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REVIEW

Yield stress fluids and ageing

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Abstract
Many high-concentration multiphase materials that are industrially and academically important do not reach thermodynamic equilibrium because of kinetic constraints originating from the structurally arrested microstructure. However, owing to thermal or elastic energy of the constituents, their microstructure progressively reorganizes to form thermodynamically more stable states. In this physical ageing process, the whole spectrum of relaxation times evolves that makes relaxation dynamics increasingly sluggish. In a process of rejuvenation, deformation field increases mobility, but non-trivially alters the shape of relaxation time spectrum. Interestingly, this class of materials also demonstrates yield stress, whose origin could be closely related to physical aging, and as a result, it depends on time and deformation history. In this review, we present an overview of experimental behaviors and theoretical advances that indicate a complex coupling between ageing and rejuvenation for this class of materials having diverse microstructures.

Keywords Yield stress · Thixotropy · Physical aging · Soft solids

Introduction

A large variety of systems, such as granular materials, foams, concentrated colloidal suspensions, dense emulsions, polymers etc. exhibit a complex viscoelastic or viscoplastic mechanical response that deviates strongly from that of a simple Newtonian liquid or Hookean solid (Larson 1999; Mewis and Wagner 2012). In a classic paper (Bingham 1916) defining the general laws of plastic flow that many materials exhibit, Bingham distinguished plastic from viscous flow by the requirement that for the former a finite "friction" needs to be overcome in order for flow to be achieved while the "fluidity" becomes zero at the concentration of solids where the plastic flow begins. Such systems, which in current terminology are called "*yield stress fluids*", exhibit an infinite zero shear viscosity and start to flow when the stress exerted on them exceeds a certain *yield stress* value (Bird et al. 1987).

An underlying physical mechanism that is related with such macroscopic flow behavior in these systems is the transition from an equilibrium fluid to an ordered solid phase (liquid-crystal transition) or to frustrated disordered solid state (glass or gel transition) (Hunter and Weeks 2012; Lu and Weitz 2013; Pusey 1991; Zaccarelli 2007). These kinds of transitions take place with increasing concentration or interparticle interactions that may be tuned by temperature, pH, or external electric or magnetic fields. Glasses and gels are typical examples of such dynamically arrested non-ergodic states, and generically, such materials have been termed as soft glassy materials in the literature (Fielding et al. 2000; Sollich et al. 1997).

In this class of materials, their viscoelastic or viscoplastic response is determined largely by the intermolecular (or particle) interactions, the number concentration, and the molecular architecture or particle shape. The above essentially determine the enthalpic and entropic contributions dictating their thermodynamic or kinetic transitions. In this way, for example, the viscoelastic properties of polymer melts are related with chain conformations, molecular architecture, and entanglements; while for colloidal suspensions, the particle size and shape, interparticle interactions, and volume fraction are important.

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The glass transition arises when many constituents interact cooperatively and prevent the system from reaching the thermodynamic equilibrium. It thus lies at the heart of many phenomena, where disorder and meta-stability result at low temperatures or high densities. Not only are glassy states common in molecular, metallic, polymeric liquids, and dispersions of various kinds but also biological, magnetic, and computer systems can arrest into glassy states. The nature of glass and the glass transition is one of the most profound problems in soft material research and was considered one of the most outstanding problems in condensed matter physics (Debenedetti and Stillinger 2001). A similar kinetic transition in the presence of attractive interactions both in polymers and colloids has been identified with the formation of gels, where a space filling network is formed by the attractive constituents providing an elastic resistance to deformation (Lu and Weitz 2013). On the other hand, jamming is a notion that is commonly used in granular systems and colloids to describe the transition to state where flow is halted due to particle contacts and formation of stress bearing structures often termed as force chains (Cates et al. 1998). In general, this kinetic arrest describes the different ways (density, temperature, flow) by which the ability of a system to flow is lost (Bonn et al. 2017b; Liu and Nagel 1998; Trappe et al. 2001).

While a complete understanding of the glass transition in quiescent systems has remained elusive, there already exist some successful investigations where external fields have been used to manipulate and control glass (or gel) formation and flow (Ballauff et al. 2013; Jatav and Joshi 2016; Jatav and Joshi 2017; Koumakis et al. 2015; Koumakis et al. 2012b; Moghimi et al. 2017; Negi and Osuji 2010b; Raghavan and Khan 1995; Vlassopoulos and Cloitre 2014). The ability to tailor soft glassy materials by physical means is interesting in its own right and is important technologically (e.g., during vitrification, applied stresses may be frozen into glass panels controlling their behavior under fracture (Herman and Sheldon 1962)). Equally importantly, these studies provide novel insights into the mechanisms of frustration and into transport mechanisms and flow of colloids and polymer melts.

Every material, which is not at thermodynamic equilibrium, by virtue of its constituent's mobility, explores its phase space to attain the lowest free energy state. In the soft glassy materials, on the other hand, the constituting entities are physically arrested over the mesoscopic length scales. As a result, the constituents have limited mobility, which constrains access to the entire phase space, and the material falls out of thermodynamic equilibrium. However, the limited access to the phase space that such material enjoys is sufficient to progressively lower its free energy as a function of time. This behavior has been termed as physical ageing (Hodge 1995; Struik 1978). A central question in ageing systems is whether and how the structure evolves and how this is linked with the internal relaxation timescales and the macroscopic mechanical or other properties (Cipelletti and Ramos 2005a; Cipelletti et al. 2003; Cloitre et al. 2000; Coussot et al. 2006; Derec et al. 2003; McKenna et al. 2009; Shahin and Joshi 2012a). In principal, during a process of physical ageing, one would expect that the microstructure of a glassy material attains increasingly more stable structures as a function of time. Consequently, in most cases as the time passes, the mobility of the constituents progressively decreases, and as a result, the time over which stress relaxes, which is also the characteristic relaxation time of a material, increases as a function of time (Fielding et al. 2000). The ultimate fate of ageing frustrated states, such as glasses and gels, through a slow evolution, depends upon whether the thermodynamic equilibrium phase (for example a crystal or phase separation) is accessible to it or not. If the thermodynamic equilibrium state is not accessible then eventually, a system may remain trapped in a local, but deeper, minimum. Such systems exhibit complex dynamics and rheology that due to a slow structural evolution (ageing) renders their microscopic dynamics and mechanical properties dependent on the waiting time and the past flow history of the sample. The application of a deformation field, in principle, usually slows down or even eliminates (or reverses) the effects of ageing by inducing fluidity in the material, a procedure known as partial or full rejuvenation (Viasnoff et al. 2003). This complex behavior is also linked to thixotropy (Mewis 1979; Mewis et al. 1975), a property wherein the viscosity of a material decreases continuously as a function of time under the application of deformation (or flow) field (such as shear), while it slowly recovers once the flow field is removed (physical ageing) (Mewis and Wagner 2009; Mewis and Wagner 2012; Moller et al. 2006). However, thixotropic materials may also show continuous increase in viscosity when the deformation field is not sufficiently strong to fully rejuvenate them. In such case, the rate of the viscosity increase would be in principle slower than that under quiescent conditions.

Some of the thixotropic materials also exhibit a yield stress behavior as pointed out in the original work of Bingham (Bingham 1916). Strictly speaking, the yield stress is defined as a threshold stress below which the material does not flow but undergoes only elastic deformation, while for larger stresses, it undergoes (at least partly) a viscous flow. In a generalized Newtonian framework (Bird et al. 1987), the constitutive equation for a very general class of yield stress fluids is given by (Denn 1998; Shaukat et al. 2012a):

$$\begin{aligned} \underset{\approx}{\sigma} &= G\underset{\approx}{\gamma}, \text{for } \sqrt{\underset{\approx}{\sigma} : \underset{\approx}{\sigma}/2} < \sigma_y \\ \underset{\approx}{\sigma} &= \left(\frac{\sigma_y}{\dot{\gamma}} + \eta\right)\underset{\approx}{\dot{\gamma}}, \text{for } \sqrt{\underset{\approx}{\sigma} : \underset{\approx}{\sigma}/2} \geq \sigma_y, \end{aligned} \tag{1}$$

where $\underset{\approx}{\sigma}$ is the deviatoric stress tensor, $\underset{\approx}{\gamma}$ and $\dot{\underset{\approx}{\gamma}}$ are, respectively, the strain and rate of strain tensors, while $\dot{\gamma}$ is the second invariant of $\dot{\underset{\approx}{\gamma}}$ given by $\left(\sqrt{\dot{\underset{\approx}{\gamma}} : \dot{\underset{\approx}{\gamma}}/2}\right)$, G is the elastic modulus, σ_y is the yield stress, and η is $\dot{\gamma}$ -dependent viscosity (and/or σ_y depending upon the model). When η is a constant, Eq. (1) represents a Bingham model, while for $\eta = m\dot{\gamma}^{n-1}$, where m and n are the model parameters, we get the Herschel-Bulkley model (Herschel and Bulkley 1926). Note that additional empirical models exist in the literature that aim to fit the rate-dependent viscosity. Furthermore, a fundamental question that arose was whether such systems have a true yield stress and therefore are really solids (Barnes and Walters 1985) or if the quantity is apparent one due to experimental limitations, such as not waiting for long enough times or reaching low enough shear rates where one would be able to detect a slow liquid-like response with very high but finite viscosity. We discuss this aspect below as well as in Appendix 1 in greater details.

Shear is expected to affect the internal relaxation spectrum of a system and therefore ageing of most related physical quantities. To this end, a central question is to what extent is ageing of soft glassy materials affected by shear and whether a well-defined shear protocol is able to reproducibly halt or revert the effects of ageing, i.e., whether an efficient shear rejuvenation exists. Moreover, one would also like to know if shear slows down ageing (under-ageing) and partially rejuvenates the system or even under certain conditions may speed-up ageing (over-ageing) (Ballesta and Petekidis 2016; Bandyopadhyay et al. 2010; Viasnoff et al. 2003; Viasnoff and Lequeux 2002). In practical applications, such complex mechanical response has an impact on both the production and proccessability of a variety of products as well as their shelf-life and final use. In fact, it has been proposed that an externally applied deformation field (such as shear flow) can be used to tune and optimize the mechanical properties of the soft glassy materials (Kanai and Amari 1993; Kaushal and Joshi 2013; Kaushal and Joshi 2016b; Koumakis et al. 2015; Moghimi et al. 2017; Raghavan and Khan 1995). For example, the processing and transport of paints; slurries; crude oils; foodstuff, such as yogurt, and mayonnaise; and homecare products, such as toothpastes, cosmetic, and pharmaceutical creams, etc., are affected by the existence of a low yield stress and the time evolution (ageing) or an influence of pre-shear history (thixotropy) on mechanical properties (Coussot 2007; Coussot 2014).

Several reviews of yield stress systems exist in literature (Bonn et al. 2017a; Bonn et al. 2017b; Cipelletti and Ramos 2005a; Cloitre and Bonnecaze 2017; Coussot 2014; Joshi 2014a), focused on colloidal systems (Lu and Weitz 2013; Zaccarelli 2007) or shear localization phenomena (Fielding 2014; Fielding 2016; Jain et al. 2018; Ovarlez et al. 2009), and mesoscopic modelling approaches (Coussot 2007). Here, we mainly focus in discussing the effects of ageing in such systems and the way this is influenced by an application of external shear fields and in turn how it affects the yield stress behavior of a material. We thus review the experimental studies, computer simulations, and theoretical models of soft yield stress materials (with particular emphasis on colloidal systems) that exhibit ageing and thixotropy. The effects of ageing are followed at the level of the microscopic dynamics and structure probed experimentally by techniques such as light (or X-ray/neutron) scattering (SLS, DLS), diffusive wave spectroscopy (DWS), optical microscopy, and computer simulations. Moreover, the rheological properties of such systems are followed as a function of waiting time discussing ageing effects both on the linear viscoelasticity and non-linear mechanical response. The paper is organized as follows: We first review, in "The structure of ageing soft glassy materials", the structure of ageing soft glassy materials and then in "Ageing at rest—evolution of the internal relaxation time", ageing effects on the slow internal relaxation probed by DLS/DWS at various yield stress samples at rest or under shear and then "Rheological behavior of ageing soft materials", present experimental behaviors dealing with the rheological ageing in the similar systems. In "Definitions and methods to determine the yield stress", we review definitions and methods to determine the yield stress, while in "Shear banding" and "Residual stresses", respectively, we discuss shear banding and an issue of residual stresses in ageing yield stress fluids. In "Modelling approaches for the physically ageing soft glassy materials", we discuss theoretical models and computer simulations of ageing systems both with regard to their phenomenology and their internal relaxations. Finally, in "Conclusions", we present the concluding remarks. We also enclose two appendices. In the first one, the matter of true yield stress is discussed, while in the second, we provide a creep flow analysis of ageing single mode Maxwell model.

The structure of ageing soft glassy materials

There are many soft materials with distinctly different microstructures that show yield stress as well as physical ageing. The common aspect in these different soft materials is that, owing to structural arrest of their constituents, the microstructure is kinetically constrained from attaining the thermodynamic equilibrium state. In this section, we discuss in this respect the microstructure of various commonly employed soft glassy materials.

One of the most commonly used soft glassy materials is highly concentrated particulate suspension of submicron sized particles in a supercooled/glassy domain (Hunter and Weeks 2012; Pusey 1991). The particulate glassy state primarily

originates from interparticle repulsive interactions and the equilibrium phase behavior or the non-equilibrium state behavior is well documented in the literature (Jones 2002; Joshi 2014a; Larson 1999; Mewis and Wagner 2012; Pusey 1991). For monodisperse spherical particles in suspension with hard-sphere interactions, liquid state ceases to exist beyond volume fraction (ϕ) of 0.494 (Pusey and van Megen 1986; Pusey and van Megen 1987). Beyond this concentration, suspension enters a biphasic region, and for $\phi > 0.54$, a crystal is formed. However, if the suspension concentration in fluid state is increased beyond $\phi > 0.494$ fast enough to avoid nucleation of crystals, the suspension enters the super-cooled region. The super-cooled state is thermodynamically out-of-equilibrium wherein caging of individual particles by their neighbors kinetically constraints the crystal formation. The mean time required for particles to diffuse out of cage, which defines the characteristic alpha-relaxation time of the system, increases with concentration and diverges as the glass transition $\phi_g \rightarrow 0.58$ is approached (Pusey and van Megen 1987). Above this concentration, the suspension enters a glassy state that persists up to random close packing threshold ϕ_{rcp}, which for monodispersed spherical particles is 0.64. In Fig. 1a, a confocal image of a colloidal glass of PMMA particles at $\phi = 0.6$ is shown where amorphous order is obvious. Recent computer simulations suggest that for particle polydispersities lower than about 7%, not only super-cooled states crystalize through nucleation and growth or spinodal decomposition but also glassy states may also slowly crystalize via small cooperative particle non-diffusive motion (Pusey et al. 2009; Sanz et al. 2011; Zaccarelli et al. 2009). Experimentally, a polydispersity of above 7–8% is often used to suppress crystallization (Hunter and Weeks 2012; Pusey 1991), at rest or even under shear shifting however the threshold associated with the formation of super-cooled state, glassy state, and ϕ_{rcp}.

