

Chapter 1

SOFT GLASSY RHEOLOGY

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Abstract We review models for the rheology of soft glasses, a class of materials including e.g. emulsions, foams, colloidal glasses and possibly—but with substantial caveats—gels. The main focus is on the soft glassy rheology (SGR) model, and in particular on the occurrence of rheological aging effects. We first review appropriate definitions of rheological response functions suited to aging samples (in which time translation invariance is lost). These are then used to study aging effects within the SGR model. Its constitutive equations relate shear stress to shear strain among a set of elastic elements, with distributed yield thresholds, undergoing activated dynamics governed by a “noise temperature”, x . For $1 < x < 2$ there is a power-law fluid regime in which transients occur, but no aging. For $x < 1$, the model has a macroscopic yield stress. So long as this yield stress is not exceeded, aging occurs, with a sample’s apparent relaxation time being of the order of its own age. The (age-dependent) linear viscoelastic loss modulus $G''(\omega, t)$ rises as frequency is *lowered*, but falls with age t , so as to always remain less than $G'(\omega, t)$ (which is nearly constant). Significant aging is also predicted for the stress overshoot in nonlinear shear startup and for the creep compliance. We discuss an extension of the model to include a proper tensorial description of stress and strain, and survey some related rheological models that have recently been developed.

1.1 Introduction

The main purpose of this chapter is to describe a theoretical model developed to rationalize the rheology of a large class of soft materials. The members of this class, which we take to include e.g. foams, dense emulsions, pastes and slurries, display intriguing features in their low frequency shear rheology. In oscillatory shear, for example, their viscoelas-

tic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, are often weak power laws of shear frequency,^{1–7} while their nonlinear stress response σ to shear strain of constant rate $\dot{\gamma}$ is often fit to the form $\sigma = A + B\dot{\gamma}^n$ (known as the Herschel-Bulkley equation, or when $A = 0$, the power-law fluid).^{8–10} The fact that such a broad family of soft materials exhibits similar rheological anomalies is suggestive of a common cause, and it has been argued that these anomalies are symptomatic of the generic presence in such materials of slow, glassy dynamics.^{11,12} Indeed, all the above materials share features of structural disorder and metastability: large energy barriers impede reorganization into states of lower free energy because this would require rearrangement of local structural units, such as the droplets in a dense emulsion. The term “soft glassy materials” (SGMs) has therefore been proposed to describe such materials.^{11,12} A prime manifestation of glassy dynamics is rheological *aging*, where e.g. the elastic modulus increases as time goes by, while the loss modulus decreases. Effects of this type can be rather complicated, with e.g. the rate of aging depending on stress.¹³ Rheological aging effects have seen intense experimental interest recently,^{13–18} stimulated (we may hope) at least in part by the theoretical developments that will be reviewed below.

We will focus, in this chapter, on the “soft glassy rheology” (SGR) model which has been developed over the last few years to describe the rheology of soft glasses.^{11,12,19,20} As will be clear from the above introduction, this model was designed for what can be termed *repulsive glasses*, in which metastability arises because the particles (or droplets etc) that make up the material are too compressed to easily move past each other and rearrange. Gels, on the other hand, can be thought of as *attractive glasses*, where particles form tenuous networks but are held together by bonds that are sufficiently strong to again hinder rearrangements.²¹ This aspect is not captured by the SGR model. The model also does not incorporate structural changes during aging. This is appropriate for repulsive glasses: e.g. in a compressed assembly of colloidal particles, only very weak changes in the overall structure are expected while the material ages by local rearrangements which bring particles into energetically more favourable positions. For gels, on the other hand, structural changes during aging are surely important, with e.g. characteristic lengthscales of network structures growing in time. A final deficiency of the SGM model is that it assumes local elastic properties to be essentially homogeneous, whereas in gels strong inhomogeneities must be expected.

In spite of these shortcomings, the present chapter will describe the SGM model “as is”, without modifications that could be contemplated

to make it more appropriate for gels. It is hoped that the approach presented, which attempts to capture complex rheological phenomena using minimal models, will nevertheless prove useful. One key advantage of the SGR model is its simplicity, which allows for a full study of a broad range of nontrivial rheological effects including aging. Confronting the resulting predictions with experiment for verification or falsification should help to stimulate the development of more sophisticated models, both for the “traditional” soft glasses and for gels.

We begin in Sec. 1.2 by briefly introducing rheology and aging. Then in Sec. 1.3 we review the SGR model and its recent generalization to a tensorial description of stress and strain, and review its rheological predictions under non-aging conditions. Sec. 1.4 begins with a discussion of the origin of the SGR model’s glass transition and the nature of the glass phase, and then describes the predicted rheological aging phenomena for conditions of controlled strain. The corresponding results for imposed stress are given in Sec. 1.5. We close in Sec. 1.6 by summarizing and discussing our results; a brief comparison with related rheological models that have recently been developed is also provided.

1.2 Rheology

Here we review the basic definitions of rheology. Unlike most in the literature, our formulation¹⁹ does not assume time translational invariance (TTI). The formalism allows in principle an arbitrary dependence of the material properties on time; we defer to Sec. 1.2.8 a discussion of what form this dependence might take in materials which exhibit aging effects (rather than other, more trivial time dependencies).

1.2.1 Constitutive properties

In general, deformation can comprise volume changes, extensional strain, and shear strain; here we consider incompressible materials and assume that only shear strains arise. A system’s shear stress $\sigma(t)$ then depends functionally on its strain rate history $\dot{\gamma}(t' < t)$, where $\dot{\gamma}$ is the strain rate. Conversely, $\gamma(t)$ can be expressed as a functional of the preceding stress history. A specification of either type is referred to as a *constitutive equation*. In general, of course, the constitutive equation is a relationship between stress and strain *tensors*; see e.g. Doi and Edwards²² for an introduction. We mainly ignore the tensorial aspects here, because the original SGR model is too simple to include them. A recent tensorial generalization²⁰ will be described in Sec. 1.3.

1.2.2 Step strain

A standard rheological test consists of suddenly straining a previously undeformed material by an amount γ_0 . Suppose this to be done at time t_w : then $\gamma(t) = \gamma_0 \Theta(t - t_w)$, where Θ is the usual step function. (For the moment, t_w is an arbitrary time label, but later we will take it as the time that the strain is applied, relative to the preparation of the sample in some prescribed state, at time zero.) The subsequent stress can be written

$$\sigma(t) = \gamma_0 G(t - t_w, t_w; \gamma_0) \quad (2.1)$$

thereby defining the step strain response, $G(t - t_w, t_w; \gamma_0)$.

