Delayed solidification of soft glasses: new experiments, and a theoretical challenge

Yogesh M. Joshi,*[a] A. Shahin[a] and Michael E. Cates*[b]

When subjected to large amplitude oscillatory shear stress, aqueous Laponite suspensions show an abrupt solidification transition after a long delay time t_c. We measure the dependence of t_c on stress amplitude, frequency, and on the age-dependent initial loss modulus. At first sight our observations appear quantitatively consistent with a simple soft-glassy rheology (SGR)-type model, in which barrier crossings by mesoscopic elements are purely strain-induced. For a given strain amplitude γ_0 each element can be classified as fluid or solid according to whether its local yield strain exceeds γ_0. Each cycle, the barrier heights E of yielded elements are reassigned according to a fixed prior distribution $\rho(E)$: this fixes the per-cycle probability $R(\gamma_0)$ of a fluid elements becoming solid. As the fraction of solid elements builds up, γ_0 falls (at constant stress amplitude), so $R(\gamma_0)$ increases. This positive feedback accounts for the sudden solidification after a long delay. The model thus appears to directly link macroscopic rheology with mesoscopic barrier height statistics: within its precepts, our data point towards a power law for $\rho(E)$ rather than the exponential form usually assumed in SGR. However, despite this apparent success, closer investigation shows that the assumptions of the model cannot be reconciled with the extremely large strain amplitudes arising in our experiments. The quantitative explanation of delayed solidification in Laponite therefore remains an open theoretical challenge.

1 Introduction

Soft materials such as concentrated suspensions, foams, emulsions and pastes are widely used in products such as foodstuffs, cosmetics, paints, pharmaceuticals, and ceramic precursors. Many of these systems show slow dynamics that are attributed to the trapping or jamming of mesoscopic constituents, creating barriers that the system can cross only slowly.[1,2] Such materials can fall out of thermodynamic equilibrium, evolving by slow "physical aging" towards lower energy states, with progressive slowing down of their relaxational dynamics and rheological response.[3,4] Macroscopic sample deformation can in turn promote barrier-crossing rearrangements, restoring fluidity.[5,6] The resulting interplay between aging, flow and rejuvenation in soft glasses leads to complex rheological effects including overaging,[7,8] viscosity bifurcations,[9–11] and shear banding.[12–15]

Here we present new experiments on a model soft glassy material, an aqueous suspension of Laponite,[16] under oscillatory shear of fixed stress amplitude. Building on a preliminary study,[17] we find that, despite the high fluidity present initially, the

[a]*Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, INDIA. E-mail: joshi@iitk.ac.in; Fax: +91 512 259 0104; Tel: +91 512 259 7993*
[b]*SUPA, School of Physics & Astronomy, University of Edinburgh, James Clerk Maxwell Building, The King's Buildings, Mayfield Road, Edinburgh EH9 3JZ, UK. E-mail: mec@ph.ed.ac.uk; Fax: +44 131 650 5902; Tel: +44 131 650 5296*

material abruptly solidifies after a certain critical time, t_c. Such "delayed solidification" could have serious consequences if it arose, for instance, during the sustained vibratory stresses that arises during transportation (*e.g.*, in road tankers) of soft materials, or in some cases during their manufacture. The sudden solidification of a supposedly fluid formulation risks catastrophic failure of expensive equipment – a situation comparable to the issue of silo rupture, caused when granular materials cease suddenly to flow.[18] The problem is all the more serious because of its apparent unpredictability: nothing obvious about the initial sample indicates that its fluidity will later be lost in this way.[17] The phenomenon of delayed solidification is thereby reminiscent of (and yet almost opposite to) that of "delayed sedimentation" in which an apparently stable colloidal gel suddenly collapses after sustained exposure to gravitational stress.[19] There are some reports in the literature where different soft glassy materials have been observed to undergo delayed solidification in creep flow.[9,11,20] The major difference between these reports and our work is the nature of the applied deformation field. We employ a stress-controlled oscillatory flow field, in which the strain induced in the material remains bounded (and therefore decreases with increasing viscosity and/or elasticity). On the other hand, in creep flow the strain induced in the material never decreases with time.

In this Discussion Paper we attempt to shed light on the physics of delayed solidification, by performing new quantitative experiments to explore the dependence of the delay time t_c on the stress amplitude, frequency, and the (age-related) loss modulus of the sample prior to the oscillatory stress being applied. Alongside this we develop a simple yet semi-quantitative theory that apparently relates these dependences directly to the distribution of energy well depths in soft glasses. Initially we will present this theory at face value, in tandem with our new experimental results (Sections 2 and 3). However, in Section 4 we will show that the model's assumptions cannot be reconciled with the extremely large strain amplitudes that arise in our experiments throughout the prolonged delay period prior to final solidification. In Section 5 we discuss delayed solidification in the context of food materials. Our reluctant conclusion (Section 6) is that, at least in its present form, our theory is not quantitatively credible in the context of the Laponite system studied here, although it may well be applicable to delayed solidification in other soft glasses. Thus our data poses an open challenge: to create a consistent quantitative theory of delayed solidification in Laponite.