In experimental systems, it is not easy to achieve pure hard-sphere interactions; however, to obtain a closer match, a short range repulsion among the particles is induced (Royall et al. 2013; Russel et al. 1989). A common way is to add a short polymer brush chemically attached to the particle, which introduces a steric stabilization due to entropic penalty upon interpenetration of the polymer brush in good solvent. Depending upon the size of the particle (core) and that of hairs a spectrum of interparticle interactions ranging from hard to soft are possible (Vlassopoulos and Cloitre 2014). In ultra-soft polymer colloids with longer-range repulsive interactions, such as polymer grafted particles, multi-arm star polymers, and star-like micelles or soft deformable microgel particles, local effects due to polymer interdigitation or outer shell deformability (Vlassopoulos and Cloitre 2014) may add further complexity to the entropically driven frustrated states. In addition, jamming transition may be reached above the overlap concentration with entanglement effects and local lubrication between deformed particles altering the micromechanics and local friction between the particles. The glassy dynamics of grafted particles in solution (Christopoulou et al. 2009) as well as in the melt (Agarwal et al. 2009) have been studied quite extensively (Vlassopoulos and Cloitre 2014).

Repulsion can also be induced among the particles via electrostatic interactions, tuning the charges on the particles by controlling pH. For sufficiently large magnitude of charges (typically magnitude of ζ potential > 40 mV), interparticle bond formation can be avoided for a very long period leading to a stable dispersion (Hanaor et al. 2012). Concentrated suspensions in the super-cooled as well as in the glassy region are viscoelastic and exhibit yield stress as well as physical ageing. In colloidal glasses, elasticity and yield stress originate from the effect of caging. However, due to thermal energy, the particles can still undergo local (in-cage) Brownian motion, while larger scale dynamic heterogeneities are also observed. Such mobility is expected to lead the kinetically frustrated

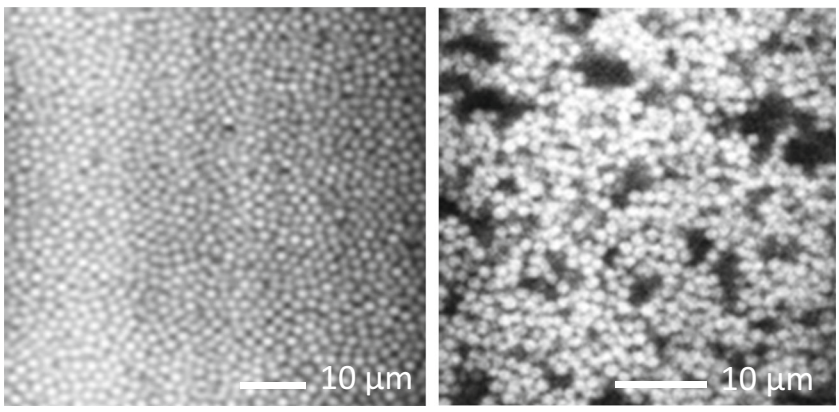


Fig. 1 Confocal microscopy images from **a** PMMA hard-sphere glass $\phi = 0.6$ and **b** depletion gel at intermediate volume fraction ($\phi = 0.44$, $U = -16$ kT, and range of attraction $\xi = 0.05$). Figures adapted from Koumakis et al. (2015). Published by The Royal Society of Chemistry

metastable system to states with progressively lower free energy, causing physical ageing.

Compared to repulsive interactions, many types of interparticle interactions, such as van der Waals, electrostatic interactions between dissimilar charges, depletion interactions, hydrophobic, and hydrophilic, etc., are attractive in nature (Israelachvili 2010; Russel et al. 1989). For highly concentrated colloidal glasses, changing the interparticle interactions from repulsive to attractive, at the same concentration, eventually leads to the attractive glasses (although a reentrant liquid might also be observed) (Pham et al. 2004; Pham et al. 2002). On the other hand, decreasing the volume fraction keeping the interparticle interaction unchanged transforms a repulsive glass to liquid, while attractive glasses turn into colloidal gels (Zaccarelli and Poon 2009). At low volume fractions, often, colloidal gels have fractal structure such that mass (M) of a percolated network enclosed in a sphere of radius R scales as: $M \propto R^{d_f}$, where d_f is a fractal dimension. When attractive interactions are strong enough, particles need fewer collisions before forming an interparticle bond. This leads to a rather open structure with low fractal dimension in the range 1.7 to 1.9, and the gelation process is termed as diffusion-limited cluster aggregation (DLCA). On the other hand, if attractive interactions are not strong compared to thermal energy, then particles may rearrange, breaking and reforming bonds. In this reaction-limited cluster aggregation (RLCA) process, the microstructure is more compact with a fractal dimension in the range 2 to 2.1 (Lu and Weitz 2013). In such fractal gels, the elasticity and yield stress originate from the elasticity of the backbone formed by interparticle bonding and in turn the strength of the interparticle interactions (Coussot 2007; Mewis and Wagner 2012). Figure 1b shows a depletion gel for an intermediate volume fraction $\phi = 0.44$ (Koumakis et al. 2015).

The coarsening of the microstructure through bond restructuring during physical ageing usually leads to an increase of the gel strength and an evolution of its rheological properties (Joshi 2014a; Zia et al. 2014), while often times, gravitational effects intervene causing a delayed gel collapse (Harich et al. 2016; Poon et al., 1999). The latter may in return affect mechanical measurements for example creating a thin liquid layer at the top in the case of plate-plate or cone-plate geometries, which qualitatively alters the rheological response from solid- to pseudo-liquid (Ballesta et al. 2013) or through larger-scale delayed collapse in a Couette cell geometry which affects in a complex way the average measured viscoelastic properties (Kamp and Kilfoil 2009). The phenomenon of delayed sedimentation in colloidal gels originates from an interplay of structural coarsening (ageing) of the gel, which is more pronounced at low and intermediate volume fraction colloidal gels with attractive interactions of few $k_B T$, and gravitational force induced stresses exerted on the microstructure of the gel network. In this sense, it is indeed a manifestation of the way external fields affect structural stability and macroscopic flow in analogy with the delayed yielding discussed below. The phenomenon has been studied in detail experimentally in various regimes of the colloid-polymer mixture phase diagram (Allain et al. 1995; Bartlett et al. 2012; Buscall et al. 2009; Poon et al., 1999; Teece et al. 2014) as well as by computer simulations (Landrum et al. 2016), although in the latter, the consideration of hydrodynamic interactions or not is important.

Unlike concentrated colloidal suspensions, wherein the glassy state is caused above a certain volume fraction by entropic caging of solid colloids in various other soft materials, jamming of liquid drops, soft deformable particles, or gas droplets also lead to glassy states (Larson 1999). Common examples are emulsions, foams, and microgel pastes, where liquid, gas, and soft solid are, respectively, dispersed in continuous liquid media. In the former two, each droplet or bubble is stabilized by surfactants or particles (Höhler and Cohen-Addad 2005; Mason et al. 1997), while microgel pastes comprise of swollen polymeric gels of submicron size (Bonnecaze and Cloitre 2010; Meeker et al. 2004). At low concentrations in the liquid state, the dispersed entities acquire their equilibrium shapes (spherical for liquid drop and gas bubble); however, at high concentrations, the dispersed entities are forced to interact and deform acquiring a polygonal shape, leading to a jammed state. Representing images of foam and emulsion is shown in Fig. 2a, b, respectively, that clearly show polygonal shaped bubbles/drops. Deformation from their equilibrium shape induces repulsive interactions and raises the free energy of a system. The elasticity and yield stress in concentrated emulsions and foams are due to the surface tension, while that of microgel paste originates from the osmotic pressure of intersegmental interactions. In all these cases, the constituents undergo microscopic motion and structural rearrangements that allows the system to lower its free energy during ageing.

Various commercial systems, such as toothpaste (Ardakani et al. 2011; Liu et al. 2015), hair gel (Shahin and Joshi 2011), cosmetic and pharmaceutical creams (Kwak et al. 2015), drilling mud (Livescu 2012), bitumen (Lesueur 2009), industrial pastes (Shukla et al. 2015; Shukla et al. 2016), polymer clay nanocomposite melt (Kaushal and Joshi 2014; Ren et al. 2003), and different pasty food materials (wheat dough, tomato ketchup, fruit jam, mayonnaise, etc.), contain variety of components

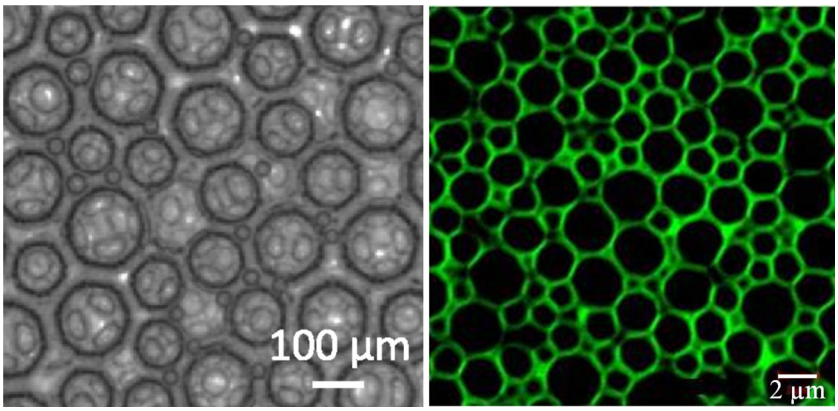


Fig. 2 **a** Microstructure of aqueous foam with gas volume fraction 0.64. **b** Oil in water emulsion with dispersed phase volume fraction 0.80. **a** Reprinted from Cohen-Addad and Höhler (Cohen-Addad and Höhler 2014) with permission from Elsevier and **b** Courtesy M. Cloitre, ESPCI France

including particles, surfactants, salts, polymers, etc., (Alam et al. 2014; Rao 2013) that share very complex inter-component interactions. Elasticity and yield stress in such materials originate from caging/jamming as well as complex inter-entity interactions. The evolution of the rheological properties in such systems is reminiscent of the physical ageing observed in model colloidal glasses and gels, as those discussed above.

Ageing at rest—evolution of the internal relaxation time

A sensitive probe of the time evolution (ageing) of soft materials is their internal relaxation times representing the relaxation of spontaneous concentration or density fluctuations. These are related with motions at different time and length-scales and are measured experimentally by scattering or microscopy techniques, such as dynamic light scattering (DLS) and X-ray photon correlation spectroscopy (XPCS) (Bandyopadhyay et al. 2004; Guo et al. 2007) or confocal microscopy (Cianci et al. 2006; Cipelletti and Ramos 2005b; Courtland and Weeks 2003; Lynch et al. 2008). Similarly, with molecular glasses, soft glassy materials exhibit multiple relaxation processes related with different length-scales. The faster modes are attributed to in-cage motion in colloidal suspensions, or local polymer dynamics are generally viewed as stationary, unless chemical or physical bonding process is involved. On the other hand, the slowest final relaxation is less well understood and most of the times exhibits ageing. These slow modes may have a variety of microscopic origins, such as out-of-cage dynamics related with dynamic heterogeneities in colloidal glasses (Hunter and Weeks 2012; Weeks et al. 2000), structural rearrangements and cluster coarsening in colloidal gels (Landrum et al. 2016), and relaxation of frozen-in stresses (Ballauff et al. 2013; Cipelletti and Ramos 2005b) etc., and may be of diffusive, sub-diffusive, or super-diffusive/ballistic and intermittent character. Usually, such slow internal relaxations, which slow down during ageing, are detected under single scattering conditions by multi-speckle DLS (MSDLS) (Cipelletti and Ramos 2005b; Cipelletti et al. 2003), echo-light scattering (Pham et al. 2004), or brute force rotation (Martinez et al. 2008; Martinez et al. 2010) in the multiple scattering regime by DWS (Ballesta et al. 2008) or for smaller particles by XPCS, in all cases in a manner that should enable proper statistical averaging of non-stationary dynamics in non-ergodic systems (Cipelletti and Ramos 2005b).

A typical ageing example of the slow relaxation mode in concentrated suspensions and glasses of model nearly hard-spheres (sterically stabilized PMMA particles) (Brambilla et al. 2009; El Masri et al. 2009) measured by mutlispeckle DLS (MSDLS) is shown in Fig. 3. The average long-time α-relaxation time τ_α, deduced from the two-time intermediate scattering function (ISF), $f(t_w, t_w+\tau) = \sqrt{g^{(2)}(t_w,\tau)-1}$, (where $g^{(2)}(t_w, \tau)$is the scattered intensity autocorrelation function), is reaching a steady-state value after a waiting time, t_w, which is diverging at the glass transition volume fraction. The latter being an increasing function of polydispersity (Martinez et al. 2008; Martinez et al. 2010). Moreover, the dynamics followed by the two-time degree of correlation, $c_I(t_w,\tau) = \frac{\langle I_p(t_w) I_p(t_w+\tau)\rangle}{\langle I_p(t_w)\rangle\langle I_p(t_w+\tau)\rangle}$ correlating the scattering intensity $I_p(t)$ (at a pixel/speckle p), and the fluctuations in the correlation function strongly indicate intermittent dynamics. In the glassy state, the α-relaxation is diverging with waiting time and thus no stationary state seems to be reached (Brambilla et al. 2009; Cianci et al. 2006; Courtland and Weeks 2003; El Masri et al. 2009; Lynch et al. 2008; Martinez et al. 2008; Martinez et al. 2010; Simeonova and Kegel 2004). Moreover, in hard-sphere glasses, ageing of the slow dynamics, suppressing crystallization, is wave-vector (q) dependent, while the non-

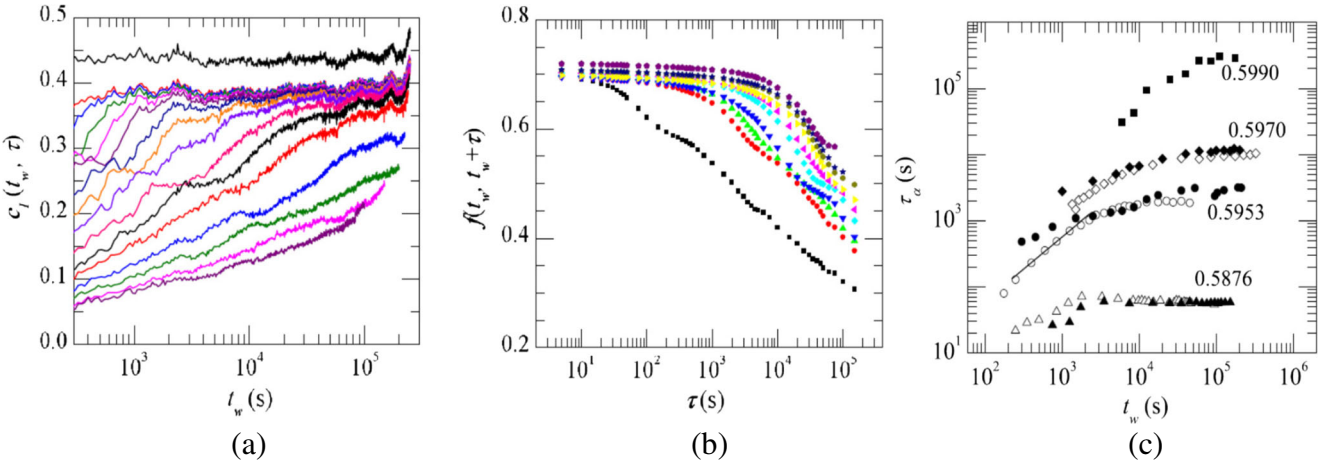


Fig. 3 DWS measurements of hard-sphere glasses: **a** Degree of correlation, c_I, for a nearly hard-sphere PMMA suspension ($\phi = 0.599$) as a function of waiting time, t_w, for different delay times, from top to bottom, $\tau = 0$ to 150 ks. **b** Two-time ISF obtained from c_I, for different waiting times from 500 s to 170 ks. Note the temporary fluctuation in c_I that produce strong deviations from a single stretched exponential decay in ISF, due to strongly heterogeneous dynamics. **c** Waiting time dependence of the α-relaxation time at different volume fractions and two separate runs. Figures adapted from El Masri et al. (El Masri et al. 2009) IOP Publishing Ltd and SISSA

ergodic plateau $f(q, t \to \infty)$ (i.e., the plateau of the correlation function after the short-time relaxation, or Debye-Waller factor) is not affected by waiting time, which suggests that any structural changes may be of longer length scales than the cage size.