1.2.3 Linearity

In the small deformation limit ($\gamma_0 \rightarrow 0$), a regime may exist for which σ is linearly related to γ_0 :

$$\lim_{\gamma_0 \rightarrow 0} G(t - t_w, t_w; \gamma_0) = G(t - t_w, t_w) \quad (2.2)$$

In this linear regime, by decomposing the applied strain $\gamma(t)$ into a series of infinitesimal steps, one finds that

$$\sigma(t) = \int_{-\infty}^t G(t - t', t') \dot{\gamma}(t') dt' \quad (2.3)$$

which represents the most general (nontensorial) linearized constitutive equation. Note that there is no unique extension of this to the nonlinear case: the response to an arbitrary flow cannot in general be written solely in terms of $G(t - t_w, t_w; \gamma_0)$, although this is assumed for certain constitutive models.²³

If the material exhibits TTI, then $G(t - t_w, t_w; \gamma_0)$ can be written as $G(t - t_w; \gamma_0)$ – it depends only on the elapsed time since the step strain was imposed. Only by assuming *both* linearity and TTI do we obtain

$$\sigma(t) = \int_{-\infty}^t G(t - t') \dot{\gamma}(t') dt' \quad (2.4)$$

where $G(t - t_w)$ is the linear step-strain response as usually defined. In the steady state (constant $\dot{\gamma}$) one recovers:

$$\sigma = \dot{\gamma} \int_0^{\infty} G(t'') dt'' \quad (2.5)$$

The integral, whenever it exists, defines the material's zero-shear viscosity η . For many soft materials, however, $G(t)$ decays to zero so slowly that the integral diverges. In this case, there can be no regime of linear response in steady shear flow, although there may be a linear regime in, say, oscillatory shear.

1.2.4 Behaviour of the linear response function

The principle of causality demands that the response function $G(t - t_w, t_w)$ is zero for times $t < t_w$. At $t = t_w$, G typically increases very rapidly (in effect discontinuously) to a value G_0 , the instantaneous elastic modulus. Thereafter, $G(t - t_w, t_w)$ is (almost always) a decaying function of its first argument. Specializing to the TTI case, we recall that for a purely Newtonian liquid of viscosity η , the function $G(t)$ approaches a delta function $\eta\delta(t)$, whereas an ideally Hookean elastic solid has $G(t) = G_0$.

Most real materials display intermediate behaviour and are thus *viscoelastic*; for the soft materials of interest here, the timescale of the viscoelasticity is readily observable in rheological experiments. The simplest (TTI) example is the Maxwell fluid, which is solid-like at short times and liquid at longer ones, with a simple exponential response function $G(t) = G_0 \exp(-t/\tau)$ connecting the two (so that $\eta = G_0\tau$). This behaviour is seen in a few experimental systems,²⁴ but $G(t)$ is usually not an exponential.

1.2.5 Creep compliance

Arguing along parallel lines to those developed above, we can write the strain response to a step stress $\sigma(t) = \sigma_0\Theta(t - t_w)$ as

$$\gamma(t) = \sigma_0 J(t - t_w, t_w; \sigma_0) \quad (2.6)$$

The linear creep compliance $J(t - t_w, t_w)$ is then found by letting $\sigma_0 \rightarrow 0$ (assuming this limit exists).

For a system exhibiting TTI, the linear compliance reduces to a function of elapsed time, $J(t - t_w)$. (For a viscous liquid, an elastic solid, and a Maxwell material we have $J(t) = t/\eta$, $J(t) = 1/G_0$, and $J(t) = 1/G_0 + t/\eta$, respectively.) The zero-shear viscosity η can then be defined as the limiting ratio of stress to strain rate long after application of an infinitesimal step stress; it therefore obeys $\eta^{-1} = \lim_{t \rightarrow \infty} dJ(t)/dt$, which may be shown to be equivalent to (2.5) whenever the required limit exists (see also Sec. 1.2.7 below).

1.2.6 Viscoelastic spectra

A common experiment is to apply a steady oscillatory strain and measure the resulting stress, or vice versa. For example, suppose that a sample is prepared in a known state at time zero. The choice

$$\gamma(t) = \Theta(t - t_s) \text{Re} \left[\gamma_0 e^{i(\phi + \omega t)} \right] \quad (2.7)$$

then describes an oscillatory flow started at time t_s after sample preparation, and continued up to (at least) the time t at which the stress is measured. For small enough γ_0 , we can use the linear constitutive equation (2.3) to obtain

$$\begin{aligned}\sigma(t) &= \text{Re} \left[\gamma_0 i\omega \int_{t_s}^t e^{i(\phi+\omega t')} G(t-t', t') dt' + \gamma_0 e^{i(\phi+\omega t_s)} G(t-t_s, t_s) \right] \\ &\equiv \text{Re} \left[\gamma_0 e^{i(\phi+\omega t)} G^*(\omega, t, t_s) \right]\end{aligned}\quad (2.8)$$

where the second term in (2.8) accounts for any step strain arising at the switch-on time t_s . This procedure defines a *time-varying* viscoelastic spectrum as

$$G^*(\omega, t, t_s) = i\omega \int_{t_s}^t e^{-i\omega(t-t')} G(t-t', t') dt' + e^{-i\omega(t-t_s)} G(t-t_s, t_s) \quad (2.9)$$

A similar compliance spectrum, $J^*(\omega, t, t_s)$ can be defined by exchanging stress and strain in this protocol.

Note that in principle, to identify by experiment the real and imaginary parts of G^* for given ω, t, t_s one would require the experiment to be repeated for two different phases ϕ (e.g., pure sine and cosine deformations). A more common procedure for TTI systems is to maintain the oscillatory strain over many cycles and record the “steady state” amplitude and phase response of the stress. However, in systems without TTI this will only give a unique result when material properties vary slowly enough; whenever it does, it will coincide with (2.9).

Since it depends on two time arguments as well as frequency, $G^*(\omega, t, t_s)$ is a cumbersome object. However, simplifications arise in the limit $\omega(t-t_s) \gg 1$. In the TTI case, where $G^*(\omega, t, t_s)$ depends only on the time interval $t-t_s$, the further condition $\omega(t-t_s) \gg 1$ can be used to eliminate simple transients. The stress then settles to a simple harmonic function of time and we can write $\sigma(t) = \text{Re} [G^*(\omega)\gamma(t)]$ where

$$G^*(\omega) = i\omega \int_0^\infty e^{-i\omega t} G(t) dt \quad (2.10)$$

Traditionally one writes $G^*(\omega) = G'(\omega) + iG''(\omega)$ where G', G'' , the storage and loss moduli, give the in-phase (elastic) and out-of-phase (dissipative) response to an applied strain.