2   Experimental methods and results

In this work we have used aqueous suspensions of 3.2 and 2.8 wt% Laponite RD® (Southern Clay Products, Inc.), prepared as described elsewhere.[16] Each Laponite suspension was stored in a sealed polypropylene bottle at 30 °C for a predetermined "idle time" t_i (7–28 days), then loaded in a Couette cell (bob diameter 28 mm, gap 1 mm) of an AR1000 stress controlled rheometer, and shear-melted for 15 min by applying oscillatory shear stress of amplitude 80 Pa at frequency 0.1 Hz. Immediately after this shear melting, an oscillatory stress of amplitude (in the range 5–40 Pa) and frequency f was applied, and the strain evolution was recorded. Experiments were performed at 25 °C; the free surface of the sample was covered with a thin layer of inviscid silicone oil to avoid water evaporation.

Our Laponite suspensions generally have a paste-like consistency. Aging in these systems increases both the elasticity and the relaxation time. Fig. 1 shows the elastic modulus G' as a function of time elapsed (after the shear-melting pre-treatment ends) for experiments at various idle times. Although the strain induced in the material is large, the characterization of the aging data in terms of the linear storage modulus G' in Fig. 1 is justified, as the third strain harmonic is less than 20% of the first.[17] The modulus G', initially too small to detect, shows a sudden and dramatic increase (delayed solidification) beyond a critical time t_c. This arises despite the very large
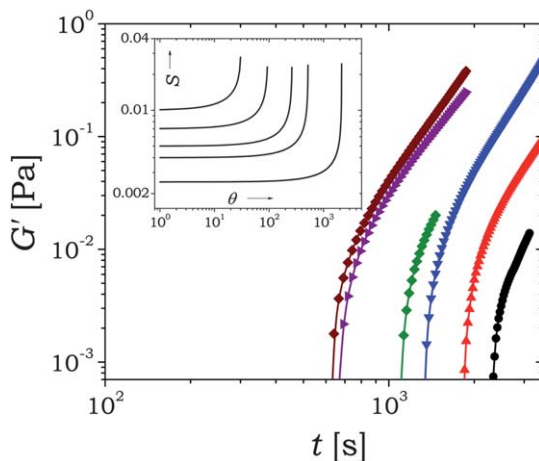
Fig. 1 Evolution of G' for various idle times. Evolution of G' subsequent to shear melting as a function of time for various idle times (from right to left: $t_i = 7, 10, 13, 15, 24, 28$ days) under application of oscillatory shear stress of 30 Pa at 0.1 Hz frequency for 3.2 wt% suspension. Inset shows prediction of eqn (1)–(3) for $\lambda/E_{min} = 0.01$ and $y = 3$, with various initial solid fractions $S(0)$.

fluidizing strains, in the range 10–200, experienced by the material in the first few (post-shear-melting) cycles.

Interestingly, t_c decreases markedly as the idle time is raised. Thus, in contrast to many soft glasses, the aging of Laponite is partly irreversible: subsequent shear melting does not rejuvenate all samples to the same state.[16] Although the microscopic details of this are debatable,[21,22] an aging Laponite suspension at rest clearly crosses some barriers too high to be reversed by our shear-melting protocol, allowing faster delayed solidification in older samples (Fig. 1). However, the evolution of G'
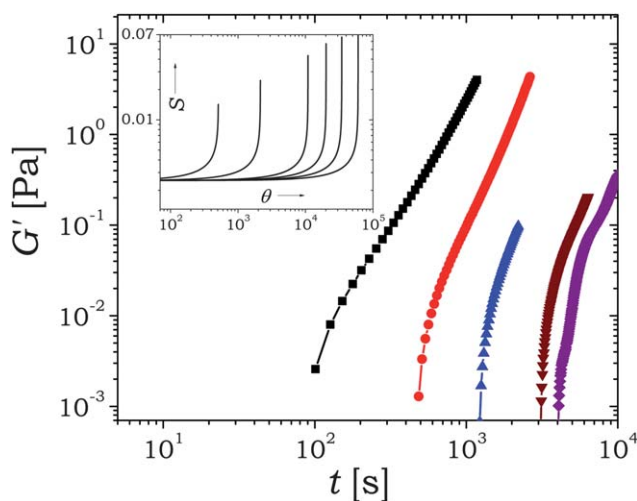

Fig. 2 Evolution of G' at various stresses. Evolution of G' with respect to time under oscillatory flow field having various magnitudes of stresses (from left to right: 20, 25, 30, 35, 40 Pa) at 0.1 Hz frequency for idle time $t_i = 13$ days for 3.2 wt% suspension. Inset shows prediction of eqn (1)–(3) for $y = 3$ (from left to right: $\lambda/E_{min} = 0.005, 0.01, 0.023, 0.031, 0.04, 0.053$).

after t_c is similar in all cases, suggesting that idle time and aging time are partly interchangeable.[16] Fig. 2 shows how the evolution of G' depends on σ at fixed idle time t_i. In this set of experiments each initial state is completely equivalent before the final oscillatory stress is applied. We see that t_c gets larger as the stress is increased. In addition, Fig. 3 shows that t_c is reduced as f is raised.