Similar ageing studies have been performed with closely packed soft spheres, such as microgel particles (Mazoyer et al. 2006; Mazoyer et al. 2009; Yunker et al. 2009), attractive colloidal gels (Cipelletti et al. 2000; Duri and Cipelletti 2006; Manley et al. 2005), and more complicated soft glassy material systems, such as Laponite clay particles (Abou et al. 2001; Bandyopadhyay et al. 2004; Bonn et al. 2002; Di Leonardo et al. 2006; Fielding 2016; Ianni et al. 2007; Kaloun et al. 2005; Saha et al. 2015; Saha et al. 2014). In all these cases, the samples remain amorphous during ageing. On the other hand, there is experimental evidence that in ultra-soft multi-arm stars, ageing of a metastable glassy state does lead to crystallization (Stiakakis et al. 2010), i.e., thermodynamic equilibrium is reached through a transition from a glass where the slow relaxation modes are not diffusive. Figure 4 shows the correlation functions and corresponding degree of correlation measured by MSDLS in a multi-arm star glass as a function of waiting time (Stiakakis et al. 2010). The sample soon after preparation is trapped in a glassy state as indicated rheologically by a solid-like response and by DLS by ageing and non-diffusive slow α-relaxation mode. However, contrary to most soft (and hard) glasses, where the slow dynamics becomes progressively sluggish during the ageing here, the slow mode initially exhibits a slowing down, but after some time, it starts to speed up again. This latter process is related with the slow crystallization of the glass as proven by SANS measurements. Similarly, computer simulation findings for hard-sphere glasses suggest that crystallization may be induced by small cooperative particle rearrangements rather than long range out-of-cage diffusion (Sanz et al. 2011; Zaccarelli et al. 2009), although experimentally gravity-induced ageing (Simeonova and Kegel 2004) seems to prohibit rearrangements necessary for crystal nucleation corroborating evidence of glass crystallization in microgravity (Zhu et al. 1997).

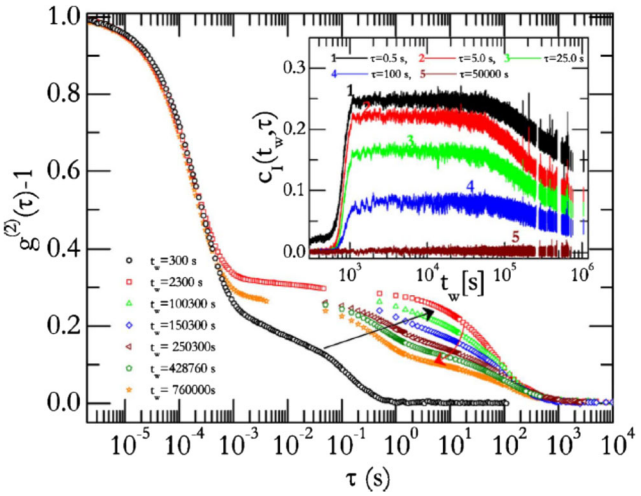


Fig. 4 Ageing dynamics of a glassy ($1.26c^*$, with c^* the overlap concentration) solution of multi-arm stars measured at $q = 0.024$ nm^{-1}. The arrows indicate the initial slowing-down and subsequent speed-up of the dynamics related with ageing and crystallization. The inset shows the corresponding degree of correlation for few sample times as a function of waiting time. Reprinted (figure) with permission from Stiakakis et al. (2010) Copyright (2010) by the American Physical Society

Slow modes that undergo ageing have a variety of origins depending on the details of the system. Nonetheless, some universal aspects do appear such as the compressed exponential decay (with exponent β in a range 1.3 to 1.5)

with non-diffusive q^{-1} scaling of the slow relaxation time, often seen in colloidal gels formed by different types of attractive particles (Chung et al. 2006; Cipelletti et al. 2000; Cipelletti et al. 2003; Guo et al. 2011), multilamellar vesicles (Ramos and Cipelletti 2001), clay suspensions (Angelini et al. 2013; Bandyopadhyay et al. 2004; Bellour et al. 2003; Schosseler et al. 2006b), pectin gel (Mansel and Williams 2015), dense ferrofluids (Robert et al. 2006), molecular (Conrad et al. 2015), and metallic glasses (Ruta et al. 2012). Similar finding has been detected by computer simulations (Bouzid et al. 2017; Chaudhuri and Berthier 2017). The behavior is attributed to super-diffusive processes associated with cluster restructuring and relaxation of internal stresses. Interestingly, such compressed exponential behavior has been observed only when the probed length-scales are of the order of micrometer or below. On the other hand, to the best of our knowledge, there is no report of compressed exponential decay in the rheological (stress relaxation) experiments that are carried out over the bulk length-scales where relaxation is always observed to be either exponential or slower than exponential (stretched exponential). Interestingly, for an ageing system containing multilamellar vesicles, Ramos and Cipelletti (2001) observed identical dependence of the relaxation time on waiting time by using bulk rheology and light scattering. However, the former exhibited stretched exponential relaxation ($\beta \approx 0.19$) over bulk length-scales, while the latter demonstrated compressed exponential behavior ($\beta \approx 1.46$). Similar findings have also been reported for aqueous suspension of Laponite wherein light scattering data indicated compressed exponential behavior (Bandyopadhyay et al. 2004; Bellour et al. 2003; Schosseler et al. 2006b), while rheology experiments only show stretched exponential relaxations (Bandyopadhyay et al. 2010; Kaushal and Joshi 2014). Relaxation dynamics over length-scales closer to the characteristic length scale of system are influenced by mobilities of the constituents and/or any heterogeneities present in the system. The relaxation behavior over the bulk length-scales, however, depends on cooperative dynamics. It is therefore not surprising that the spectrum of relaxation times is different over different length-scales. Similar length-scale dependent rheological response has also been reported for aqueous Laponite suspensions (Oppong et al. 2008; Rich et al. 2011b). The slow relaxation time is found to increase exponentially (Abou et al. 2001; Negi and Osuji 2010c; Shahin and Joshi 2012a) or as power law with waiting time (Chung et al. 2006; Cloitre et al. 2000; Viasnoff et al. 2003) or even in some cases, a combination of the two. The exponential increase is related with the transition from a fluid to a non-ergodic state (due to the formation of cages in a glass or inter-connected network in a gel) (Joshi 2007; Schosseler et al. 2006a), while once in the frustrated state, the time dependence is linear or power law increase (Bellour et al. 2003; Cipelletti et al. 2000; Greinert et al. 2006; Robert et al. 2006) related with the genuine ageing of the soft glassy materials.

Experimental studies aim to understand how external perturbations, such as shear, affect ageing of the soft glassy materials and more specifically whether a shear protocol can be found that erases the sample history (thus fully rejuvenating it), or under which conditions shear may halt or accelerate ageing. Along this line, microscopic dynamics were probed via light scattering or microscopy in order to identify the origin of ageing and the mechanisms responsible for thixotropy. Figure 5 shows the time evolution of the internal dynamics probed by multi-speckle DWS in a concentrated suspension of charged stabilized polystyrene particles after a large amplitude oscillatory shear (Viasnoff et al. 2003). Measurements at different strain amplitudes have revealed that, in addition to the usual shear-induced (full or partial) rejuvenation seen at high strain amplitudes under certain conditions, moderate shear may also accelerate ageing (Viasnoff et al. 2003; Viasnoff and Lequeux 2002). Such (over-ageing) phenomenon was related with modification of the distribution of relaxation times and can be qualitatively captured by the SGR model, although it might not be a generic feature among soft glassy materials (Kaushal and Joshi 2016a).

Scattering experiments have been utilized to probe internal dynamics of yield stress soft matter systems such as colloidal glasses and gels under shear. The evolution of DLS correlation function in a hard-sphere glass under constant stress, below the yield stress, was measured by Ballesta and Petekidis (2016). As the shear rate progressively decreases, internal slow dynamics becomes sluggish and strong fluctuations appearing in the shear rate are linked with intermittent particle dynamics and large fluctuations of the slow relaxation mode. Internal dynamics are another manifestation of continuous increase of the apparent viscosity (or decrease of shear rate) under constant low stress indicating a system with finite yield stress.

On the other hand, in colloidal gels, structural evolution at rest is much more pronounced, while external flow and shear fields profoundly alter the structure and mechanical properties. In this respect, in-situ microscopic probes are more valuable to provide valuable links between microstructure, dynamics, and mechanical properties. For example, combined rheometry and XPCS (Guo et al. 2010; Guo et al. 2011) have related the increase of the elastic modulus with particle localization during gel formation and ageing. Microrheological measurements were also used to determine the local viscoelastic properties of ageing systems (Rich et al. 2011a; van den Ende et al. 2010) and probe, via optical trapping of probe particles, the effective temperature

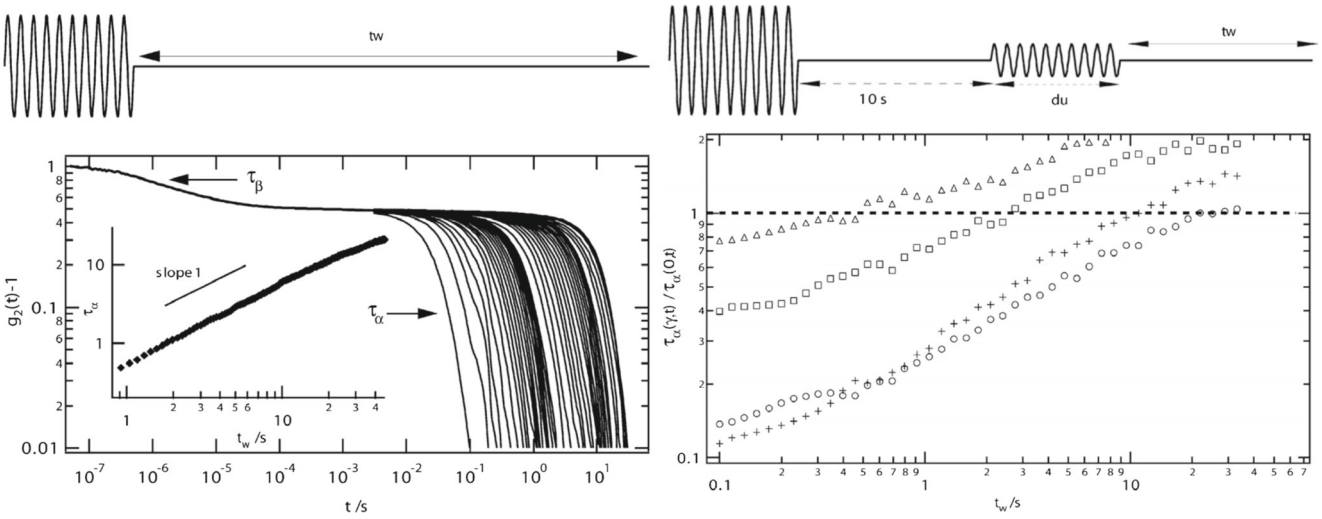


Fig. 5 Internal dynamics after a shear-induced rejuvenation in concentrated suspension ($\phi = 50\%$) of polystyrene particles. Left: ISF after full rejuvenation and waiting time dependence of the α-relaxation time. Right: Scaled α-relaxation time after a second burst with strain amplitude of $\gamma_0 = 7.9\%$ (which should be in the weakly non-linear regime) at different frequencies. The effect of over-ageing is evident and stronger with increasing frequency (10 to 0.1 Hz, from left to right). Figure adapted from Viasnoff et al. (Viasnoff et al. 2003) with permission of The Royal Society of Chemistry

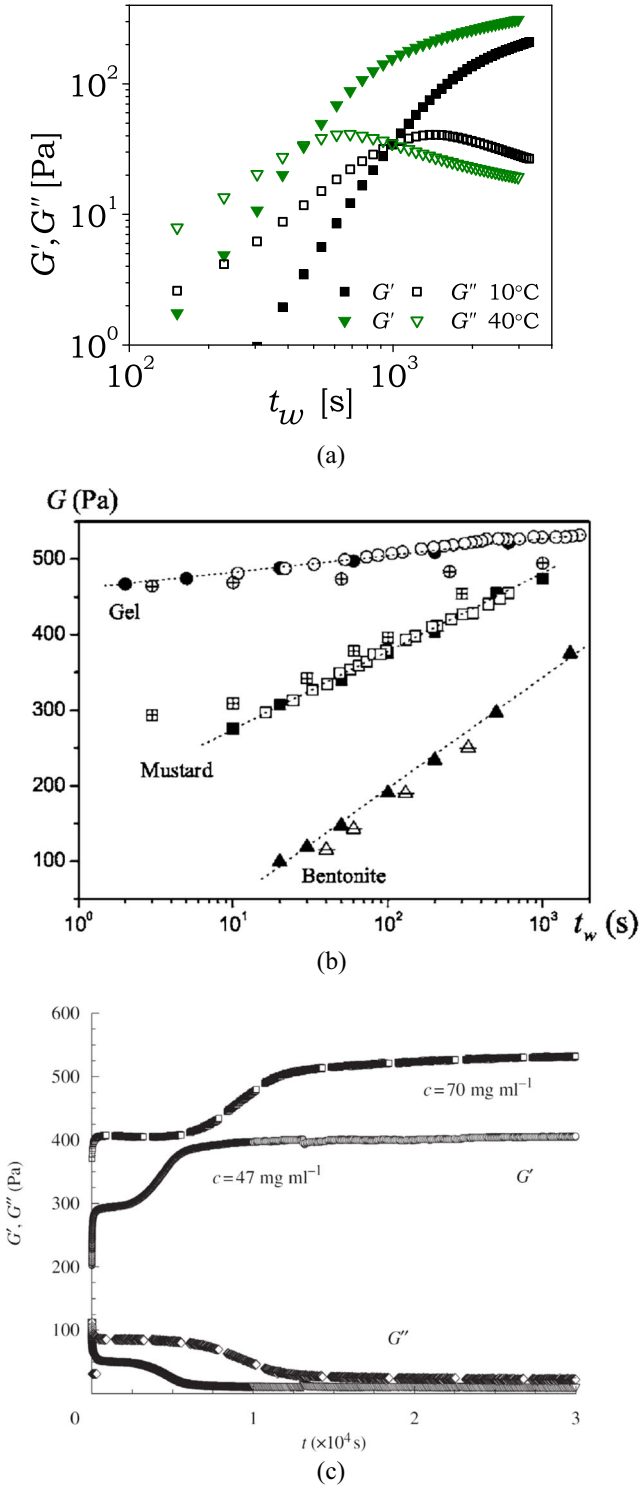
(Greinert et al. 2006) of an ageing colloidal suspension during liquid-glass transition. Relevant Brownian dynamics simulations (Zia et al. 2014) also follow the coarsening of colloidal gels with time as discussed below.