Clearly one can reach an identical steady state by applying a small amplitude oscillatory stress and measuring the resulting strain. This defines, for the TTI case, a complex compliance $J^*(\omega)$ via $\gamma(t) = \text{Re}[J^*(\omega)\sigma(t)]$, which is just the reciprocal of $G^*(\omega)$. But by an argument similar to that given above for (2.10) one also has $J^*(\omega) = i\omega \int_0^\infty e^{-i\omega t} J(t) dt$.

Hence, within the linear response regime of a system with TTI, knowledge of any one of $G(t)$, $J(t)$, $G^*(\omega)$, $J^*(\omega)$ is enough to determine the other three.

A similar set of simplifications are certainly not guaranteed in the absence of TTI. However, the transient dependence on t_s *may* become negligible when $\omega(t - t_s) \gg 1$, in which case we have

$$G^*(\omega, t, t_s) \rightarrow G^*(\omega, t) \quad (2.11)$$

giving a viscoelastic spectrum that depends only on the measurement time t . If, in addition, the time evolution of the underlying material properties is negligible on the timescale of one oscillation, then $G^*(\omega, t)$ *may* obey the relation

$$G^*(\omega, t) = i\omega \int_0^\infty e^{-i\omega t'} G(t', t) dt' \quad (2.12)$$

Similar statements apply to the compliance spectrum $J^*(\omega, t, t_s)$. Finally, $G^*(\omega, t)$ and $J^*(\omega, t)$ *may* obey the usual reciprocal relation $G^*(\omega, t) = 1/J^*(\omega, t)$. Indeed, we shall find that all the above simplifying relationships are true for the SGR model (subject to an additional requirement that $\omega t_s \gg 1$; see below). As discussed by Fielding et al.¹⁹ they may also hold more generally for systems with “weak long term memory”, but there is no general proof of this that we are aware of. The above simplifications cannot therefore be assumed for all non-TTI systems, and should be verified, for each system studied. This *prima facie* breakdown of conventional linear viscoelastic relationships in aging systems was emphasized by Struik²⁵ though he argued that they are recovered in sufficiently ‘short-time’ measurements. It does not (as Struik seems to suggest) extend necessarily to breakdown of linear superposition itself, which survives in the form of (2.3). In fact, breakdown of TTI is a quite separate issue from nonlinearity; neither implies the other.

1.2.7 Steady state response: The flow curve

Consider now the ultimate state of a material, with TTI, long after an infinitesimal step stress of amplitude σ_0 has been applied. The ultimate deformation may involve a limiting strain $\gamma = \sigma_0 J(t \rightarrow \infty)$, in which case the steady state elastic modulus is $G_\infty = \sigma_0/\gamma$. Alternatively, it may involve a limiting strain rate, in which case the zero-shear viscosity is $\eta = \sigma_0/\dot{\gamma}$. However, neither outcome need occur. If, for example, one has “power law creep”, *i.e.*, $J(t) \sim t^y$ with $0 < y < 1$, the material has both zero modulus (infinite compliance) and infinite viscosity in steady state.

What if the stress amplitude is larger than infinitesimal? The ultimate steady state can again be that of a solid, a liquid, or something in between. When a liquid-like response is recovered, it is conventional to measure the “flow curve”, or steady state relationship between stress and strain rate: $\sigma_{ss} = \sigma(\dot{\gamma})$. In many materials, the following limit, called the yield stress

$$\sigma(\dot{\gamma} \rightarrow 0) = \sigma_y \quad (2.13)$$

is nonzero. (The experimental existence of a true yield stress, in this sense, is debatable,¹⁰ though behaviour closely approaching it is often reported.)

The presence of nonzero yield stress does not necessarily imply a finite Hookean modulus G_∞ : for $\sigma < \sigma_y$, the material could creep forever, but at an ever decreasing rate. (Alternatively, it could reach a steady strain γ that is not linear in σ even as $\sigma \rightarrow 0$.) Nor does the *absence* of a finite yield stress imply a finite viscosity; a counterexample is the power law fluid, for which $\sigma \sim \dot{\gamma}^p$. This has $\sigma_y = 0$ but, for $p < 1$, infinite viscosity $\eta = \lim_{\dot{\gamma} \rightarrow 0} \sigma(\dot{\gamma})/\dot{\gamma}$.

What about the flow curve for materials without TTI? For these, no meaningful definition of “steady state response” exists in general. However, in the SGR model considered below, TTI is restored for nonzero $\dot{\gamma}$,^{11,12} and this may be generic for certain types of aging.^{11,12,26,27} If so the flow curve, including the value of the yield stress σ_y (but *not* the behaviour for $\sigma < \sigma_y$) remains well-defined.

1.2.8 Aging

Aging has been intensively studied in the context of both spin glasses^{26,28–30} and structural glasses.³¹ Some of the earliest experimental investigations of aging in fact involved rheological studies of glassy polymers.²⁵ Nevertheless, in much of the rheological literature aging effects have traditionally been regarded as unwanted obstacles to observing the “real” behaviour of the system, and not in themselves worthy of study. But this may be illusory: aging, when present, can form an integral part of a sample’s rheological response. For example, the literature contains many reports of viscoelastic spectra in which the loss modulus $G''(\omega)$, while remaining less than the (almost constant) storage modulus $G'(\omega)$ in a measured frequency window, appears to be increasing as frequency is lowered (see Fig. 1.1, bold lines). The usual explanation³² is that some unspecified relaxation process is occurring at a lower frequency still, giving a loss peak (dashed), whose true nature could be elucidated if only the frequency window was extended. This may often be the case, but an alternative explanation, based on explicit calculations for the