3 A simple model and its predictions

The microstructure of Laponite suspensions is variously argued to be a repulsive glass or an attractive gel;[21,22] under our conditions (without added salt), repulsions and attractions probably both are important.[16] Nonetheless, whether caging or bonding dominates locally, mesoscopic elements can be considered trapped in energy wells of various depths. These elements are forced out of their traps by macroscopic deformation, whereupon they form new cages or bonds that in turn present new barriers to rearrangement.

Our model for this process is essentially a soft-glassy-rheology (SGR) model,[5,7,23,24] considered for simplicity in the noise-free limit whereby elastic elements cross barriers only when their local mechanical yield threshold is exceeded. One important simplification within the SGR approach, which our model inherits, is the assumption that all elements strain affinely with the imposed flow between one jump and the next. Allied with the further simplifying assumptions of harmonicity within each trap and a uniform elastic constant for all traps,[23] this represents a picture in which the intra-jump elastic deformation is that of a parallel mechanical circuit. The opposite assumption would be to suppose equal stress in all elements, *i.e.*, a series mechanical circuit. The real distribution of local elastic deformations and stresses must lie somewhere between these extremes; we return to this point in Section 4.

Within the SGR framework, the arrested state (an amorphous solid) of a soft glass is described, as indicated above, in terms of mesoscopic elements trapped in energy wells created by neighbors.[5] A crucial postulate of SGR is that these well depths
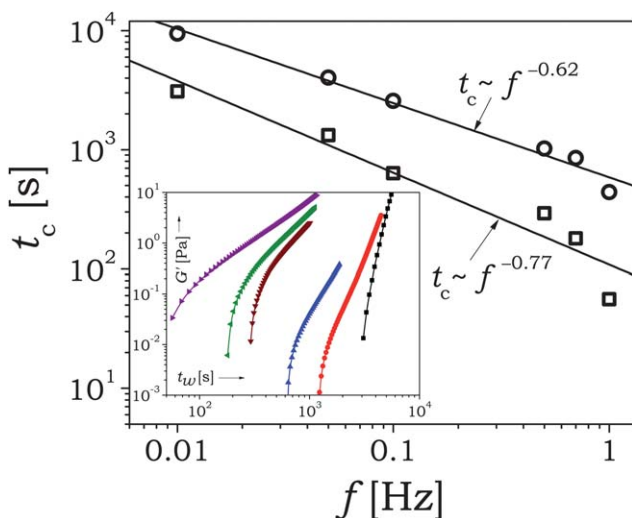

Fig. 3 Evolution of G' at various frequencies and dependence of critical time on frequency. The critical time for delayed solidification plotted against frequency of oscillations (open squares: 3.2 wt% suspension, $t_i = 28$ days, $\sigma_0 = 30$ Pa; open circles: 2.8 wt% suspension, $t_i = 21$ day, $\sigma_0 = 20$ Pa). Inset shows corresponding evolution of G' as a function of time for various frequencies (from right to left: 0.01, 0.05, 0.1, 0.5, 0.7, 1 Hz) for 3.2 wt% suspension.

(or barrier heights) are distributed broadly. As shown by Bouchaud,[4] if the *a priori* (prior) distribution of well-depths varies as $\rho(E) \sim \exp[-E/\langle E \rangle]$, ergodicity is lost at a glass transition temperature T_g, obeying $k_B T_g = \langle E \rangle$. All other forms of $\rho(E)$ lie either in the glass or the fluid according to whether their decay is slower or faster than exponential. The SGR model[23,24] further allows for deformations, and replaces the thermal energy $k_B T$ by a nonequilibrium noise amplitude. Assuming exponential $\rho(E)$, the SGR model offers a unified phenomenological model of soft-glass rheology, whose predictions include power-law fluid and Herschel–Bulkley behaviours.[5]

Although theoretical arguments suggest it asymptotically,[4,24] there is so far no direct experimental test of whether the well-depth distribution in soft glasses is indeed exponential, as SGR assumes. (Other forms might still support an arrest transition, but only if more complicated cooperative dynamics are considered.[23,24]) It would therefore be useful to gain clearer experimental insight into the true form of $\rho(E)$.