Rheological behavior of ageing soft materials

In frustrated systems, such as soft glassy materials, an application of external fields (for example shear or extensional flow) changes the relative position of the constituents increasing the energy (or decreasing the well depth). This holds for both the colloidal glasses and attractive gels as the description in terms of energy acquired by trapped entities (whether entropic crowding as in glasses or enthalpic bonding as in attractive gels) with respect to the well depth is generic. Thereby, this procedure facilitates out-of-cage diffusion (for hard-sphere glasses or soft particle jammed states) or bond breaking/restructuring (for attractive particle gels) and eventually large-scale rearrangements. Subsequent to cage or bond breaking, new cages or interparticle bonds are formed reversing the effect of ageing. Immediately after the full rejuvenation, the material is in its highest free energy state; and since a successful rejuvenation erases all the history, soft glassy materials are usually subjected to strong enough deformation fields to obtain a reproducible initial state before carrying out any rheological experiments.

The process of physical ageing is primarily due to the mobility of the constituents, albeit limited, which form the microstructure of a material. In athermal systems, ageing is either absent or weak (like for example in hard-sphere glasses) and only large-scale rearrangements not easily detectable drive the slowing down of the slow relaxation modes, while the material remains arrested in an out of equilibrium microstructure. On the other hand, systems that are brought in thermodynamic equilibrium from an arrested state (for example shear-induced hard-sphere crystals) stop exhibiting ageing (Koumakis et al. 2008). Moreover, the greater is the mobility of the constituents, the faster is the exploration of the phase space, leading to faster ageing. As a result, temperature plays an important role in an ageing process. Particularly, enhanced thermal energy is observed to accelerate ageing so that, an evolution of G' and G'' (as well as that of the distribution of relaxation times) has been observed to shift to lower timescales with increase in temperature as shown in Fig. 6a (Dhavale et al. 2013; Gupta et al. 2012; Ovarlez and Coussot 2007; Shahin and Joshi 2012b). Similarities exist also with molecular glasses, wherein ageing is known to involve free volume relaxation (Struik 1978). However, in molecular glasses, the change in the specific volume upon temperature step-up or step-down jumps has been observed to be asymmetric due to a competition between expansion/contraction of the cages vis a vis trapped molecules (Shaw and MacKnight 2005). Interestingly, in soft glasses, the probed experimentally measurable parameter (such as G' in clay suspensions (Dhavale et al. 2013) and occupied volume in thermosensitive microgel paste (Di et al. 2011)) has also been observed to show asymmetric variation. The reasons, however, differ depending upon the specific aspects of the studied soft glassy materials.

In some simple colloidal glasses with an amorphous microstructure, the average slow relaxation time (τ) as well as its distribution scale linearly with ageing (or waiting) time, t_w, i.e., the time elapsed since rejuvenation, $\tau \propto t_w$ (in Figs. 3



◀ **Fig. 6** Ageing of the linear viscoelastic properties: **a** Evolution of G' and G'' as a function of time at two temperatures for Laponite dispersion. Immediately after shear melting, both G' and G'' show initial increase with time. However, beyond cross-over, G' shows logarithmic increase, while G'' shows a decrease with time. Increase in temperature shifts the evolution to smaller timescales (data from Shahin and Joshi 2012b). **b** Logarithmic evolution of elastic modulus as a function of time for a hair gel, mustard, and bentonite suspension (reprinted with permission from Coussot et al. (2006) Copyright (2006), The Society of Rheology). **c** Evolution of elastic and viscous moduli in concentrated glassy multi-arm star polymer solutions at two concentrations. Note the two-stage evolution of the viscoelastic properties (figure adapted from Christopoulou et al. 2009)

and 4 and in the related discussion symbol, τ has been used to represent lag time in ISF. This should not be confused with τ represented as relaxation time). In the inset of Fig. 5, the slow relaxation time of an ageing colloidal glass of polystyrene particles, determined by multispeckle DWS, has been plotted as a function of time. It can be seen that τ indeed scales linearly with t_w. However, in general, very few soft glassy systems follow such linear time dependence; instead more often the relaxation times follow a power law dependence on t_w given by: $\tau \sim \tau_m^{1-\mu} t_w^{\mu}$, where τ_m is the microscopic relaxation time, while μ is the power law exponent (τ_m can be considered as unit time associated with structural reorganization (Shahin and Joshi 2012b)). Interestingly such power law dependence of τ on t_w has been observed not only for soft glassy materials (Cipelletti et al. 2000; Cloitre et al. 2000; Derec et al. 2003; Negi and Osuji 2010c; Shahin and Joshi 2011) but also for molecular glasses including polymeric glasses (Struik 1978) and spin glasses (Sibani and Hoffmann 1989). Depending upon the values of μ, the ageing behavior is classified as sub-ageing ($\mu < 1$), full ageing ($\mu = 1$) and hyper or super-ageing ($\mu > 1$). The origin and implications of such behavior have been discussed extensively, for example in reference (Bouchaud 2000; Cipelletti and Ramos 2005a; Joshi 2014a; Shahin and Joshi 2012a).

Usually for materials with entropic frustration, such as hard-sphere glasses, the increase of the modulus is almost absent or very weak (Ballesta and Petekidis 2016; Derec et al. 2003; Koumakis et al. 2016; Koumakis et al. 2008). As mentioned above, in comparison with hard-sphere glasses, their shear-induced crystal counterparts (formed when a glassy sample is subjected to oscillatory shear) do not exhibit any ageing of their linear viscoelastic properties (Koumakis et al. 2008), as expected from a system that has reached thermodynamic equilibrium. On the other hand, in materials where the non-ergodic transition has at least partly an enthalpic origin, such as clay suspensions, attractive emulsions, colloidal gels, industrial pastes etc., the elastic modulus, G', shows a prominent increase as a function of time (Coussot et al. 2006; Dhavale et al. 2013; Koumakis et al. 2015; Koumakis and Petekidis 2011). In such systems with attractive interactions, arrested particles still may undergo cooperative motions, due to thermal energy, with time scale τ_m, and progressively occupy energy landscapes with increased well depths with lower mean value E. The modulus can be represented as an energy density given by, $G \propto E/b^3$, where b is a characteristic length-

scales of the system (Jones 2002). If the characteristic relaxation time of a material is considered to have an Arrhenius dependence on E, $\tau = \tau_m \exp(E/k_B T)$, a power law dependence of τ on time, leads to logarithmic dependence of modulus on time (Joshi 2014a; Shahin and Joshi 2012b). Indeed, many soft glassy materials that exhibit a relaxation time $\tau \sim \tau_m^{1-\mu} t_w^{\mu}$ do also show a logarithmic dependence of G' on time as shown in Fig. 6b (Coussot et al. 2006). In Fig. 6a, evolution of G'' subsequent to rejuvenation has also been plotted along with that of G' for aqueous Laponite suspension. It can be seen that initially, both the moduli ($G'' > G'$) increase with time, with G' increasing at a faster rate and crossing over G''. After the crossover, G'' decreases after showing a maximum, while G' shows a logarithmic increase with time. If the rheological behavior of a material is approximated by the single-mode Maxwell model, G'' can be related to G' as $G'' \approx G'/\omega\tau$. Consequently, a logarithmic time dependence of G' and a power law time dependence of τ on time indeed predict G'' to decrease with time as observed experimentally (Shahin and Joshi 2012b). However, depending upon the specific nature of a soft glassy material, more complicated dependences of G' on time are possible. For example, in concentrated multi-arm star polymer solutions and glasses, the evolution of G' follows a two-step increase as seen in Fig. 6c. The first fast step is attributed to cage formation, while the second step is proposed to be due to cage rearrangement (Christopoulou et al. 2009), both specific to the multiarm microstructure and related with arm fluctuations and interdigitation, which macroscopically lead to a soft shear-thinning system at intermediate times and a more solid shear banding one at longer timescales (Erwin et al. 2010). In jammed systems (compressed emulsions, multilamellar vehicles, etc.), ageing can be induced by stresses built in the system during shear rejuvenation and then triggered by temperature fluctuations (Mazoyer et al. 2006), inducing local shear that lead to the exponential increase of slow relaxation times. In cytoskeletal networks, stresses induced during gel formation are relaxing during ageing through chemical unbinding of actin filaments (Lieleg et al. 2011) causing a drop of both G' and G''.

In some thixotropic systems, pre-shear history creates a temporary change of mechanical properties, or time hysteresis. In this way, different pre-shear protocols may be used to tune the viscoelastic properties (and the yield stress) of attractive systems, such as clay suspension and fumed silica (Kaushal and Joshi 2013), carbon black suspensions (Helal et al. 2016; Ovarlez et al. 2013; Radhakrishnan et al. 2017), and depletion colloid-polymer gels (Koumakis et al. 2015; Moghimi et al. 2017) (Koumakis et al. 2015). Recently, Kaushal and Joshi (2016b) also used the SGR model to address the possibility of tailoring viscoelastic properties by varying magnitude of pre-shear.

The time dependency induced in a material due to physical ageing manifests itself not only in the oscillatory flow experiments in the linear regime but also in standard rheological experiments, such as step stress (creep), step strain (stress relaxation), and step shear rate (start-up shear) carried out in non-linear regime. In a typical protocol, a rejuvenated material is kept under quiescent condition before being subjected to the above-mentioned flow/shear fields. It is usually observed that in creep experiments started at progressively longer t_w, the strain induced in an ageing material is lower while its evolution is weaker as manifested in Fig. 7a for a microgel paste (Cloitre et al. 2000). If ageing during creep time ($t - t_w$) is neglected in the limit of $t - t_w << t_w$, horizontally shifting creep curves on a logarithmic time axis often lead to time-ageing time superposition (Joshi and Reddy 2008; Negi and Osuji 2010b; Struik 1978), as shown in Fig. 7b. The corresponding horizontal shift factor yields then the dependence of the average τ on t_w. As discussed above, ageing materials have also been investigated by passive microrheology, wherein mean square displacement (MSD) of probe particles embedded in the material is measured (Oppong et al. 2008; Rich et al. 2011a; van den Ende et al. 2010). Interestingly, similar to creep compliance, MSD at any given time is also observed to decrease with waiting time, and its time evolution is also observed to be sluggish for experiments started at higher waiting times. Furthermore, MSDs can also be superimposed via a horizontal shifting on logarithmic axis, similar to the response of the creep compliance (Vyas et al. 2016).

Cloitre and coworkers (Cloitre et al. 2000) obtained independent time-ageing time superpositions for different values of constant stress and indeed observed $\tau \sim \tau_m^{1-\mu} t_w^{\mu}$, irrespective of value of stress. As shown in the inset of Fig. 7b, they observed that in a limit of small values of stress $\mu \approx 1$ that decreased beyond what they termed as critical shear stress. Furthermore, increasing stress leads to a decrease in μ, which eventually goes to zero at a stress where ageing stops (or complete rejuvenation takes place). Interestingly, in this system, this stress closely matched with independently measured yield stress as shown in the inset of Fig. 7b. Note that the very existence of superposition shown in Fig. 7b implies that all the relaxation modes in the distribution show identical dependence on t_w (for simple ageing t_w is the only relevant internal time, while for subageing or hyperageing, there would be additional influences) for a given stress and the shape of distribution remains preserved over a duration of the creep measurement (Struik 1978). Joshi and coworkers observed that, in some systems, the corresponding superpositions at various stresses have similar curvature and therefore lead to time-ageing time-stress superposition (Baldewa and Joshi 2012; Joshi and Reddy 2008), suggesting that the shape of the

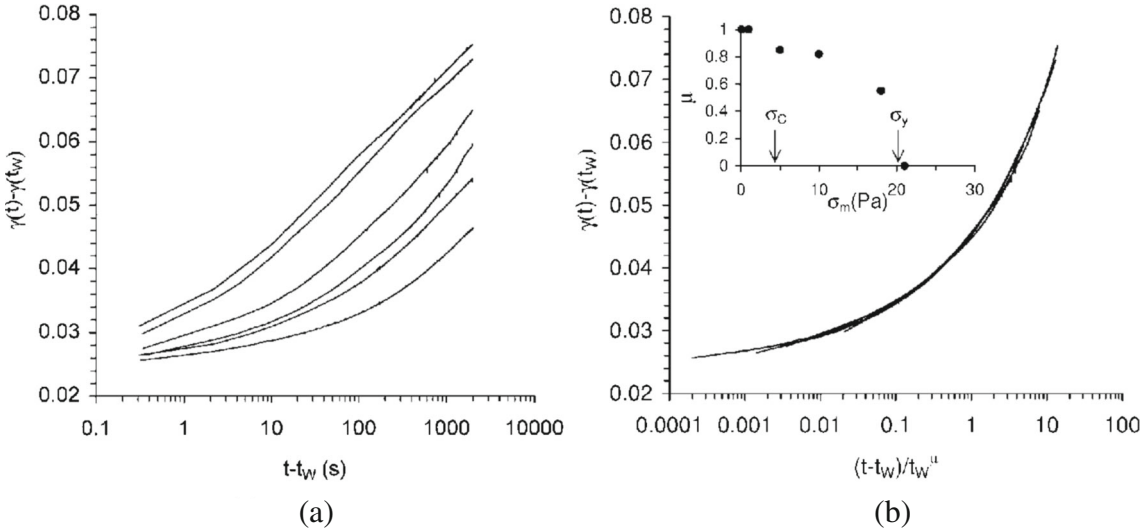


Fig. 7 Ageing effect in the non-linear creep measurements: **a** Strain is plotted as a function of time elapsed, since application of stress applied at different waiting times for microgel paste. It can be seen that with increase in waiting time, the magnitude of strain decreases and the evolution of strain weakens. **b** All the strain curves superpose to form a master-curve when plotted as a function of $(t-t_w)/t_w^{\mu}$. The corresponding value of μ is plotted as a function of stress in the inset of figure (**b**). Reprinted with permission from Cloitre and coworkers (Cloitre et al. 2000). Copyright (2000) by the American Physical Society

relaxation time distribution remains constant for the explored time duration irrespective of a value of stress. In the observed power law relation: $\tau \sim \tau_m^{1-\mu} t_w^{\mu}$, the prefactor $\tau_m^{1-\mu}$ is a requirement to fulfill dimensional consistency. Under the application of different creep stresses, the existence of time-ageing time-stress superposition not only verifies the relation $\tau \sim \tau_m^{1-\mu} t_w^{\mu}$ but also leads to a constant numerical value of τ_m (Baldewa and Joshi 2012; Joshi 2014b; Shukla and Joshi 2017).