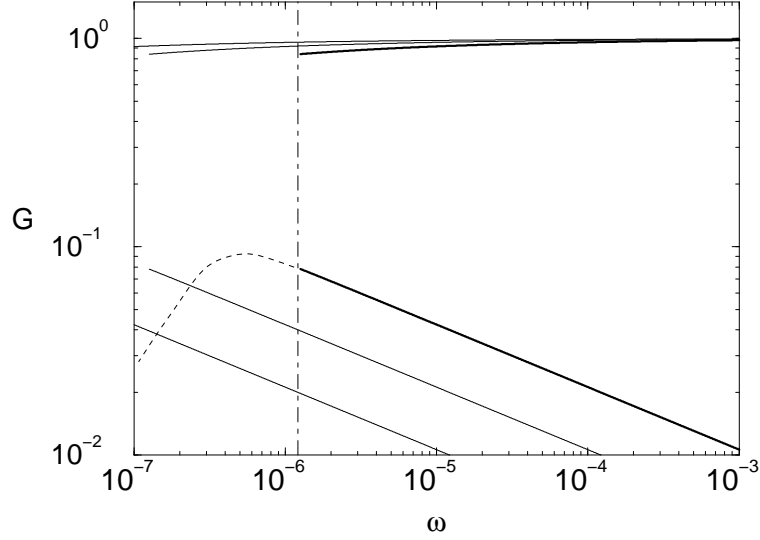


Figure 1.1. Sketch of aging scenario for dynamic moduli G' (top) and G'' (bottom). Thick and thin solid lines: initial spectrum and two subsequent ones. Dashed: putative loss peak. Dot-dashed: limit to frequency window set initially by sample age. (In fact, the solid lines are calculated from the SGR model at noise temperature $x = 0.7$; see Sec. 1.4.) From Fielding et al.¹⁹. Copyright The Society of Rheology.

SGR model, is shown by the thin solid lines in Fig. 1.1, representing subsequent observations in a wider frequency window. No oscillatory measurement can probe a frequency far below the reciprocal of the sample's age; yet in aging materials, it is typically the age itself which sets the relaxation time of whatever slow relaxations are present. Accordingly, the putative loss “peak” can never be observed and is, in fact, a complete figment of the imagination. Instead, a rising curve in $G''(\omega)$ at low frequencies will *always* be seen, but with an amplitude that decreases as the system gets older (typically ensuring that $G''(\omega)$ never exceeds $G'(\omega)$).

In the previous section, we set up a general framework for describing the rheological properties of systems without TTI. Time translation invariance can be broken, in a trivial sense, by the transients that any system exhibits during equilibration. We now consider how such transients can be distinguished from aging proper, considering by way of example the linear step strain response function $G(t - t_w, t_w)$. Aging can then be defined¹⁹ as the property that *a significant part of the stress relaxation takes place on timescales that grow with the age t_w of the system*. If aging is present, then in order to see the full stress relaxation we need to allow the time t at which we observe the stress to be much larger than the

time t_w at which the step strain has been applied. On the other hand, if there is no aging, then the full stress relaxation is “visible” on finite timescales: as long as $\Delta t = t - t_w$ is large enough, we observe the full stress relaxation whatever the age t_w of the system at the time when the strain was applied. (Mathematically, this means that the limits $\Delta t \rightarrow \infty$ and $t_w \rightarrow \infty$ can be interchanged.) We will refer to deviations from TTI in non-aging systems (for which all significant relaxation processes can essentially be observed on finite timescales) as *transients*; see also the discussion, in the context of the SGR model, in Sec. 1.4 below.

We have defined aging as the property that a significant part of the stress relaxation $G(t - t_w, t_w)$ takes place on timescales that grow with the age t_w of the system. In the simplest case, there is only one such growing timescale, proportional to the age of the system itself. The (aging part of the) stress relaxation then becomes a function of the scaled time difference $(t - t_w)/t_w$. We will encounter such simple aging behaviour in the glass phase of the SGR model. More complicated aging scenarios are possible, however: There may be several timescales that grow differently with the age of the system. This can be represented as

$$G(t - t_w, t_w) = \sum_i \mathcal{G}_i [h_i(t)/h_i(t_w)] = \sum_i \tilde{\mathcal{G}}_i [\xi_i(t) - \xi_i(t_w)] \quad (2.14)$$

where the functions $h_i(t)$ define the different diverging timescales and $\xi_i = \ln h_i$, $\tilde{\mathcal{G}}_i(\ln h) = \mathcal{G}_i(h)$. If there is only a single term in the sum, with $h(t) = t$, then the simplest aging scenario is recovered. But (2.14) also includes TTI and intermediate aging scenarios: for $\xi(t) = t/\tau_0$, corresponding to $h(t) = \exp(t/\tau_0)$ (where τ_0 is a microscopic time), one has TTI. More generally, $\xi(t) = (1 - \mu)^{-1}(t/\tau_0)^{1-\mu}$ interpolates between TTI for $\mu = 0$ and simple aging for $\mu \rightarrow 1$. In the regime of short time differences ($t - t_w \ll t_w$), one then finds that the response function depends on $\xi(t) - \xi(t_w) = (t - t_w)/(t_w^\mu \tau_0^{1-\mu})$, thus recovering Struik’s general ‘time waiting-time superposition principle’.²⁵

1.3 The SGR model

The phenomenological SGR model captures many of the observed rheological properties of soft metastable materials, such as foams, emulsions, slurries and pastes.^{1–7} It is based upon Bouchaud’s trap model of glassy dynamics, with the addition of strain degrees of freedom, and the replacement of the thermodynamic temperature by an effective (noise) temperature. It incorporates only those characteristics deemed common to all soft glassy materials (SGMs), namely structural disorder and metastability. We now review its essential features.

We conceptually divide a macroscopic sample of SGM into many mesoscopic elements. By mesoscopic we mean large enough such that the continuum variables of strain and stress still apply for deformations on the elemental scale, and small enough that any macroscopic sample contains enough elements to allow the computation of meaningful “averages over elements”. We then assign to each element a local strain l , and corresponding stress kl , which describe deformation away from some local position of unstressed equilibrium relative to neighbouring elements. The macroscopic stress of the sample as a whole is defined to be $\langle kl \rangle$, where $\langle \rangle$ denotes averaging over elements.

For a newly prepared, undeformed sample, we make the simplest assumption that $l = 0$ for each element. (Physically, of course, $\langle l \rangle = 0$ would be sufficient and is indeed more plausible.) The subsequent application of a macroscopic strain at rate $\dot{\gamma}$ causes each element to strain relative to its local equilibrium state and acquire a non-zero l . For a given element, this continues up to some maximal strain l_y , at which point that element yields, and rearranges into a new configuration of local equilibrium with local strain $l = 0$. This ignores possible “frustration” effects: an element may not be able to relax to a fully unstrained equilibrium position due to interactions with neighbouring elements. Such effects can be incorporated into the model, but are not expected to affect the results in a qualitative way.¹² Under continued macroscopic straining, the yielded element now strains relative to its new equilibrium, until it yields again; its local strain (and stress) therefore exhibits a saw-tooth dependence upon time.