The prior distribution of well depths, $\rho(E)$, is not their occupancy probability $P(E)$ since deeper wells have lower escape rates and are more likely to be occupied. However $\rho(E)$ is the distribution from which E is drawn once a rearrangement is made and a new barrier height chosen. If oscillatory shear of amplitude σ is imposed, creating a strain amplitude γ_0, then assuming affine intra-jump deformation (as SGR does) each individual element will gain an energy $k\gamma_0^2/2 \equiv E_0$, where k is a spring constant, at the extremes of each cycle. (As in SGR, k is here taken independent of well-depth E;[5] we partially relax this assumption below.) We assume that any element of well-depth $E < E_0$ is rejuvenated during the given strain cycle, while all those occupying deeper wells are not.

We now distinguish a liquid fraction F and solid fraction $S = 1 - F$, representing in turn the fractions of elements occupying wells shallower or deeper than E_0. Taking for convenience a time coordinate $\theta = ft$, we propose F to obey:

$$\frac{dF}{d\theta} = -FR \tag{1}$$

where R is the fraction of jumps into the solid state:

$$R = \frac{\displaystyle\int_{E_0(\gamma_0)}^{\infty} \rho(E)\,dE}{\displaystyle\int_0^{\infty} \rho(E)\,dE} \tag{2}$$

Eqn (1) models the random events by which 'fluid' elements—those that cross their barriers by strain-induced dynamics during one cycle—become 'solid' elements (those that don't) in the next. In a material having solid fraction S and thus modulus GS, the strain induced by the stress of amplitude σ is then taken to be:

$$\gamma_0 = \frac{\sigma}{SG} \tag{3}$$

The threshold energy at given stress σ and solid fraction S then obeys $k\gamma_0^2/2 = E_0$, or equivalently $E_0 = \lambda/S^2$ where $2\lambda = k\sigma^2/G^2$.

Eqn (1)–(3) can now be solved to give $S(\theta)$ in terms of $\rho(E_0)$ and the initial solid content which we denote as $S(0) = \varepsilon$. We consider two cases: first the exponential distribution $\rho(E) = e^{-\alpha E}/\alpha$ for which $R(E_0) = e^{-\alpha E_0}$, and secondly a power law, $\rho(E) = A E^{-y}$ for $E > E_{min}$, with a cutoff E_{min}. The cutoff is defined so that

$\rho(E < E_{min}) = 0$. By normalization we then have $A = E_{min}^{1-y}/(1-y)$; the resulting R is given by $R(E_0) = (E_0/E_{min})^{1-y}$.

Fig. 1 (inset) shows for the power-law case the time evolution of the solid fraction $S(\theta)$, for various initial solid contents ε, but the same values of λ/E_{min} (equivalently, the same stress σ). Our simple model captures both the sudden solidification at t_c, and the decrease in t_c with increasing initial solid content. Fig. 2 (inset) shows $S(\theta)$ for various values of λ/E_{min} (or equivalently various σ) but the same initial solid content ε. As observed experimentally, the delayed solidification time t_c is predicted to increase with stress. Since $\theta = ft$, eqn (1) directly implies $t_c \propto f^{-1}$. Fig. 3 (inset) shows a decreasing trend, although the best fit power laws (albeit with limited data) are $t_c \propto f^{-0.77}$ for the 3.2% sample and $t_c \propto f^{-0.62}$ at 2.8%. Given the simplicity of the model, these are close enough to the f^{-1} prediction to be broadly encouraging.

Moreover, integrating eqn (1) gives the time at which a given solid fraction is attained:

$$\theta(S) = \int_{\varepsilon}^{S} \frac{1}{(1-S')R(S')} \, \mathrm{d}S' \tag{4}$$

The critical value θ_c identifies the time where S "ceases to be small". The precise definition of this quantity is clearly somewhat arbitrary, but once it is no longer small, $S(\theta)$ increases so steeply that the details of the definition barely matter. Thus, it suffices to ignore the saturation that occurs as $S \to 1$ in the denominator, and then set $S = 1$ as the upper limit of the integral above; these two simplifications give the following expression for the solidification time $\theta_c = ft_c$:

$$\theta_c \approx \int_{\varepsilon}^{1} \frac{1}{R(S')} \, \mathrm{d}S' \tag{5}$$

For our exponential and power law distributions the results are respectively:

$$\theta_c = \frac{2\varepsilon^3 G^2}{\alpha k \sigma^2} \exp\left[\frac{\alpha k \sigma^2}{2\varepsilon^2 G^2}\right] \tag{6}$$

$$\theta_c \propto \varepsilon^{3-2y}\sigma^{2(y-1)} \tag{7}$$

Fig. 4 shows t_c, now experimentally defined by $G'(t_c) = 5$ mPa, as a function of G'', the initial loss modulus measured directly after shear melting. Strictly speaking, our model relates the solid fraction only to G', which is too small to measure in this early time regime. Therefore we assume that the loss modulus is a similar indicator of solid content: $G'' \propto \varepsilon = S(0)$. If so, eqn (6) demonstrates a poor fit to the experimental data but the power law result (eqn (7)) fits well, with $y = 3.15 \pm 0.13$ at 3.2% and $y = 3.3 \pm 0.18$ at 2.8%.