However, prolonged application of stresses is also observed to cause delayed yielding, both experimentally in various soft glassy materials (Baldewa and Joshi 2012; Coussot et al. 2002b; Divoux et al. 2011; Divoux et al. 2012; Gibaud et al. 2009; Gibaud et al. 2010; Gopalakrishnan and Zukoski 2007; Grenard et al. 2014; Kamp and Kilfoil 2009; Sprakel et al. 2011) and by computer simulations in colloidal gels (Landrum et al. 2016). A common aspect in all these observations is that the compliance, $J(t) = \gamma(t)/\sigma$, which temporarily exhibits an apparent plateau, demonstrates a sudden upturn indicating that the sample starts flowing. The delay time associated with such yielding exhibits an inverse power law dependence on stress (Gopalakrishnan and Zukoski 2007), though an exponential dependence has also been reported in the literature (Gibaud et al. 2009; Grenard et al. 2014; Sprakel et al. 2011). Therefore, this behavior, in principle, suggests a possibility of a material to yield at any stress, around the apparent yield stress, if one waits for a long enough period of time. Furthermore, it has been observed that during yielding, the flow field may become heterogeneous exhibiting shear bands, bulk flow regions, and slip at the boundary, with the nature of heterogeneity being sensitive to interparticle interactions and detailed system microstructure (Divoux et al. 2011; Divoux et al. 2016; Divoux et al. 2012; Gibaud et al. 2009; Gibaud et al. 2010; Grenard et al. 2014). Note that creep curves associated with the delayed yielding do not participate in the time-ageing time superposition (Baldewa and Joshi 2012).

In a completely opposite behavior, a soft glassy material subjected to stresses around the yield stress that cause flow for a prolonged time has been observed to suddenly get arrested (Christopoulou et al. 2009; Joshi et al. 2012; Negi and Osuji 2010a; Shukla and Joshi 2009). Both these behaviors stem from strong alteration of relaxation time distribution that in turn affects the strain field generated for a given stress and suggest that the yield stress has complex dependence on t_w when the materials are subjected to stress.

As expected, ageing also affects the stress relaxation after a step strain. Under such conditions, typically the stress relaxation gets sluggish with increasing ageing time (t_w) (Bandyopadhyay et al. 2010). All stress relaxation curves obtained at different t_w usually show the same curvature leading to a time-ageing time superposition when shifted suitably on a logarithmic time axis (Kaushal and Joshi 2014).

In a step shear rate experiment, the stress evolution is often used to analyze a material's viscoelastic character and yielding response. In several soft glassy materials or even concentrated hard-sphere suspensions, the stress shows an overshoot before reaching a steady-state value (Koumakis et al. 2016). However, unlike in any equilibrium viscoelastic material and even in the absence of any time evolution of the linear viscoelastic moduli (such as in the case of hard-sphere glasses), the

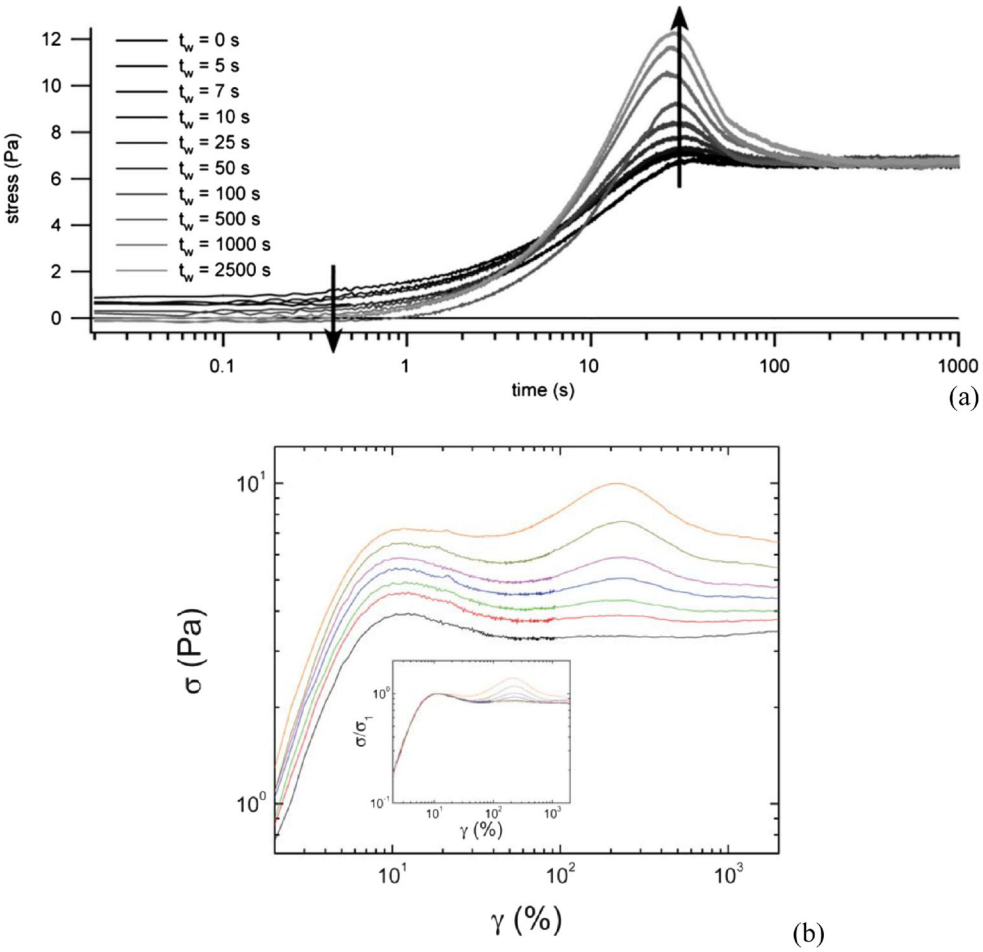


Fig. 8 Effect of ageing in the non-linear transient rheology: **a** Stress overshoot subsequent to application of step shear rate at different waiting times for ultra-soft multi-arm star glass (reprinted with permission from Rogers et al. (2010). Copyright 2010, The Society of Rheology. The magnitude of the overshoot is increasing with waiting time. **b** Similar stress overshoots as a function of waiting time (increasing waiting time from bottom to top) in attractive colloid-polymer gels. Note the evolution of the second stress overshoot (inset of **b** where the stress is normalized by the stress at the first overshoot) as the gel ages (figure adapted from Koumakis and Petekidis (2011) with permission of The Royal Society of Chemistry)

magnitude of the overshoot has been observed to increase with increasing t_w (Derec et al. 2003; Koumakis et al. 2016; Siebenbürger et al. 2012). Such increase mainly affects the strength of the overshoot, while the long time steady-state stress remains the same (see Fig. 8a), as has been detected in various yield stress soft glassy materials from hard-sphere glasses, glasses of core-shell microgels, waxy crude oil, clay suspensions (Dimitriou and McKinley 2014; Koumakis et al. 2016; Rogers et al. 2010; Siebenbürger et al. 2012), as well as for multi-arm star polymers as shown in Fig. 8a (Christopoulou et al. 2009). Another example is shown for attractive colloidal gels in Fig. 8b where in a two-step yielding process, the second stress overshoot is found to be affected stronger by ageing due to large scale coarsening of the gel microstructure with waiting time as also found in similar systems by computer simulations (Zia et al. 2014). The double overshoot is another manifestation of the two-step yielding due to the existence of two confining mechanisms at two distinct length-scales, the bond range, and the cage size in attractive glasses (Pham et al. 2008) or the cluster size in lower volume fraction colloidal gels (Koumakis and Petekidis 2011). Therefore, the stronger ageing dependence of the second overshoot reflects the structural evolution and the coarsening of the gel at the cluster length-scales level. This points out to the microscopic origins of thixotropy in these systems; moreover, it relates with the mechanism via which mechanical properties can be tuned by pre-shear as discussed above. In fact, it has been shown that the two-step yielding process itself can be also altered by pre-shear with the second overshoot being promoted through by specific pre-shear conditions, which create larger structural inhomogeneities (Koumakis et al. 2015; Moghimi et al. 2017).

Ageing under quiescent (or weak flow) conditions and rejuvenation under strong flow conditions are characteristic features of the soft glassy materials (Cipelletti and Ramos 2005). During rejuvenation under strong flow field as the material gets fluidized, all relaxation modes get faster as the arrested entities diffuse out of their respective physical cages thereby acquiring a higher energy states. However, for some materials, moderate flow fields have been observed to cause a bifurcation of the relaxation time spectrum in such a way that some of the entities that diffused out of their cages or constraints get trapped in deeper ones. This causes the relaxation of a material to get

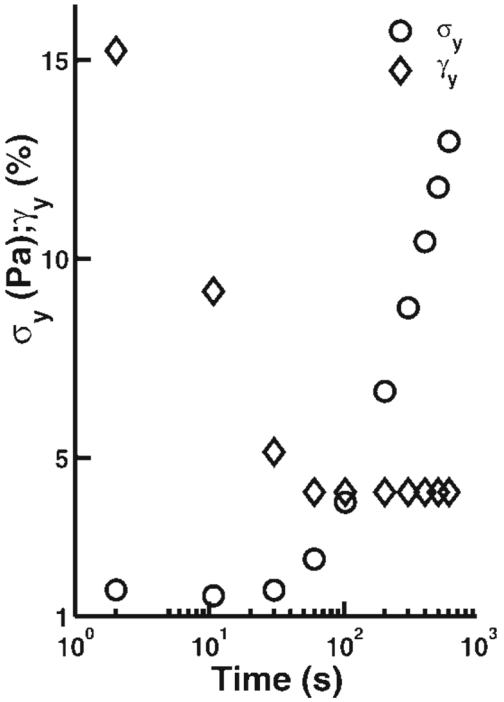


Fig. 9 Yield stress and yield strain are plotted for an aqueous suspension of Laponite as a function of waiting time. The yield stress and yield strain have been obtained by examining the stress-strain curve and denoting the yield point where the slope deviates more than 5% from linearity. It can be seen that the yield stress remains constant initially and then increases as a function of time. Reprinted with permission from Negi and Osuji (2010c). Copyright (2010) by the American Physical Society

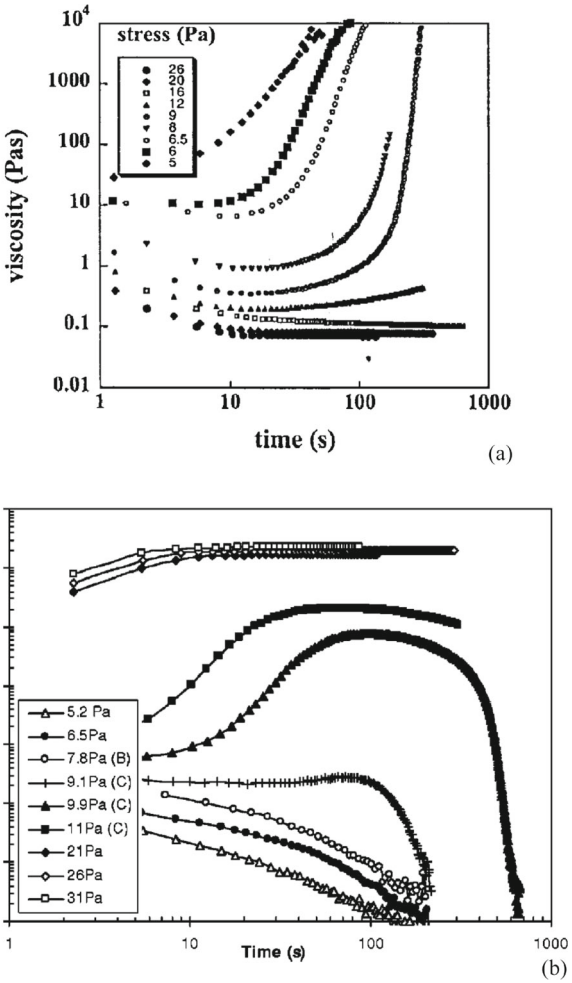


Fig. 10 **a** Bifurcation of viscosity as a function of time for a 4-wt% bentonite suspension above and below the yield stress (reprinted with permission from (Coussot et al. 2002a). Copyright (2002) by the American Physical Society). **b** Viscosity bifurcation represented in terms of evolution of shear rate for 4.5-wt% bentonite suspension. For intermediate stress of 9.9 Pa, delayed solidification can clearly be seen (reprinted with permission from Coussot et al. (2002b). Copyright 2002, The Society of Rheology)

slower over certain timescales and is related with the shear-induced over-ageing detected by multispeckle DWS as discussed above (Viasnoff and Lequeux 2002). The same phenomenon could be viewed in the compactification of clusters at intermediate volume fraction colloidal gels under weak steady shear or intermediate strain amplitudes under oscillatory shear that leads to microstructural evolution towards phase separation that would otherwise be very slow or not possible at all under quiescent conditions (Koumakis et al. 2015; Moghimi et al. 2017). Interestingly, soft glassy rheology (SGR) model proposed by Sollich and coworkers qualitatively predicts the over-ageing behavior (Kaushal and Joshi 2016b; Viasnoff et al. 2003). It is important to note that not all ageing soft glassy materials demonstrate over-ageing. Over-ageing has also been reported for molecular glasses (Lacks and Osborne 2004; Wallace and Joós 2006).

The phenomena of ageing and rejuvenation demonstrated by soft glassy materials are linked with their thixotropic character (Mewis and Wagner 2012; Moller et al. 2009). However, the mere presence of thixotropy does not render a material a yield stress. It has been observed that the materials that show strong slow relaxation time, as well as G' enhancement with t_w, exhibit peculiar yielding characteristics (Coussot et al. 2002b; Paredes et al. 2011). One such prominent example is aqueous suspension of Laponite that shows constant yield stress up to a certain age followed by a logarithmic increase as shown in Fig. 9 (Negi and Osuji 2010c). Interestingly, the corresponding yield strain has been observed to decrease with age over a duration when yield stress remains constant (Negi and Osuji 2010c). On the other hand, the yield strain reaches a plateau when yield stress starts increasing. This unusual behavior has been attributed to non-monotonic constitutive relationship (steady-state shear stress-shear rate) (Coussot et al. 2002b). Joshi (Joshi 2015) proposed that non-monotonic steady-state flow curve is possible only when τ increases faster than linearly with t_w in addition to the modulus showing a logarithmic or stronger increase with time, with both these conditions detected in Laponite suspensions (Negi and Osuji 2010c; Shahin and Joshi 2012a).

This discussion makes it amply clear that for ageing materials, there exists a threshold stress—that depends on time—below which the material indeed undergoes a creep deformation with diminishing increment in creep compliance and eventually reaches a constant plateau leading to flow halt in a delayed solidification scenario (Ballesta and Petekidis 2016; Christopoulou et al. 2009). Just above this threshold, on the other hand, the compliance induced in the material keeps on increasing leading to a steady flow. This phenomenon wherein below and above the threshold stress viscosity keeps on increasing (and approaches infinity), whereas below this stress it decreases to a constant value that has been used to define the yield stress (Cloitre et al. 2000), was termed as viscosity bifurcation and is observed for variety of soft glassy materials (Baldewa and Joshi 2012; Ballesta and Petekidis 2016; Christopoulou et al. 2009; Coussot et al. 2002b; Vasu et al. 2013). In Fig. 10, a typical viscosity bifurcation behavior is plotted for a bentonite suspension and the corresponding threshold stress has been used to determine the yield stress. A comparison of this definition with other conventional definitions of yield stress is discussed in detail next.