The simplest assumption to make for the behaviour between yields is that $\dot{\gamma} = \dot{l}$: the material deformation is locally affine.²² Yield events apart, therefore, the SGR model behaves as an elastic solid of spring constant k . Yields confer a degree of liquidity by providing a mechanism of stress relaxation.

Although we have introduced yielding as a purely strain-induced phenomenon, we in fact model it as an “activated” process.^{11,12} We assume that an element of yield energy $E = \frac{1}{2}kl_y^2$, strained by an amount l , has a certain probability for yielding in a unit time interval. We write this rate as τ^{-1} , where the characteristic yield time

$$\tau = \tau_0 \exp \left[\left(E - \frac{1}{2}kl^2 \right) / x \right] \quad (3.1)$$

is taken to be the product of an attempt time and an activation factor which is thermal in form. This captures the strain-induced processes described above since any element strained beyond its yield point will yield exponentially quickly; but it also allows even totally unstrained

elements to yield by a process of activation over the energy barrier E . These activation events mimic, within our simplified model, nonlinear couplings to other elements. A more complete model would treat these couplings explicitly. However, in the SGR model, which does not, x is regarded as an effective “noise” temperature to model the process. (Alternatively, we can think of x as the typical *energy* available for an activated processes. We use units in which the Boltzmann constant $k_B = 1$ throughout, so there is no need to distinguish between these two interpretations of x as either a temperature or an energy.) Because the energy barriers are (for typical foams, emulsions, etc.) large compared to the thermal energy $k_B T$, so are the energy changes caused by these nonlinear couplings, and so to mimic these, one expects to need x of order the mean barrier height $\langle E \rangle$. Whether it is fully consistent to have a noise temperature $x \gg k_B T$ is a debatable feature of the model.^{11,12} However, similar “macroscopic” effective temperatures, which remain nonzero even for $k_B T \rightarrow 0$, have been found in other theories of out-of-equilibrium systems with slow dynamics.^{27,33}

The disorder inherent to SGMs is captured by assuming that each element of a macroscopic sample has a different yield energy: a freshly yielded element is assigned a new yield energy selected at random from a “prior” distribution $\rho(E)$. This suggests the following alternative view of the dynamics: each material element of a SGM can be likened to a particle moving in a landscape of quadratic potential wells or “traps” of depth E . The depths of different traps are uncorrelated with each other and distributed according to $\rho(E)$. The bottom of each trap corresponds to the unstrained state $l = 0$; in straining an element by an amount l , we then effectively drag its representative particle a distance $\frac{1}{2}kl^2$ up the sides of the trap, and reduce the effective yield barrier height ($E \rightarrow E - \frac{1}{2}kl^2$). Once the particle has got sufficiently close to the top of its trap ($E - \frac{1}{2}kl^2 \approx x$), it can hop by activated dynamics to the bottom of another one. This process corresponds to the yielding of the associated material element.

A specific choice of $\rho(E)$ is now made: $\rho(E) = (1/x_g) \exp(-E/x_g)$, where $x_g = \langle E \rangle$ is the mean height of a barrier chosen from the prior distribution $\rho(E)$. As shown by Bouchaud,³⁴ the exponential distribution, combined with the assumed thermal form for the activated hopping, is sufficient to give a glass transition in the model. The transition is at $x = x_g$ and divides the glass phase ($x \leq x_g$), in which “weak ergodicity breaking”³⁴ occurs, from a more normal phase ($x > x_g$). In the glass phase, the Boltzmann distribution (which is the only possible steady state for activated hopping dynamics, in the absence of strain), $P_{\text{eq}}(E) \propto \rho(E) \exp(E/x)$ is not normalizable: thus there is no steady

state, and the system must age with time. The converse applies for $x > x_g$: there is then a unique equilibrium state, which is approached at long times. Apart from our use of an effective temperature x , the only modification to Bouchaud's original model of glasses lies in our introduction of dynamics within traps coupled to strain.

It may appear suspicious that, to obtain a glass transition at all, an exponential form of $\rho(E)$ is required. In reality the glass transition is certainly a collective phenomenon: the remarkable achievement of Bouchaud's model is to represent this transition within what is, essentially, a single-particle description. Thus the chosen "activated" form for the particle hopping rates, and the exponential form of the trap depth distribution, should not be seen as two independent (and doubtful) physical assumptions, but viewed jointly as a tactic that allows glassy dynamics to be modelled in the simplest possible way.^{11,12}

From now on, without loss of generality, we choose units so that both $x_g = k = 1$. This means that the strain variable l is defined such that an element, drawn at random from the prior distribution, will yield at strains of order one. Since the actual value of the strain variable can be rescaled within the model (the difference being absorbed in a shift of k), this is purely a matter of convention. Our choice should nevertheless be borne in mind when interpreting the results: where strains "of order unity" arise, these are in fact of order some yield strain l_y , which may in reality be a few percent or less. In addition we choose by convention $\tau_0 = 1$; the timescale in the SGR model is scaled by the mesoscopic "attempt time" for the activated dynamics. The low frequency limit, which is the main regime of interest, is then defined by $\omega\tau_0 = \omega \ll 1$. Note that, with our choice of units, $\langle E \rangle = 1$ so that we expect the interesting physics to involve $x \simeq 1$.

1.3.1 Constitutive equation

The SGR model is exactly solved by two coupled constitutive equations,¹² the first of which expresses strain as an integral over stress history, while the second embodies the conservation of probability. We assume that the sample is prepared (in a known initial state of zero stress and strain) at time zero and that a time dependent macroscopic strain $\gamma(t)$ is applied thereafter, so $\gamma(t) = 0$ for $t \leq 0$. The constitutive equations are then

$$\sigma(t) = \gamma(t)G_0(Z(t, 0)) + \int_0^t [\gamma(t) - \gamma(t')] Y(t') G_\rho(Z(t, t')) dt' \quad (3.2)$$

$$1 = G_0(Z(t, 0)) + \int_0^t Y(t') G_\rho(Z(t, t')) dt' \quad (3.3)$$

In these equations

$$Z(t, t') = \int_{t'}^t \exp \left([\gamma(t'') - \gamma(t')]^2 / 2x \right) dt'' \quad (3.4)$$

while $Y(t')$ is the average yield rate rate at time t' . The functions $G_\rho(Z)$ and $G_0(Z)$ obey

$$G_\rho(Z) = \int_0^\infty \rho(E) \exp \left(-Z e^{-E/x} \right) dE \quad (3.5)$$

$$G_0(Z) = \int_0^\infty P_0(E) \exp \left(-Z e^{-E/x} \right) dE \quad (3.6)$$

where $P_0(E)$ is the probability distribution for the yield energies (or trap depths) in the initial state of preparation of the sample at time $t = 0$.