Fig. 5 shows how t_c depends on σ for the 3.2% data of Fig. 2, and for two datasets at 2.8%. Here stress was varied at fixed idle time, so we expect ε to be fixed, giving $t_c \sim \sigma^{2(y-1)}$ by eqn (7) (note however that the measured initial G'' decreases with σ; see the Appendix for a discussion). Fig. 5 confirms this power law, and again contrasts with the prediction for exponential $\rho(E)$. A fit gives $y = 3.4 \pm 0.3$ for the 3.2% sample and $y = 3.6 \pm 0.1$ for both 2.8% samples.

To summarize, fitting separately the dependences of t_c on initial solid content and on stress leads to very similar y values for three different samples, suggesting a fairly robust power law. This is interesting from a glass physics viewpoint: any power law
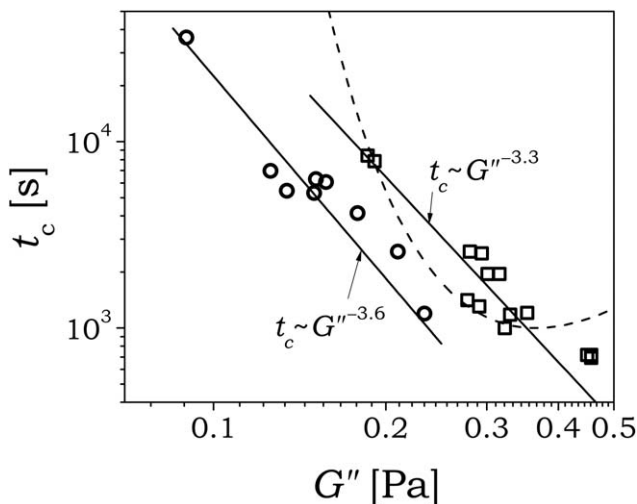
Fig. 4 Dependence of critical time on initial G''. The critical time for delayed solidification plotted against G'' measured directly after the shear-melting protocol is complete (open squares: 3.2 wt% suspension, $\sigma = 30$ Pa, $f = 0.1$ Hz; open circles: 2.8 wt% suspension, $\sigma = 20$ Pa, $f = 0.1$ Hz). Solid lines represent fit of eqn (7) while the dashed line represents fit to eqn (6) with $G'' \propto \varepsilon$ assumed in both cases. The stated exponents for the modulus dependence translate into the y values quoted in the text.
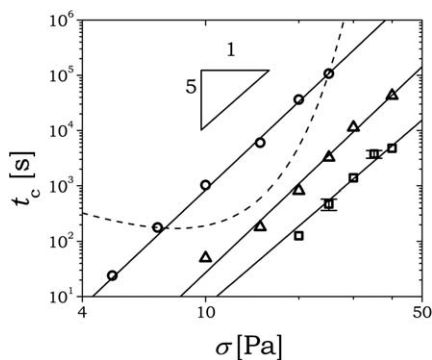

Fig. 5 Dependence of critical time on stress. The critical time for delayed solidification plotted as a function of applied stress amplitude σ (circles: 2.8 wt% suspension, $t_i = 9$ days, $f = 0.1$ Hz; triangles: 2.8 wt% suspension, $t_i = 15$ days, $f = 0.1$ Hz (data from), squares: 3.2 wt% suspension, $t_i = 13$ days, $f = 0.1$ Hz.) Solid lines represent fit of eqn (7) to the experimental data; the dashed line is a fit of eqn (6) for the uppermost dataset only.

distribution should, by the arguments of Bouchaud,[4] lie deep in the aging glass regime. In the Appendix, we generalize our simple model to allow the elastic constant k of an element to vary as $k \propto E^p$. This gives the same results as above, but with y replaced by $y_{eff} = (y + p)/(1 + p)$; the same conclusion applies. Thus we have found that, when interpreted within the precepts of the SGR-inspired model presented above, our quantitative delayed solidification measurements for Laponite indicate a power law distribution of the energy well depths. This apparently direct connection between macroscopic rheological observations and the mesoscopic energetics is tantalizing: it holds out the prospect for "spectroscopic" analysis of the energy landscape through careful study of the nonlinear rheology. In turn this

might provide new insight into aging and rejuvenation in this important class of materials.

4 What's wrong with this picture?

Before answering this question, it is interesting to speculate where power laws in the local yield energy and/or elastic constant might come from. At the low volume fractions present in our Laponite samples, bonding might lead to some sort of percolation transition. Near such a transition the elastic elements comprise clusters of all sizes, whose moduli are controlled by power laws (coinciding in the scalar limit with those for resistivity.[25]) The corresponding yield energy distribution is model-dependent, but seemingly can itself exhibit power laws over one or two decades, or more in some limits,[26,27] although not enough is yet known to suggest specific values for the relevant exponents.