Definitions and methods to determine the yield stress

In the literature, various methods have been employed to determine the yield stress by continuous and/or oscillatory shear. Depending upon the exact experimental protocol, the estimated yield stress can be characterized as static or dynamic (Bonnecaze and Brady 1992; Pham et al. 2008). For example, during a *start-up shear experiment*, the stress may exhibit a peak after an initial linear increase with strain and before reaching a steady-state flow. In this case, the static yield strain is defined at the peak stress beyond which a material starts to flow. In such an experiment, the values of the steady-state stress reached after the maximum maybe used to determine the dynamic yield stress at the limit of zero shear rate upon decreasing shear rates progressively along the *flow curve*. Moreover, by subjecting the initially quiescent material to increasing deformation field and noting the point at which a material starts not to fully recover upon stress removal (*creep and recovery*), one can define an elastic yield stress (Petekidis et al. 2004; Pham et al. 2008). This point may be near or above the limit of linear stress-strain response. Beyond this point, the system may deform plastically. Such plastic deformation may occur before the stress peak or the steady-state regime, where it finally reaches flow with a constant viscosity during start-up shear test. In a creep flow field, the application of stress below the static yield stress leads to a strain plateau, while for the stresses above the static yield stress, the strain continuously increases as a function of time showing viscosity bifurcation.

Depending upon the history dependence of a material, the static and dynamic yield stresses may significantly differ from each other. For thixotropic materials, the dynamic yield stress is always smaller than or equal to the static yield stress as the protocol for determining the former (for example a progressive decrease of the shear rate in a flow curve) does not allow a material to rebuilt the structure (or age), at least fully. Both yield stresses can also be obtained by applying *large amplitude oscillatory shear*, wherein a material is subjected to an increasing or decreasing stress or strain amplitude at a constant frequency. Monitoring a decrease in G' (often coinciding with the limit of linearity and harmonic response), a peak in G'' (point of maximum dissipation) and a cross-over point of G' and G'', respectively, leads to yield stress/strain related to deviation from linearity, maximum energy dissipation, and the point where viscous response starts dominating over the elastic one. The counterparts of the first two under steady shear were the ones identified above and defined as the elastic and static yield stresses/strains.

In oscillatory shear, the values of resultant yield stress (or strain) depend also on the frequency, as well as on the ramp rate, as they depend on rate of deformation under steady shear. While the yield stress obtained by various methods does differ, the difference is usually not significant (Dinkgreve et al. 2017; Pham et al. 2008). Various issues associated with different yield stress/strain measurement techniques have been recently discussed by Dinkgreve and coworkers (Dinkgreve et al. 2016). Moreover, conventional as well as non-conventional techniques including those employed in industry are also discussed by Coussot (Coussot 2005).

The above defined yield stress determinations assume that the material does not evolve with time and therefore, they represent a time invariant quantity. Ageing not only complicates the determination of yield stress/strain quantities but introduces the need of additional definitions and analysis. For strongly physically ageing (thixotropic) materials though, one gets a time-dependent yield stress (see Fig. 9) (Negi and Osuji 2010c; Shaukat et al. 2012b). Furthermore, in ageing systems, strain evolves under constant stress (creep) to eventually reach a plateau (shear rate approaching zero and viscosity diverging) reflecting a solid-like response below the yield stress (Baldewa and Joshi 2012; Coussot et al. 2006; Petekidis et al. 2004; Uhlherr et al. 2005). Above the yield stress, the sample eventually flows with a constant viscosity, even if one has to wait for some, often long, time. The critical stress at which this viscosity bifurcation occurs has been termed as a threshold that separates solid-like from liquid-like behavior. *This definition suggests the yield stress as the lowest stress at which, if we wait adequate time, the sample will reach a final steady state with constant viscosity.*

As observed experimentally (Cloitre et al. 2000; Joshi and Reddy 2008), the mean relaxation time (τ) shows a power law

dependence on time: $\tau = A\tau_m^{1-\mu}t^{\mu}$, with power law exponent (μ) that decreases with the applied stress and eventually goes to $\mu = 0$. Since in a completely rejuvenated state ($\mu = 0$), the relaxation time is given by $\tau = A\tau_m$, where A is a factor associated with the relaxation time, which does not depend upon ageing. In Appendix II, we solve the single mode Maxwell model with a time-dependent relaxation time $\tau = A\tau_m^{1-\mu}t^{\mu}$. Our calculation suggests that for $\mu > 1$ (hyper-ageing), the strain reaches a plateau over finite creep time, while for $\mu \leq 1$, it is expected to reach a plateau only in the limit of infinite creep time. Furthermore, for $\mu > 0$, the material undergoes indefinite viscous deformation before reaching a plateau. Interestingly, the minimum stress to stop ageing ($\mu = 0$) is the same as the minimum stress for which material attains a steady state. Note that real materials have distribution of relaxation times; however, if any of the modes age with time ($\mu > 0$), the material will not reach a steady state. Consequently, this minimum stress should be equivalent to the minimum stress to reach a steady-state viscosity at some point during the viscosity bifurcation (as steady state requires no ageing). Therefore, the yield stress obtained from viscosity bifurcation study should coincide with the minimum value of stress for which $\mu = 0$. Although the minimum value of stress that is necessary to completely erase ageing leading to a steady flow in a material is an important information, whether this should be identified as the yield stress is probably still a matter of semantics as the material can indeed undergo indefinite viscous flow below this stress.

Therefore, the protocol used to obtain the yield stress, particularly for ageing systems, depends on its precise definition. Currently, there is no clear criterion to suggest that any definition is more accurate than the others as each one portray an important information about the yielding behavior of a material. Nonetheless, while choosing a protocol to obtain the yield stress, not only an intended application but also the corresponding flow field and timescales of application are needed to be taken into account.

Shear banding

Ageing yield stress materials have been observed to show steady state as well as transient shear banding. Shear banding is common wherever a yield stress fluid is experiencing a flow field with stress gradient. The stress gradient is very common in the pressure flows through pipe or slit (Bird et al. 1987). However, there are a number of studies wherein many ageing soft glassy materials demonstrate steady as well as transient shear banding in a simple shear flow in which stress across the flow field, in principle, remains constant (Balmforth et al. 2014; Divoux et al. 2016; Kurokawa et al. 2015; Martin and Thomas Hu 2012; Ovarlez et al. 2009; Paredes et al. 2011). In a typical example, as shown in Fig. 11a for bentonite suspension, it has been observed that when the shear rate of a flowing soft glassy material having very high shear rate with homogeneous flow profile has been dropped below a certain critical shear rate ($\dot{\gamma}_c$), shear banding is observed with coexisting regions of flowing and stationary bands. By increasing the imposed shear rate ($\dot{\gamma}_i$), the width of the flowing band increases, and in a limit of $\dot{\gamma}_i = \dot{\gamma}_c$, the stationary band vanishes. The shear rate in the flowing band has always been observed to be equal to $\dot{\gamma}_c$, if $\dot{\gamma}_i < \dot{\gamma}_c$ (Kurokawa et al. 2015; Ovarlez et al. 2009; Paredes et al. 2011). Interestingly, the non-monotonic steady state-shear rate constitutive relationship explains the observed experimental behavior very well, wherein $\dot{\gamma}_c$ is the minimum shear rate associated with the non-monotonic constitutive curve (Coussot et al. 2002b; Joshi 2015). Consequently, below $\dot{\gamma}_c$, the flow is linearly unstable. On the other hand, if a shear rate is imposed on the material after allowing it to age, transient as well as steady-state shear

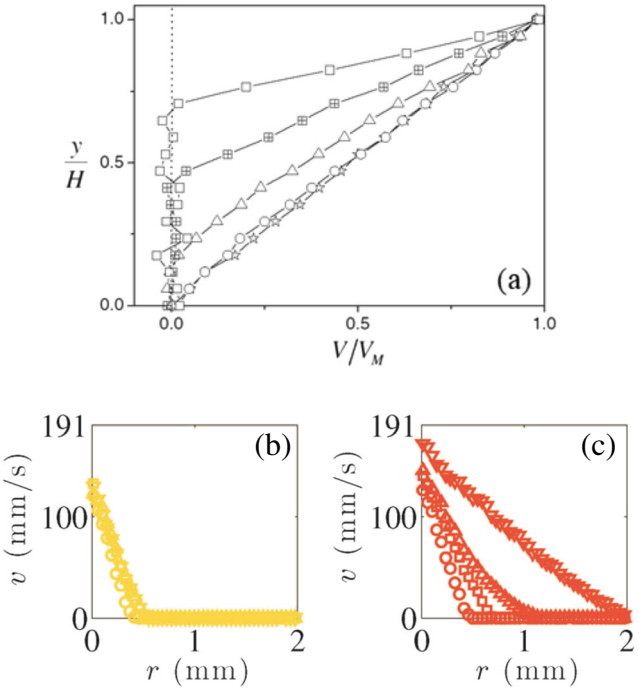


Fig. 11 **a** Velocity (V) is plotted as a function of fractional distance (y/H) from the stationary bottom plate for bentonite suspension. V_M is the maximum velocity associated with top moving surface. The various apparent steady-state velocity profiles correspond to those obtained after step down in shear rate from a large value to a small value. With increase in a magnitude of the final velocity (curves top to bottom), the flowing band expands and eventually the flow becomes homogeneous. Reprinted by permission from Springer Nature from (Ovarlez et al. 2009). **b** and **c** Velocity (v) is plotted as a function of distance to rotor (r) for Ludox gel. In these experiments, after the rejuvenation, the sample was kept at rest for different times: **b** 100 and **c** 30 min before applying shear rates. The various velocity profiles belong to different times (circles 30 s, squares 400 s, up triangles 800 s and down triangles 1100 s) after applying the shear rate of 100/s. Figures adapted from Kurokawa et al. (2015). Published by The Royal Society of Chemistry

banding is observed as shown in Fig. 11c, b, respectively (Kurokawa et al. 2015; Martin and Thomas Hu 2012). Particularly for smaller values of $\dot{\gamma}_i$, the flowing band shrinks during a transient eventually leading to steady-state shear banding. On the other hand, for higher values of $\dot{\gamma}_i$, the flowing band expands leading to steady shear banding. With increase in $\dot{\gamma}_i$, the width of stationary band decreases in such a way that at high value of $\dot{\gamma}_i$ steady-state banding completely disappears (Martin and Thomas Hu 2012). Kurokawa et al. (2015) observed steady-state shear banding for an aged Ludox gel even for $\dot{\gamma}_i > \dot{\gamma}_c$. At higher shear rates ($\dot{\gamma}_i >> \dot{\gamma}_c$), the material eventually demonstrates homogeneous flow, although during the transient wall slip and (transient) shear banding take place accompanied by spike-like events in the stress overshoot. The observed shear banding behaviors in both Laponite suspensions and Ludox gels, which show significant physical ageing, have also been attributed to non-monotonic steady state-shear rate constitutive relationship, wherein a balance of rejuvenation in the flowing band (close to rotor) with ageing in the stationary band (close to stator) controls the nature of transient banding and the threshold for steady-state banding (Coussot and Ovarlez 2010). Moreover, the boundary conditions have also been observed to influence on the shear banding behavior. Gibaud et al. (2008, 2009) observed that for a Laponite suspension, during start-up shear, smooth walls leading to wall slip induce fragmentation of suspension which eventually results in homogeneous flow. For rough walls that ensure no-slip conditions, on the other hand, steady-state shear banding is observed. Recently, Mendes et al. (2015) reported shear banding for thixotropic waxy crude oil whose banding behavior showed strong dependence on the temperature history of the same. Therefore, shear banding behavior might be affected by sample history, loading, and other effects, which may introduce heterogeneities in the system that will then promote banding (Ovarlez et al. 2013a).

Recently, Fielding (2016) proposed that in order to observe transient shear banding, the stress needs to be a decreasing function of strain before attaining a steady state. Equivalently, in order to observe steady-state shear banding, the stress needs to be a decreasing function of shear rate. Interestingly, a different kind of shear banding is reported for hard-sphere suspension, which does not require flow curve to be non-monotonic or any shear localization. This kind of shear banding is attributed to an instability due to shear-concentration coupling and to migration of particles towards the low shear rate region within a flow field. This occurs due to strong dependence of the yield stress on the concentration, so that a small variation in the latter leads to a banded profile (Besseling et al. 2010). Note that in such hard-sphere glasses, shear banding is observed in steady state at very low shear rates, where essentially no stress overshoot is seen in start-up shear, whereas at higher rates stress overshoots are indeed observed without necessarily been related with shear banding as suggested by complementary computer simulations (Koumakis et al. 2012a; Koumakis et al. 2016). Recently, Jain et al. (2018) solved the fluidity model proposed by Coussot et al. (2002b) that employed inelastic constitutive relation and showed that there is no correlation between the stress overshoot and shear banding. In a stress-controlled or a rate-controlled flow field, shear start up experiments on Carbopol gel show that system does remain in shear banded state over a time that varies in an inverse power law fashion as a function of stress in excess of yield stress for the former (Divoux et al. 2011) or shear rate for the latter (Divoux et al. 2010; Divoux et al. 2012). Transient shear banding has also been reported for various kinds of other non- or weakly ageing yield stress materials (Grenard et al. 2014; Ovarlez et al. 2013a).

Residual stresses

Soft glassy materials, under application of constant strain, exhibit incomplete stress relaxation leading to residual stresses. Residual stresses have been reported for aqueous suspension of Laponite (Negi and Osuji 2010b), microgel glasses (Ballauff et al. 2013; Mohan et al. 2013; Mohan et al. 2015), Carbopol microgels (Lidon et al. 2017), hard-sphere glasses (Ballauff et al. 2013), and colloidal gels (Moghimi et al. 2017). Usually, it is observed that the extent of relaxation increases with increase of the preshear shear rate (Ballauff et al. 2013; Mohan et al. 2013) as shown in Fig. 12 for the hard-sphere suspensions. Lidon et al. (2017), however, did not observe any effect of duration of pre-shear on the residual stresses. Figure 12 also suggests that below the concentration associated with glass transition (< 0.58), the stress is expected to relax fully, while in the glassy regime significant residual stress remains over the practical timescales. Similar findings

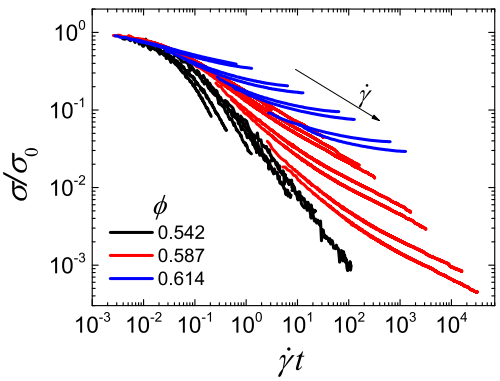


Fig. 12 Normalized stress is plotted as a function of $\dot{\gamma}t$ for three concentrations of hard-sphere particles, where $\dot{\gamma}$ is the steady-state shear rate prior to measuring the stress relaxation. The figure shows that above the concentration associated with the glass transition (> 0.58), the relaxation of stress is incomplete. Furthermore, for a given concentration of the suspension, greater extent of relaxation is observed for increase in $\dot{\gamma}$. The data taken from (Ballauff et al. 2013)

have been revealed by computer simulations and mode coupling theory by Ballauff et al. (2013), although the latter predicts an ideal stress plateau that is not observed in real systems. Simulations on jammed non-Brownian elastic microgel spheres attributed the long-time relaxation and residual stresses to local in cage adjustments of the elastic contacts among the particles (Mohan et al. 2013). They propose that while the contacts reorganize locally, the process is cooperative: a slight movement of a facet causes a reorganization far apart. Such cooperativity is responsible for long-time modes in the stress recovery (Mohan et al. 2013). By solving a fluidity model, Joshi (2015) suggested that residual stresses could originate from a stronger than linear increase of the relaxation time with respect to waiting time during physical ageing that makes relaxation of stress difficult over the usual observation timescales. It is important to note that the simulations as well as the experimental results show a partial relaxation of stress before plateauing out. This behavior, therefore, suggests two possibilities depending upon whether ageing is responsible for residual stresses or not. In a non-ageing or weakly (weaker than linear dependence) ageing systems, subsequent to rejuvenation (or shear switch-off), some relaxation modes remain finite leading to partial relaxation, while the remaining modes diverge giving rise to residual stresses. In hyper-ageing systems, on the other hand, stress is unable to relax over typical observation times as the stress relaxation time grows stronger than linear with respect to waiting time.