These equations can be understood by viewing yielding as a “birth and death” process: each time an element yields it dies and is reborn with zero stress, and with a yield energy selected randomly from the prior distribution $\rho(E)$. The (average) yield rate rate at time t' is $Y(t')$; the birth rate at time t' of elements of yield energy E is therefore $Y(t')\rho(E)$. The proportion of these which survive without yielding until time t is found as $\exp[-Z(t, t')/\tau(E)]$ where $\tau(E) = \exp(E/x)$ is the (mean) lifetime that an unstrained element of yield energy E would have. The expression (3.4) for $Z(t, t')$ reflects the fact that an element that last yielded at time t' and has a yield energy E will have a yield rate of $\tau(E)^{-1} \exp \left([\gamma(t'') - \gamma(t')]^2 / 2x \right)$ at time t'' . Here the exponential factor accounts for the lowering of the yield barrier by strain applied since the element last yielded. Eq. (3.2) is then obtained by multiplying the contribution from each element by the strain (and hence stress) $\gamma(t) - \gamma(t')$ acquired since it was last “born”, and integrating over t' . The additional first term arises from elements that have never yielded since time 0. Eq. (3.3), which is an integral equation for $Y(t)$, is obtained similarly from the conservation of the total number of elements.

Under conditions where the local strain is everywhere negligible, one has $Z(t, t') \rightarrow t - t'$. More generally, $Z(t, t')$ can be thought of as an effective time interval measured on an “internal clock” within an element, which allows for the effect of local strain on its yield rate, by speeding up the clock. This speeding up effect, which describes strain-induced yielding, is the only source of nonlinearity within the (scalar) SGR model; additional nonlinearities arise in the tensorial version discussed next.

1.3.2 Tensorial SGR model

Although we focus in the rest of this chapter on the scalar SGR model as described above, it is worth outlining briefly how the model can be

extended to account fully for the tensorial nature of stress and strain.²⁰ It turns out that the modifications required are in fact rather minimal. Instead of the shear $\gamma(t)$, one now needs a tensorial quantity to describe the deformation history of the material. This is furnished by $\mathbf{E}_{tt'}$, the deformation tensor between times t' and t : a small vector $\delta\mathbf{r}$ embedded in the material is transformed to $\mathbf{E}_{tt'}\cdot\delta\mathbf{r}$ during this time interval. $\mathbf{E}_{tt'}$ thus replaces $\gamma(t) - \gamma(t')$. We can now assume as before that the deformation of local mesoscopic element follows the macroscopic deformation between yield events, and that elements are “reborn” in an unstrained state after a yield event. The constitutive equation (3.2) is then replaced by

$$\boldsymbol{\sigma}(t) = \mathbf{Q}(\mathbf{E}_{t0})G_0(Z(t, 0)) + \int_0^t \mathbf{Q}(\mathbf{E}_{tt'})Y(t')G_\rho(Z(t, t')) dt' \quad (3.7)$$

while (3.3) remains as before except for the modified definition of $Z(t, t')$,

$$Z(t, t') = \int_{t'}^t \exp [R(\mathbf{E}_{t''t'})/x] dt'' \quad (3.8)$$

Here $\boldsymbol{\sigma}$ is the overall stress tensor, and \mathbf{Q} and R are tensor and scalar functions of \mathbf{E} that can in principle be freely chosen. $\mathbf{Q}(\mathbf{E})$ gives the stress contributed by an element that has been deformed by \mathbf{E} , generalizing our earlier simple linear relation between local strain l and local stress kl . $R(\mathbf{E})$ is the corresponding increase in internal energy of the element which lowers the yield barrier and generalizes the earlier $kl^2/2$. All other quantities have the same meaning as for the scalar model.

Suitable choices for \mathbf{Q} and R are described in detail by Cates and Sollich²⁰ with particular attention to the case of foams and emulsions. This paper also discusses the predictions of the tensorial SGR model for a range of rheological quantities and scenarios that cannot be addressed within the scalar model, including normal stress differences and extensional flows.

1.3.3 Rheological properties without aging

We now return to the scalar SGR model and review briefly its predictions in the non-aging regime where TTI applies. Solution of the constitutive equations (3.2,3.3) is then relatively straightforward.^{11,12} Only the linear spectra and the flow curve are discussed below; predictions for more complicated experiments such as large-amplitude oscillatory shear are detailed by Sollich.¹²

A regime of **linear rheological response** arises whenever the effect of strain on the effective time interval $Z(t, t')$ is small. This requires that the local strains in each element remain small; in oscillatory shear, where

$\gamma(t) = \gamma_0 e^{i\omega t}$, this is satisfied at low enough strain amplitudes γ_0 for any finite frequency ω . (The same is not true in steady shear flow; see below.) The elements' lifetimes are then, to order γ_0 , strain-independent, and in the constitutive equations $Z(t, t')$ can then be replaced by $t - t'$.

As described in Sec. 1.2.6 above, the conventional definition of the linear viscoelastic spectra $G'(\omega), G''(\omega)$ (Eq. 2.10), requires not only linearity but also TTI. Thus they are well-defined only for an equilibrium state; in the SGR model, the latter exists only for $x > 1$. But even at $x > 1$ these spectra show interesting power law dependencies at low frequency; these are summarized as follows (prefactors^{11,12} are omitted):

$$\begin{aligned} G'' &\propto \omega & \text{for } 2 < x, & & \propto \omega^{x-1} & \text{for } 1 < x < 2 \\ G' &\propto \omega^2 & \text{for } 3 < x, & & \propto \omega^{x-1} & \text{for } 1 < x < 3 \end{aligned} \quad (3.9)$$

Here and throughout, “low frequency” in the SGR model means $\omega \ll 1$, that is, frequencies small compared to the mesoscopic attempt rate for activated hopping $\tau_0^{-1} = 1$ (in our units).