However the emerging picture of a buildup of the solid fraction S (from an initially minimal level) by a percolation-like process gives pause for thought. For if solidification is initiated by the formation of relatively rigid clusters within a sea of fluidized material, SGR's assumption of a parallel mechanical circuit becomes highly suspect. One could not expect such aggregates to deform affinely under any type of flow: solid objects floating in a fluid develop only small deformations before achieving stresses that match those of their continuously deformable surroundings. At first sight, this objection might not appear fatal to our model since, in its many other predictions, the SGR approach is empirically successful although in practice local deformations are never affine. Nonetheless, the percolation viewpoint argues for a model that lies much nearer the series-circuit (equal stress on all elements) end of the spectrum than the parallel-circuit assumption embodied in SGR.

A serious blow is struck by noting that, in our Laponite studies, the enormous initial strains to which the initially fluidized sample is subjected (of order 10–200, *i.e.*, 1000% to 20,000%) are maintained almost throughout the incubation period prior to the final solidification event. It is scarcely credible that *any* mesoscopic element of the type envisaged by SGR could have high enough internal or external energy barriers to sustain an affine deformation of this magnitude. By completely destroying the structures that SGR requires to survive from one cycle to the next, such strain amplitudes preclude the slow buildup of a solid component which is an essential precursor to the final dramatic solidification. (Recall that the latter occurs when the feedback between the slowly building elasticity and decreasing strain amplitude finally takes over.) The observation of delayed solidification at these initial strain amplitudes in Laponite therefore means we must look for a mechanism involving pockets of solidity that do not deform affinely, and, for that reason alone, can grow from one cycle to the next. Whatever its merits in other context, by assuming affine deformation, SGR precludes a consistent description of any such mechanism.

We can however, speculate a mechanism by assuming that the solid pockets, and the fluidized suspension surrounding these, share the same stress (series mechanical circuit). Consequently the strain induced in the solid region would be very small. Such a scenario may give rise to an apparent boundary layer around the solid pocket, wherein strain magnitude changes from practically zero at the surface to a very large value away from it. In this small strain region very near the solid surface, the liquid suspension may undergo aging following a very similar dynamics mentioned in the previous section. Owing to this aging of the liquid suspension near the solid surface, the solid region is expected to grow, which in turn will enhance the fraction of liquid suspension undergoing smaller strain. Moreover the enhanced solid fraction will also reduce the bulk strain magnitude. Through a forward feedback mechanism, the growing solids will fill the space causing jamming of the system as a whole. This picture preserves some of the physical

features of our SGR-based approach, but would require a different mathematical description from the one we present above.

5 Delayed solidification in the context of food materials

Interestingly, there are many food materials that have paste like consistency and are expected to demonstrate soft glassy rheological behavior. These include: fruit jams, mustard, jellies, mayonnaise, cheese, ice-creams, tomato and chocolate puree, tooth-paste (not exactly a food material, but edible), *etc.* Among these both mustard[28] and mayonnaise[29] have been reported to demonstrate physical aging (time dependent enhancement in viscosity and elastic modulus), which is a signature of soft glassy behavior. Rheological behavior is one of the most important characteristic features of food materials. The effects of time and deformation, which respectively tend to enhance and reduce viscosity and elasticity, is a very important consideration when designing food processing equipment and determining the shelf life of a food product. The present work suggests that under application of a sustained oscillatory deformation field, food materials may in some cases transform from an apparently fluid like state to solid state. Such materials are subjected various kinds of deformation fields during preparation, transportation and handling. The present work suggests that such deformation fields can delay but may not stop the process of aging which leads to solidification.

In addition to physical aging, which is a reversible process, food materials are also prone to undergo partly irreversible changes in their rheological behavior. Particularly enzymes, heating or acidification can induce gelation in certain food products causing an increase in viscosity and elastic modulus. Thus flowing liquids get converted to soft solids as a function of time.[30] The solidification that we discuss in this manuscript is essentially reversible. However, Laponite suspensions are also known to show partial irreversible aging behavior and therefore interestingly mirror what happens in certain types of food materials.

Besides time-dependent irreversible phenomena, irreversible aggregation induced by an applied deformation field is also possible and is particularly observed for proteins. It is known that mis-folded proteins tend to aggregate because of inter molecular hydrophobic associations.[31] In addition, one of the proposed mechanisms for spider silk formation also suggests deformation induced self-assembly of proteins which is irreversible in nature.[32–34] In colloidal suspensions, shear-induced aggregation has also been reported.[35] Interestingly, shear-induced enhancement in elasticity is also observed in some soft glassy materials[7] and in Laponite suspensions in particular.[8] However, there seems to be no direct connection between shear-induced solidification (for instance in steady shear) and the delayed solidification addressed in our work under sustained oscillatory shearing.