Modelling approaches for the physically ageing soft glassy materials

In this section, we discuss various modeling approaches aiming to capture the rheology of ageing yield stress systems. It is important to note that the rheological behavior of a material is primarily dictated by its internal relaxation time spectrum. Interestingly, in soft glassy materials, individual modes in the spectrum age differently governed by the distinct time evolution of the microstructure at different length-scales as the system explores lower energy states as a function of time. On the other hand, individual modes in the relaxation spectrum may also have unique deformation field dependency. As a result, the time and deformation field dependence of the relaxation spectrum determines the rheological behavior of the material. Clearly, modeling such complex dependencies for a given microstructure is not an easy task. However, efforts have been made to qualitatively describe and connect the microscopic physical processes with the macroscopic rheological response. Some of the common phenomena detected in soft glassy materials can be qualitatively explained by considering a single relaxation mode and its ageing and rejuvenation. On the other hand, some distinct responses certainly emanate from a spectrum of relaxation processes, which may also age or get rejuvenated differently. Modeling efforts can be divided broadly into three groups, namely fluidity models, the more rigorous SGR model, and computer simulations.

Phenomenological toy or fluidity models

The fluidity models have been developed to phenomenologically represent a thixotropic response and have been extensively reviewed in literature (Coussot et al. 2002b; Joshi 2014a; Mewis and Wagner 2009). This class of models is simplistic in their mathematical construction, with primary objective to capture the basic features of the underlying physics. Typically, a fluidity parameter λ is considered as a measure of the extent of structure formation in a material (Coussot et al. 2002b; Mewis and Wagner 2009) or inverse of characteristic relaxation time (Derec et al. 2001). In a most general representation, the evolution of λ is expressed as (Coussot 2007; Moorcroft et al. 2011):

$$\frac{d\lambda}{dt} = \frac{1}{\theta} - c\left(\lambda, \dot{\gamma}\right) + D\frac{d^2\lambda}{dy^2} \tag{2}$$

wherein the first term on the right represents physical ageing with θ being the timescale associated with λ evolution while the second term, which is a function of the shear rate is related with shear-induced rejuvenation. The third term denotes diffusion of the fluidity in the neighborhood of the flow (Moorcroft et al. 2011). The majority of the fluidity models contain only the growth and the decay terms, which influence the fluidity evolution without the diffusion term. Some models do contain more complicated ageing terms that also depend on deformation field. The diffusion term has been a part of some of the recent fluidity models (Moorcroft et al. 2011) and is particularly useful when model is to be solved for a specific geometry. It describes mobility effects in the region surrounding the one under consideration and smoothens the variation of λ at an interface of strongly ageing and rejuvenating regions. In addition to Eq. (2), a constitutive equation relating stress, strain, and their derivatives is also necessary. Finally, the relationship between λ and the rheological parameters of the constitutive relation, such as viscosity, modulus etc., complete the fluidity model (Mewis and Wagner 2009). By virtue of single parameter that describes the structure, this class of models usually has only a single relaxation mode (Joshi 2015). However, fluidity models with multiple λ parameters leading to relaxation spectrum have been proposed in the literature (Wei et al. 2016). Furthermore, since many experimental responses do not require consideration of viscoelasticity, an inelastic generalized Newtonian constitutive equation has been observed to be sufficient (Coussot et al. 2002b).

The strength of the fluidity models is in their simplicity and ability to capture the basic physical behavior. Depending upon the relationship between rheological

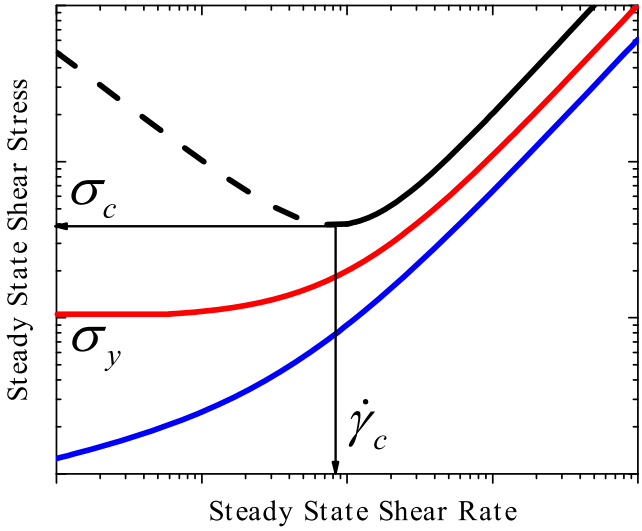


Fig. 13 Prediction of the fluidity models depending on relationship between fluidity and rheological parameters. Typically, the flow curves representing monotonic, plateau in a low shear rate regime (constant yield stress), and non-monotonic relationships between steady-state shear stress and shear rate are predicted

properties and λ, fluidity models typically predict three types of steady-state stress-strain rate relationships (flow curves), namely monotonic, non-monotonic, and with a low shear rate plateau as shown in Fig. 13 (Coussot et al. 2002b). Monotonic flow curves represent an ageing thixotropic material without yield stress or with a constant yield stress in the case when a stress plateau is measured in the limit of low shear rates. The non-monotonic flow curve, on the other hand, represents an ageing thixotropic material with a time-dependent yield stress whose minimum value is the value of stress associated with the minimum in the flow curve (σ_c). A material with such non-monotonic flow curve exhibits a constant yield stress σ_c only for a finite time after a strong shear melting; however, beyond a certain time though the yield stress starts increasing as shown in Fig. 9 (Joshi 2015; Negi and Osuji 2010c). The mechanism linking non-monotonic flow curves with the time-dependent yield stress is discussed elsewhere (Coussot et al. 2002b; Joshi 2015).

The branch of a flow curve having negative slope is always linearly unstable and is indicated by a dashed line in Fig. 13. As a result, in a rate-controlled shear flow experiment, a fluidity model predicts shear banding when an applied shear rate is in the unstable region. In such case as mentioned above, a non-flowing band coexists with a band flowing the characteristic shear rate ($\dot{\gamma}_c$) and the width of non-flowing band shrinks, while that of flowing band broadens with increasing shear rate, as observed experimentally (Coussot et al. 2002b; Kurokawa et al. 2015; Moller et al. 2009; Paredes et al. 2011). Recently, a fluidity model was proposed by considering ageing and rejuvenation to cause a decrease and increase of free energy, respectively (Joshi 2015). Within this approach in order to have non-monotonic flow curve, the relaxation time must grow faster than linearly and the material should exhibit an enhancement in modulus with time, as has indeed been found in some systems (Martin and Thomas Hu 2012; Ovarlez et al. 2009; Paredes et al. 2011). Moorcroft et al. (2011) solved a fluidity model with a diffusivity term that exhibits a low shear rate yield stress plateau. They observed that the stress overshoot during the start-up shear experiment gets more pronounced with increasing ageing time and reported transient shear banding, which they associated with the observed stress overshoot. Recently Radhakrishnan et al. (2017) showed that a fluidity model with non-monotonic flow curve explains the hysteresis during the up and down shear rate ramp seen in ageing systems, which is accompanied by shear banding.

Fluidity models for which the flow curve is monotonic with a low shear rate stress plateau as well as those that exhibit a non-monotonic flow curve both show viscosity bifurcation (Coussot et al. 2002b). In the latter case, however, the stress at which the viscosity bifurcation occurs increases with time. Furthermore, Joshi (2015) reported slowing down of rate of ageing as stress is increased and absence of ageing for stresses above the yield stress, which is in qualitative agreement with observations by Cloitre et al. (2000) (Fig. 7). However, since usually fluidity models include only a single relaxation mode, they cannot predict delayed yielding, delayed solidification and over-ageing behaviors that are attributed to alteration of relaxation time spectra by the applied deformation field.

Soft glassy rheology model

Sollich et al. (1997) proposed the SGR model that along with subsequent papers (Fielding et al. 2000; Sollich 1998) constitutes an exhaustive model of soft glassy materials that exhibit ageing and yield stress. The model considers mesoscopic entities as the building blocks that are sufficiently large in number and are trapped in energy wells whose depths (E) are assumed to follow a distribution given by: $\rho(E) = \exp(-E/\langle E\rangle)/\langle E\rangle$, with the average energy well equal to the thermal noise, $x=k_BT$, at the glass transition such that $x_g = k_BT_g = \langle E\rangle$. The Boltzmann distribution $P_{eq}(E) \propto \rho(E)\exp(E/x)$ is not normalizable for $x \leq x_g$; as a result, the system is not able to reach the steady state. Consequently E must increase with time, thereby inherently showing ageing (Bouchaud 1992). Under the application of a strain field (γ), the material is assumed to deform affinely such that individual elements gain energy $\left({}^1/_2 k\gamma^2\right)$, altering the energy barriers to: $E-{}^1/_2 k\gamma^2$, and hence the cage diffusion times to: $\tau = \tau_0 \exp\left[E-{}^1/_2 k\gamma^2\right]/x$. Thus, SGR predicts an element escape out of an energy well by two scenarios, thermally activated and/or strain induced. Upon escape, an entity chooses its potential well randomly from a preassigned distribution, $\rho(E)$. While global

strain induced in a material is affine, an individual element gets in an unstrained state upon escape from the potential well, which makes strain inhomogeneous over different elements. Sollich et al. (1997) proposed the evolution of the occupancy probability, $P(E, \gamma, t)$, of finding an element arrested in a well with depth E, subjected to strain γ at time t. The stress is then obtained by averaging the strain over all the elements, $\sigma = \langle k\gamma \rangle$, and expressing it in terms of $P(E, \gamma, t)$. The complete SGR model including detailed procedures for its solution can be found elsewhere (Fielding 2000; Fielding et al. 2000; Kaushal and Joshi 2016b).

The SGR model has a single model parameter x that determines the state of a material, which for $x \leq x_g = 1$ shows physical ageing. By virtue of having a distribution of relaxation times, with individual modes evolving with time and altered by external deformation, SGR qualitatively predicts many experimental rheological findings, such as flow curves with yield stress plateau following a Hershel-Bulkley behavior: $\sigma - \sigma_y = \dot{\gamma}^{1-x}$. The model also predicts simple ageing in the absence of a deformation field. In creep and the stress relaxation experiments, it predicts a progressive slowing-down of the dynamics with ageing time in agreement with experiments. Furthermore, the model predicts a stress overshoot in start-up shear whose magnitude goes on increasing with ageing. Very importantly, the model predicts, as an inherent feature, over-ageing wherein deformation field induced uneven alteration of the relaxation time distribution causes overall a faster slowing down of the dynamics under stress than at rest (Viasnoff et al. 2003). However, there are many soft glassy materials that do not demonstrate over-ageing. This discrepancy between model prediction and the real behavior (for some materials) could be due to an intrinsic feature of SGR model that does not foresee any correlation between the potential well depths before and after cage escape (Kaushal and Joshi 2016b). Moreover, the SGR model has been extended to include an evolution of the noise parameter x to account for fluidity in the vicinity of the neighboring elements. Such extension leads to the prediction of a non-monotonic steady flow curve (as in Fig. 13) and to a viscosity bifurcation as well as shear banding (Fielding et al. 2009). Moorcroft et al. (2011) reported transient shear banding within SGR model that was linked to the decreasing part of the stress after the stress overshoot. Radhakrishnan and Fielding (2016) also analyzed the large amplitude oscillatory shear of SGR model and reported strong shear banding that persists even in the limit of small frequencies, while more recently (Radhakrishnan et al. 2017), they analyzed the hysteresis accompanied by shear banding in shear rate ramp experiments.

In comparison to fluidity models, despite being mathematically more complicated, the SGR model provides inherent advantage as it considers ageing in a natural self-consistent manner. Moreover, it describes rejuvenation as a combined effect of strain and activation induced rearrangements. Most importantly through the incorporation of relaxation time distribution, the SGR model predicts those effects that fluidity model cannot. However, the fluidity models, owing to their inherent empiricism and simple mathematical construction, can be easily modified to accommodate additional features that are observed experimentally. Especially with the incorporation of more modes, the predictive capacity of the fluidity models is expected to enhance significantly.

Computer simulations

Several types of simulations have been carried out, at different levels of coarse graining, to investigate the flow of yield stress fluids under constant steady stress, or shear rate, as well as for transient and oscillatory tests, or related to industrial processes, through different geometries around the obstacles. In the latter case, the system is most often simulated as a continuous medium and its flow and deformation is covered by a specific constitutive relation. Although comparison between the experimental data and the simulations show generic agreement in some range of parameters partly providing the predictive power sought in the applications, the lack of underlying physical mechanisms is the main drawback. For detailed review on this topic, the reader may consult recent review articles (Balmforth et al. 2014; Mitsoulis and Tsamopoulos 2017; Saramito and Wachs 2017). Recently, Burghelea et al. (2017) and Sainudiin et al. (2015) proposed the Ising model type of approach that assumes a yield stress material to be made up of microscopic network of particles that when subjected to stress can either assemble forming bonds or to melt breaking bonds. The model considers these dynamics with only two internal parameters that captures some of the macroscopic behaviors of gelation and yielding as a function of time under a given stress field.