The **flow curve** was defined in Sec. 1.2.7 as the nonlinear stress response $\sigma(\dot{\gamma})$ to a steady strain rate $\dot{\gamma}$. For the SGR model, it shows the following scalings for $\dot{\gamma} \ll 1$:

$$\begin{aligned} \sigma &\propto \dot{\gamma} & \text{for } x > 2 \\ \sigma &\propto \dot{\gamma}^{x-1} & \text{for } 1 < x < 2 \\ \sigma - \sigma_y &\propto \dot{\gamma}^{1-x} & \text{for } x < 1 \end{aligned} \quad (3.10)$$

These results exhibit two interesting features which are explored more fully in Sec. 1.5.2. Firstly, for $x < 1$ there is a yield stress $\sigma_y(x)$. A linear response regime exists at $\sigma \ll \sigma_y$; aging can occur for all $\sigma < \sigma_y$. For $\sigma > \sigma_y$ the system achieves a steady state, and aging no longer occurs. This is because any finite flow rate, however small, causes strain-induced yielding of elements even in the deepest traps; the time required to yield, with a steady flow present, is only power law, rather than exponential in E . Thus the aging process is curtailed or “interrupted” by flow;^{11,12,19} the flow curve is well-defined even in the glass phase. The second interesting feature is that, for $1 < x < 2$ (where aging is absent) there is no linear response regime at all in steady shear: however small the applied stress, the behaviour is dominated by strain-induced yielding. There is an anomalous (power law) relation between stress and strain rate, and an infinite zero-shear viscosity (cf. Sec. 1.2.7 above). This also shows up in (3.9), where $\eta = \lim_{\omega \rightarrow 0} G''(\omega)/\omega$ is likewise infinite. More recently, it has been argued³⁵ that alternative methods of averaging the contributions to the viscosity of the local elements can give a finite zero-shear viscosity for $1 < x < 2$. This then diverges strongly as $x = 1$ is approached.

It is worth mentioning that the flow curves produced by the SGR model are all shear-thinning, with $\sigma/\dot{\gamma}$ and $d\sigma/d\dot{\gamma}$ both decreasing as $\dot{\gamma}$ is increased. The model can be modified, however, to account for shear-thickening effects. This also leads to interesting rheological instabilities and even chaotic behaviour.^{36,37}

1.4 Rheological aging: Imposed strain

Before giving the results for aging under imposed strain, it is useful to discuss some general features of aging in the SGR model. These will provide a basis for an intuitive understanding of the predicted behaviour.

As noted above, to solve the constitutive equations (3.2,3.3) the initial distribution $P_0(E)$ of yield energies at time zero must be specified. For simplicity, we choose the case where $P_0(E) = \rho(E)$; this is equivalent to suddenly “quenching” the noise temperature x , at time zero, from a very large value ($x \gg 1$) to a value within the range of interest. The effects of other initial conditions are discussed in detail in.¹⁹

Following a quench, the system will age, and this will be reflected within the SGR model in the evolution of the distribution of lifetimes (or equivalently particle hopping rates). We ignore the presence of a strain, so that the discussion applies when there is no flow, and in the linear response regime, where strain-induced hops can be ignored. Under such conditions, the hopping rate $Y(t)$ is a strain-independent function of time, and is readily found from (3.3) by Laplace transform:¹⁹ for $x > 1$, $Y(t) \rightarrow \text{const.}$ for $t \rightarrow \infty$, while for $x < 1$, $Y(t) \sim t^{x-1}$. From this, the distribution of yield energies $P(E, t)$ can be deduced. By “birth-death” arguments similar to those above, it is given by

$$P(E, t) = P_0(E) \exp[-t/\tau(E)] + \int_0^t Y(t') \rho(E) \exp[-(t-t')/\tau(E)] dt' \quad (4.1)$$

with $\tau(E) = \exp(E/x)$ as before. Equivalently, one can consider the lifetime distribution $P(\tau, t)$. As pointed out above, in the absence of strain, the only candidate for a steady state distribution of yield energies $P_{\text{eq}}(E)$ is the Boltzmann distribution: $P_{\text{eq}}(E) \propto \rho(E) \exp(E/x)$, which translates to $P_{\text{eq}}(\tau) = P_{\text{eq}}(E) dE/d\tau \propto \tau^{-x}$. In either language, the distribution is not normalizable for $x < 1$, leading to broken TTI in the model.³⁴ the probability distribution of trap lifetimes $P(\tau, t_w)$ evolves as a function of the waiting time t_w elapsed since sample preparation. The initial lifetime distribution is obtained from $P(E, 0) = \rho(E)$ as $P(\tau, 0) \propto \rho(E) d\tau/dE \propto \tau^{-(1+x)}$. Thereafter, by changing variable from E to τ in (4.1), we find the following approximate

expressions for $P(\tau, t_w)$

$$\begin{aligned} P(\tau, t_w) &\simeq xY(t_w)\tau\rho(\tau) & \text{for } \tau \ll t_w \text{ and } t_w \gg 1 \\ P(\tau, t_w) &\simeq xY(t_w)t_w\rho(\tau) & \text{for } \tau \gg t_w \text{ and } t_w \gg 1 \end{aligned} \quad (4.2)$$

For a quench “temperature” above the glass point ($x > 1$), $P(\tau, t_w)$ exhibits a transient decay; as $t_w \rightarrow \infty$, $P(\tau, t) \rightarrow P_{\text{eq}}(\tau) = (1-x)\tau^{-x}$, as expected. The nature of the approach to the long time limit is illustrated schematically in Fig. 1.2(a); the final distribution has most of its weight at $\tau = O(1)$. For $x < 1$, in contrast, $P(\tau, t_w)$ evolves as in Fig. 1.2(b).