6 Conclusions

We have studied in detail the sudden and dramatic enhancement in elastic modulus at late times seen in aqueous Laponite suspensions undergoing stress-controlled oscillatory shear. The critical time t_c for this delayed solidification is reduced for older samples, despite our use of a vigorous pre-shear protocol, whereas application of higher stress amplitude, or lower frequency, increases t_c. We have proposed a simple SGR-type model wherein a liquid fraction of fluidized elements are rejuvenated every cycle. At each such event, there is a probability R of jumping into a solid fraction of deep wells, that do not rejuvenate; R is determined by the current strain amplitude, and the prior distribution of well depths. The ever-increasing solid content slowly decreases the induced strain and increases R; this positive feedback leads eventually to sudden jamming of the whole sample. Taken at face value, the model offers a semi-quantitative explanation of our Laponite experiments, with strong evidence that a power law distribution of energy well depths must be chosen

in preference to the exponential form normally adopted in an SGR context. This offers a tantalizing glimpse of how macroscopic rheology might be directly relatable to the barrier distribution for rearrangements—a quantity that has previously eluded direct experimental characterization in soft glasses. But unfortunately this is no more than a glimpse, because on closer inspection the large strain amplitudes arising in the Laponite system cannot credibly be reconciled with one of the model's central approximations: that local deformations between rearrangement events follow affinely the macroscopic flow.

Where does this critique leave the model? Unless its foundations can be reinterpreted or repaired (and we have not managed to do this so far), then despite its semi-quantitative success at fitting the data, our SGR-based approach clearly does not offer a secure starting point to understand delayed solidification in Laponite suspensions. Accordingly, the evidence that it seemingly offers for a power-law rather than exponential barrier height distribution must now be set aside.

On the other hand, the qualitative physical predictions of our SGR-inspired model remain intact for systems that are credibly approximated by its assumption of affine deformation between rearrangements. We can see nothing to prevent the existence of soft glasses for which a delayed solidification scenario arises at much more modest strains, of order unity: our model, even if it must be rejected for Laponite, offers a ready-made description for such systems. Meanwhile it remains an open theoretical challenge to develop a more suitable quantitative model for delayed solidification in Laponite itself. Only when such a model exists can one know how much, if any, of the qualitative physics embodied in our model is also relevant to the Laponite system.

Appendix

A. Stress dependence of viscous modulus at fixed idle time

For experiments carried out on 2.8 wt% Laponite suspension on day 9, the initial G'', measured in the first cycles of oscillatory shear after shear melting, was found to decrease with stress amplitude. Since all the samples have equivalent histories prior to this point, we believe that this decrease represents shear thinning of the rejuvenated suspension, not a stress-dependent initial solid fraction. To verify this we measured viscosity (η) of a sample immediately after the rejuvenation stage. The Fig. 6 shows G''/ω and η vs. stress. Both the variables show the same dependence
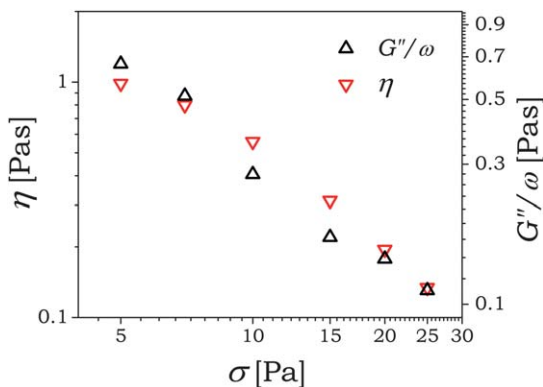

Fig. 6 Initial G''/ω for an oscillatory test (angular frequency $\omega = 0.628$ rad s^{-1}) plotted as a function of magnitude of stress for 2.8 wt% 9 days old Laponite suspension. The viscosity measured from a stress controlled shear experiment is also plotted against stress for the same system.

on shear stress, confirming that the decrease in G'' is indeed due to shear thinning of the rejuvenated suspension.

B. Modified exponents for power law traps with variable local elastic constant

Here we consider conditions where $k = k(E)$, so that the elastic modulus of a trap depends on its depth. For simplicity we assume $k(E) = E^p$. Eqn (2) for the liquid-solid conversion factor R is unaffected, where now $E_0/k(E_0) = \gamma_0^2/2$, so that $\gamma_0 \propto E_0^{(1-p)/2}$. Also the modulus of the solid material G in eqn (3) now obeys:

$$
G \propto \frac{\displaystyle\int_{E_0}^{\infty} \rho(E)k(E)\,\mathrm{d}E}{\displaystyle\int_{E_0}^{\infty} \rho(E)\,\mathrm{d}E} \propto E_0^p \tag{8}
$$

In other words, the solid fraction populates wells of depth $E > E_0$ with the prior distribution, and the modulus of the solid phase is fixed by the appropriate weighted average of the elastic constants k of the individual wells. This gives $S \propto \sigma\, E_0^{-(1-p)/2}$, while $R \propto E_0^{1-y}$ as before, and therefore $\theta_c \propto \varepsilon^{(3-2\,y+p)/(1+p)}\,\sigma^{2\,(y-1)/(1+p)}$.