The simulations explicitly introducing the interacting constituents at the particle or at more coarse-graining level, which also analyze various interaction forces, provide important insights and direct comparison with the state-of-art experiments at a range of length—and time—scales. These types of simulations include Monte Carlo (MC), molecular dynamics (MD), Brownian dynamics (BD) (including hydrodynamic interaction), Stokesian dynamics (SD), and dissipative particle dynamics (DPD) etc. As an example, BD simulations have been used to study the delayed sedimentation and coarsening of intermediate volume fraction colloidal gels (Landrum et al. 2016; Zia et al. 2014). These simulations reveal detailed microscopic mechanisms, wherein gel evolution is driven by the diffusive migration of particles at an almost liquid-like surface of space spanning clusters in the glassy interior, formed during the process of arrested phase separation. For similar low and intermediate volume fractions, computer simulations (Colombo and Del Gado 2014) probe strain hardening in

transient start-up shear as well as shear banding at low shear rates in agreement with experiments (Ballesta et al. 2013; Besseling et al. 2010). The inclusion of hydrodynamic interactions in such systems allows more accurate comparison with experimental findings in systems such as colloidal gels (Boromand et al. 2017), where BD simulations fail to capture the transient response such as two-step yielding. Nonetheless, for some systems, mainly when large density heterogeneities are not present, such as colloidal glasses, the responses are also well captured by MD or BD simulations where full HI are not included (Ballauff et al. 2013; Koumakis et al. 2013; Koumakis et al. 2012a; Koumakis et al. 2016; Moghimi et al. 2017). As an extended review of computer simulations of yield stress fluids is beyond the scope of this work, the above are just indicative examples of particle based simulations that were directly compared with the experiments.

Conclusions

Structurally arrested soft materials, which are unable to attain thermodynamic equilibrium over practical timescales, are ubiquitous in our day to day life and in industry. Under quiescent conditions, these materials undergo structural reorganization to form more stable states, and despite of having diverse microstructures, show surprisingly similar behaviors, wherein their relaxation dynamics becomes sluggish as a function of time. Interestingly, this physical ageing behavior is reminiscent of that observed in molecular and spin glasses causing this class of materials to be termed as soft glassy materials. During a process of rejuvenation, deformation field, which in principle reverses the effect of ageing, may non-trivially influence the microstructure. Most of the materials in this class also demonstrate yield stress, whose origin itself could be attributed to physical aging that depends on time and deformation field leading to a very complex rheological response.

In soft glassy materials, a spectrum of relaxation time gets profoundly altered by ageing and rejuvenation owing to, respectively, structural reorganization and deformation field induced enhanced mobility. Consequently, competition between these two opposing effects for every individual mode in the spectrum leads to a rich array of rheological behaviors, such as thixotropy, viscosity bifurcation, over-ageing, delayed yielding, delayed solidification, shear banding, and residual stresses, etc. The complex coupling of time and deformation field also influences materials' yield stress, while the richness of the rheological response has led to various definitions of the yield stresses. Over past two decades, independent optical techniques (scattering and microscopy) and in-situ rheological and optical techniques have led to significant insights into the physical behavior of this class of materials. This has opened up new avenues of tailoring and tuning the microstructure of the soft glassy materials to obtain the desired properties.

Theoretically, the SGR model has been able to capture some of the vital physics of microstructural evolution during ageing and rejuvenation associated with individual modes in a spectrum. While mathematically intricate, it predicts most of the generic rheological behaviors demonstrated by this class of materials. In parallel, there have been advances in developing fluidity models that while mathematically simple take into account some of the essential physics and predict major rheological behaviors. However, at present, the majority of these models are limited to a single relaxation mode and therefore are restricted in predictive power. There is clearly a need to develop microstructure specific theoretical models to describe different materials. Similarly, extensive work has also been carried out in simulations that provide crucial information about the nature of physical aging, various consequent rheological behaviors based on specific interparticle interactions.

In view of the above, we have also summarized the various definitions of yield stress, particularly for aging materials that have been proposed in the literature that deviate from the original proposed by Bingham. Different definitions portray important and often complementary information about the yielding behavior of a material. We also touch upon a rather philosophical issue of whether true yield stress exists and conclude that any affirmative answer to such question can always be challenged for not waiting for enough time. Nonetheless, over the practical timescale many systems do show true yielding, but may undergo plastic deformation for stresses below the yield stress for long periods of time. Finally, a designing process to obtain a yield stress material with specific properties and practical application needs to take into account the structural and rheological evolution that it undergoes during aging and rejuvenation over the relevant timescales. We believe that this review provides important insights towards this objective.

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Appendix 1: types of yield stress materials

Historical issue on the existence of true yield stress

Whether the yield stress is a true property or merely an engineering artifact is a perennial question that has been

discussed in the literature over and over again. Traditionally, the yield stress has been termed as that critical threshold below which material deforms only elastically and above which it undergoes viscous (dissipation) flow. The validity of this definition was explicitly addressed by Barnes and Walters (1985) using newly, at the time, developed constant stress rheometer that could measure stress accurately down to shear rates as small as 10^{-6}/s. Their experiments indeed showed a zero-shear viscosity plateau in a limit of very small shear stress that formed a basis of their claim that yield stress is a myth, and fluid indeed flows at all the stresses. They further claimed that at the "so called yield stress" a fluid merely undergoes a transition from high viscosity (slow flow) to a low viscosity (flow). This issue was revisited by Moller et al. (2009) more recently by performing similar experiments, wherein they showed that the apparent viscosity (obtained under constant stress) is a function of measurement time. They observed that by merely increasing the measurement time the apparent viscosity plateau keeps on shifting to the progressively higher values. This observation and estimated dependence of apparent viscosity on timescale of measurement suggested that a material must stop flowing (apparent viscosity tending to infinity) in the limit of long measurement times indicating to the existence of true yield stress. In terms of strain response to constant stress, this observation suggests that for stresses below the yield stress, a material creeps and eventually reaches a constant strain plateau. This behavior is in agreement with Kelvin-Voigt model, which represents a viscoelastic solid (therefore with infinite viscosity), that shows a retarded strain evolution towards a plateau.

The concept of true yield stress indicates a material to behave solid-like, when stressed below this value. However, this concept contradicts the concept of "everything flows" or the notion behind the Deborah number ($De = \tau/t_{obs}$, where τ is the relaxation time and t_{obs} is the observation time) that suggests that materials behave as a viscous liquid in a limit of $De << 1$. Therefore, unless the relaxation time of a material is truly infinite, it is expected to flow in a limit of very long time. Note also that while the work of Moller et al. (2009) indeed shows that there may not be a low zero shear viscosity plateau as reported by Barnes and Walters (1985) over the explored timescales, there is no clear proof that material may not yield after an ever longer time, after reaching a constant compliance plateau in a creep experiment. Interestingly, many systems have been observed to demonstrate delayed yielding wherein an apparently "solid-like" state shows a near constant compliance plateau for a very long time, but then suddenly flow suggesting yielding to be not only a stress controlled but also a time-dependent phenomenon (Baldewa and Joshi 2012; Ballesta et al. 2013; Kamp and Kilfoil 2009; Siebenbürger et al. 2012; Sprakel et al. 2011). Therefore, the question whether true yield stress exists or not may well be considered subject to the timescale of observation. It is therefore safe to assume that when the experimental timescale is smaller than the dominant relaxation time of a material ($De > 1$), it indeed shows close to true yielding behavior. However, when the experimental timescales are large enough such that $De \leq 1$, a material will exhibit some flow even under the application of infinitesimal stress.

Simple (or non-ageing) and thixotropic (or physically ageing) yield stress materials

Few experiments that have convincingly shown that there is a long-time strain plateau under constant stress below the yield stress with Moller et al. (2009) observing this dependence for a very diverse set of materials such as 0.2-mass% Carbopol sample, hair gel, foam, and emulsion. These were not observed to show any time dependency of their linear viscoelastic properties under quiescent conditions and therefore were classified as *simple yield stress fluids*. Similar behavior is also exhibited by the suspension of hard-sphere glasses, where the linear viscoelastic properties seem to not change with waiting time (Ballesta and Petekidis 2016), although the slow internal relaxation does increase with waiting time (see Fig. 3). Therefore, the definition of simple yield stress fluids can be extended to those systems that do not show any noticeable thixotropic loop even though they show time evolution (usually weaker than linear) with modulus remaining practically constant.

On the other hand, systems undergoing physical ageing, when subjected to a constant stress below the yield stress (creep experiments), exhibit a compliance that first increases with time and eventually plateaus out. Since the ageing systems demonstrate inherent thixotropy, these materials were classified as *thixotropic yield stress fluids*. In this case, owing to physical ageing even under stress the relaxation time continuously increases with time. However, if for a given magnitude of applied stress, the average relaxation time grows weaker than linear with respect to time (which is same as t_{obs}), the Deborah number will decrease with the observation time, and a material will eventually flow in a limit of $De << 1$. On the other hand, if an applied stress is such that the relaxation time increases stronger than linear, the Deborah number will continuously increase with the observation time, and in principle, the material will never yield for that stress leading to the true yield

stress. Interestingly, the fluidity model proposed by Joshi (2015) indeed suggests that linear or stronger dependence of relaxation time on time is a necessary condition for observation of (true) yield stress in ageing soft glassy materials. However, it is still an open question whether a material will continue to age with stronger than linear dependence forever; as for aqueous suspension of Laponite, it has been observed that the dependence of relaxation time on the observation time weakens from strong hyperaging dependence to linear ageing over a duration of months (Shahin and Joshi 2012a). Therefore, if eventually the dependence of relaxation time on the observation time indeed weakens, the Deborah number may decrease with the observation time leading to yielding after very long times.

Appendix 2. Creep behavior of ageing single mode Maxwell model

Let us consider a physically ageing single mode Maxwell model with constant modulus G but time-dependent viscosity $\eta(t)$. As observed for many soft glassy materials (Cipelletti et al. 2000; Cloitre et al. 2000; Derec et al. 2003; Kaushal and Joshi 2014; McKenna et al. 2009; Negi and Osuji 2009; Shahin and Joshi 2011; Viasnoff et al. 2003), we assume the mean relaxation time $\tau(=\eta/G)$ follows a power law dependence:

$$\tau(t) = A\tau_{\mathrm{m}}\left(\frac{t}{\tau_{\mathrm{m}}}\right)^{\mu}, \tag{3}$$

where A and τ_{m} are constants, while μ is stress-dependent. The constitutive equation for the Maxwell model is given by:

$$G\tau(t)\dot{\gamma} = \tau(t)\frac{d\sigma}{dt} + \sigma. \tag{4}$$

Using the dimensionless variables such as: $\overline{\sigma} = \sigma/G$ and $\overline{t} = t/(A\tau_m)$, we get:

$$\frac{d\gamma}{d\overline{t}} = \frac{d\overline{\sigma}}{d\overline{t}} + \overline{\sigma}\left(A\overline{t}\right)^{-\mu}. \tag{5}$$

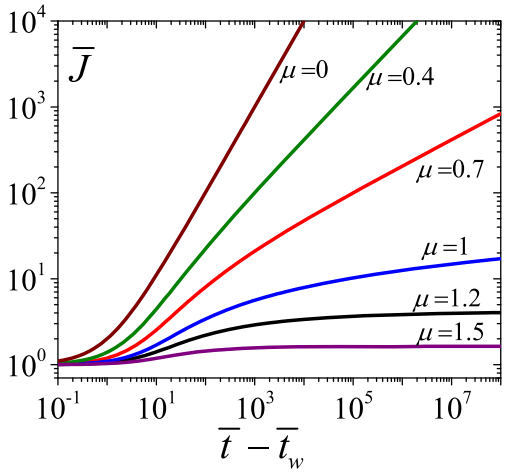

Fig. 14 The dimensionless compliance is plotted as a function of dimensionless creep time for various values of μ for $\overline{t}_{\mathrm{w}} = 10$ as described by Eqs. (8) and (9). It can be seen that for $\mu > 1$, the compliance eventually reaches a plateau for a high value of $\overline{t}-\overline{t}_{\mathrm{w}}$

Here, $A\tau_{\mathrm{m}}$ is the relaxation time associated with the completely rejuvenated state. Let us assume that the material evolved under quiescent conditions $(\overline{\sigma} = 0)$ up to time $\overline{t}_{\mathrm{w}}$ is subjected to constant stress of $\overline{\sigma} = \overline{\sigma}_0$. The corresponding induced strain rate is the following:

$$\frac{d\gamma}{d\overline{t}} = \left(A\overline{t}\right)^{-\mu}\overline{\sigma}_0, \quad \overline{t} > \overline{t}_{\mathrm{w}}. \tag{6}$$

Equation (6) shows that for $\mu > 0$, the shear rate induced in a material must decay $(d\gamma/d\overline{t} \to 0)$ as $\overline{t}-\overline{t}_{\mathrm{w}} \to \infty$. This suggests that steady state in an ageing material is possible only when ageing stops $(\mu = 0)$. Furthermore, for an initial condition of $\gamma(\overline{t}_{\mathrm{w}}) = \overline{\sigma}_0$ (strain induced in spring), the strain induced in the material is given by (Joshi and Reddy 2008):

$$\gamma = \overline{\sigma}_0 + \frac{A^{-\mu}\overline{\sigma}_0}{(1-\mu)}\left(\overline{t}^{\,1-\mu} - \overline{t}_{\mathrm{w}}^{\,1-\mu}\right), \quad \overline{t} \geq \overline{t}_{\mathrm{w}}, \tag{7}$$

which can be written in compliance form as:

$$\overline{J} = 1 + \frac{A^{-\mu}}{(1-\mu)}\left(\overline{t}^{\,1-\mu} - \overline{t}_{\mathrm{w}}^{\,1-\mu}\right) = 1 + \frac{A^{-\mu}}{(1-\mu)}\left(\left[\left(\overline{t}-\overline{t}_{\mathrm{w}}\right) + \overline{t}_{\mathrm{w}}\right]^{1-\mu} - \overline{t}_{\mathrm{w}}^{\,1-\mu}\right), \quad \overline{t} \geq \overline{t}_{\mathrm{w}} \tag{8}$$

where $\overline{t}-\overline{t}_{\mathrm{w}}$ is the dimensionless creep time. For a special case of $\mu = 1$, integration of Eq. (6) leads to:

$$\overline{J} = 1 + A^{-1}\ln\left(\frac{\left(\overline{t}-\overline{t}_w\right)+\overline{t}_w}{\overline{t}_w}\right), \quad \overline{t}\geq\overline{t}_w. \tag{9}$$

We plot $\overline{J}$ as a function of $\overline{t}-\overline{t}_w$ for $\overline{t}_w = 10$ and $A = 1$, for various values of μ in Fig. 14. It should be noted that at any point in time, elastic strain in the material is that of associated with the spring and is given by: $\gamma_s = \overline{\sigma}_0$ (or $\overline{J}_s = 1$). Consequently, viscous strain (strain induced in dashpot) is given by $\gamma_d = \gamma - \overline{\sigma}_0$ (or $\overline{J}_d = \overline{J} - 1$).

Figure 14 shows that for $\mu > 1$, the compliance is eventually set to reach a plateau. Such behavior was indeed experimentally observed by Shahin and Joshi (2011). On the other hand, for $\mu \leq 1$, the compliance is expected to plateau in the limit of $\overline{t}-\overline{t}_w \to \infty$. Discussion on viscosity bifurcation in "Definitions and methods to determine the yield stress" suggests that the yield stress maybe defined as the stress in the limit of $\mu \to 0$, where the ageing stops. The above discussion clearly suggests that material undergoes indefinite viscous flow for $0 < \mu \leq 1$, while undergoing ageing but without attaining a steady state, whereas it achieves a steady-state flow (with constant viscosity) only in a limit of $\mu \to 0$.

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