Acknowledgements

References

1 L. Cipelletti and L. Ramos, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 228–234.
2 P. G. Debenedetti and F. H. Stillinger, *Nature*, 2001, **410**, 259–267.
3 L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier, Houston, 1978.
4 J. P. Bouchaud, *J. Phys. I*, 1992, **2**, 1705–1713.
5 S. M. Fielding, P. Sollich and M. E. Cates, *J. Rheol.*, 2000, **44**, 323–369.
6 L. M. Falk and J. S. Langer, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 1998, **57**, 7192–7205.
7 V. Viasnoff and F. Lequeux, *Phys. Rev. Lett.*, 2002, **89**, 065701.
8 R. Bandyopadhyay, H. Mohan and Y. M. Joshi, *Soft Matter*, 2010, **6**, 1462–1466.
9 P. Coussot, Q. D. Nguyen, H. T. Hyun and D. Bonn, *J. Rheol.*, 2002, **46**, 573–589.
10 C. Derec, A. Ajdari and F. Lequeux, *Eur. Phys. J. E: Soft Matter Biol. Phys.*, 2001, **4**, 355–361.
11 C. Christopoulou, G. Petekidis, B. Erwin, M. Cloitre and D. Vlassopoulos, *Philos. Trans. R. Soc. London, Ser. A*, 2009, **367**, 5051–5071.
12 P. Coussot, J. S. Raynaud, F. Bertrand, P. Moucheront, J. P. Guilbaud, H. T. Huynh, S. Jarny and D. Lesueur, *Phys. Rev. Lett.*, 2002, **88**, 218301.
13 F. Varnik, L. Bocquet, J. L. Barrat and L. Berthier, *Phys. Rev. Lett.*, 2003, **90**, 095702.
14 M. L. Manning, J. S. Langer and J. M. Carlson, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2007, **76**, 056106.
15 S. M. Fielding, M. E. Cates and P. Sollich, *Soft Matter*, 2009, **5**, 2378–2382.
16 A. Shahin and Y. M. Joshi, *Langmuir*, 2010, **26**, 4219–4225.
17 A. Shukla and Y. M. Joshi, *Chem. Eng. Sci.*, 2009, **64**, 4668–4674.
18 J. M. Rotter, *Guide for the economic design of circular metal silos*, Taylor and Francis, London 2001.

19 L. Starrs, W. C. K. Poon, D. J. Hibberd and M. M. Robins, *J. Phys.: Condens. Matter*, 2002, **14**, 2485–2505.
20 B. M. Erwin, D. Vlassopoulos and M. Cloitre, *J. Rheol.*, 2010, **54**, 915–939.
21 P. Mongondry, J. F. Tassin and T. Nicolai, *J. Colloid Interface Sci.*, 2005, **283**, 397–405.
22 B. Ruzicka and E. Zaccarelli, *Soft Matter*, 2011, **7**, 1268–1286.
23 P. Sollich, F. Lequeux, P. Hebraud and M. E. Cates, *Phys. Rev. Lett.*, 1997, **78**, 2020–2023.
24 P. Sollich, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdisc. Top.*, 1998, **58**, 738–759.
25 D. Stauffer, *Phys. Rep.*, 1979, **54**, 1–74.
26 Y. M. Strelniker, S. Havlin, R. Berkovits and A. Frydman, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2005, **72**, 016121.
27 A. G. Hunt, *Transp. Porous Media*, 1998, **30**, 177–198.
28 P. Coussot, H. Tabuteau, X. Chateau, L. Tocquer and G. Ovarlez, *J. Rheol.*, 2006, **50**, 975–994.
29 F. Da Cruz, F. Chevoir, D. Bonn and P. Coussot, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdisc. Top.*, 2002, **66**, 051305.
30 D. Eric, *Food Hydrocolloids*, 2012, **28**, 224–241.
31 K. M. N. Oates, W. E. Krause, R. L. Jones and R. H. Colby, *J. R. Soc. Interface*, 2006, **3**, 167–174.
32 A. K. Lele, Y. M. Joshi and R. A. Mashelkar, *Chem. Eng. Sci.*, 2001, **56**, 5793–5800.
33 H. J. Jin and D. L. Kaplan, *Nature*, 2003, **424**, 1057–1061.
34 C. Holland, J. S. Urbach and D. L. Blair, *Soft Matter*, 2012, **8**, 2590–2594.
35 A. Zaccone, D. Gentili, H. Wu, M. Morbidelli and E. Del Gado, *Phys. Rev. Lett.*, 2011, **106**, 138301.

This journal is © The Royal Society of Chemistry 2012