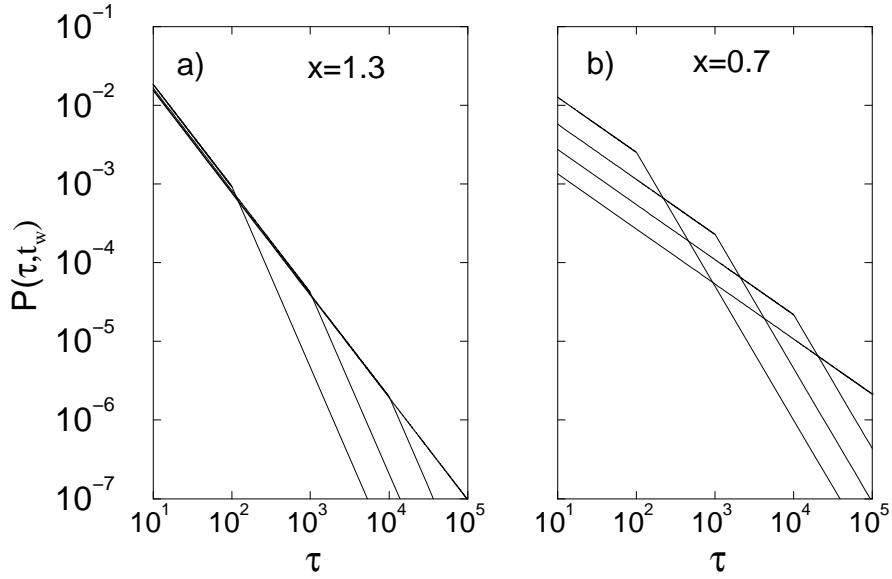


Figure 1.2. Schematic evolution of the relaxation time distribution (a) above the glass transition; (b) below it. The first shows a transient decay onto a steady state, the second shows aging behaviour. The curves lie in order of increasing t_w at the bottom of each figure. From Fielding et al.¹⁹. Copyright The Society of Rheology.

Since $Y(t_w) \sim t_w^{x-1} \rightarrow 0$ at long times, the limit of $P(\tau, t_w)$ is zero for any finite τ as $t_w \rightarrow \infty$. Thus, the proportion of elements having yield time of order unity tends to zero as $t_w \rightarrow \infty$; the bulk of the distribution’s weight is at $\tau \simeq t_w$. This is consistent with the idea that, in a system undergoing aging, the characteristic relaxation time is typically of the order of the age of the system itself.

We are now ready to present the predictions of the SGR model in the aging regime. Because the constitutive equations (3.2, 3.3) are more readily solved to find the stress response to an imposed strain, rather

than vice-versa, we discuss first strain-controlled experiments and defer the stress-controlled case to Sec. 1.5.

1.4.1 Linear response

As described in Sec. 1.3.3 above, when local strains are negligible, the SGR model displays a linear response regime, with the effective time interval $Z(t, t')$ becoming the actual time interval $t - t'$, and the hopping rate $Y(t')$ a strain-independent function of time. The stress response to any strain history then follows directly from (3.2).

For a **step strain**, the amplitude γ_0 gives the maximum local strain experienced by any element, making the condition for linearity $\gamma_0 \ll 1$. The linearized step strain response, defined in (2.2), can be found in the SGR model by rewriting the constitutive equation (3.2) as

$$G(t - t_w, t_w) = 1 - \int_{t_w}^t Y(t') G_\rho(t - t') dt' \quad (4.3)$$

Limiting analytic forms for $G(t - t_w, t_w)$ can be obtained when experimental timescales are large on the scale of the mesoscopic attempt time $\tau_0 = 1$, so that $t - t_w \gg 1$ and $t_w \gg 1$. We then identify two distinct regimes: a short time interval regime $t - t_w \ll t_w$ and long time interval regime $t - t_w \gg t_w$ (where the measure of “short” and “long” is not now τ_0 but t_w itself). The limiting forms in each case depend on the value of x . For $x > 1$, one has $G \sim (t - t_w)^{1-x}$ for short time intervals and $G \sim t_w(t - t_w)^{-x}$ for long ones; here and in the following we omit all numerical prefactors. In the glass phase ($x < 1$), on the other hand, one has $G \sim 1 - [(t - t_w)/t_w]^{1-x}$ and $G \sim [(t - t_w)/t_w]^{-x}$, respectively. These results can be motivated physically by recognizing that $G(t - t_w, t_w)$ just measures the fraction of elements that have not yielded between t_w and t . To a good approximation, this is the fraction of elements that have a lifetime $\tau > t - t_w$ at time t_w , $\int_{t-t_w}^{\infty} P(\tau, t_w) d\tau$. Inserting the approximate forms (4.2) for P one then indeed recovers the predicted scalings of G .

Numerical results for $G(t - t_w, t_w)$ are shown in Fig. 1.3. For $x > 1$, one has no aging and only transients, as displayed in the left panel: the curves coincide at short time intervals $t - t_w \ll t_w$. At large t_w , this regime accounts for more and more of the decay of G ; the remaining t_w -dependence is only through an unimportant tail. For $t_w \rightarrow \infty$, the “short time” regime extends to all finite values of $t - t_w$; one recovers the equilibrium response which decays to zero on a t_w -independent timescale. Equivalently, if we assume that $G(t - t_w, t_w)$ can be measured reliably only as long as it remains greater than some specified value (a small

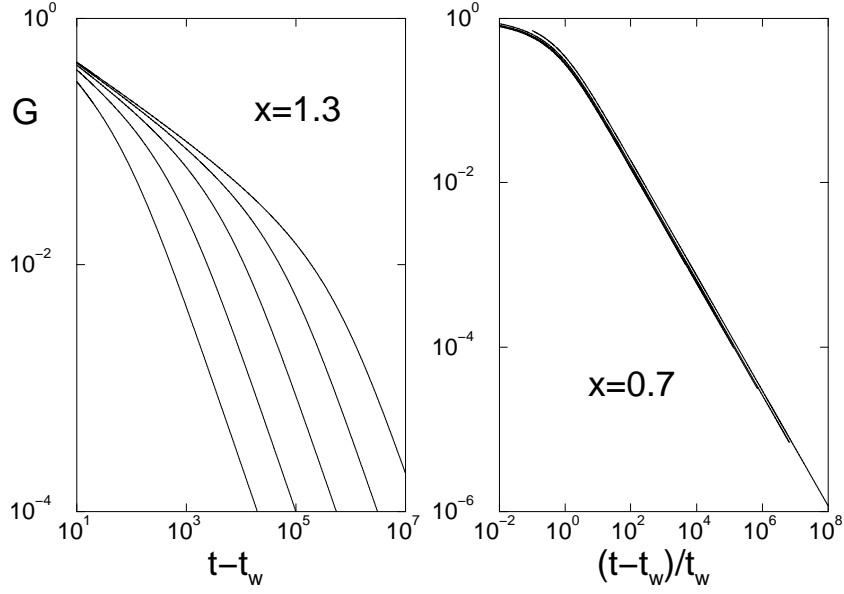


Figure 1.3. Stress relaxation modulus $G(t - t_w, t_w)$, for $x = 1.3$ against $t - t_w$ (left) and for $x = 0.7$ against the scaled time interval $(t - t_w)/t_w$ (right). Shown are data for waiting times $t_w = 10^2, 10^3 \dots 10^6$ (left to right in left panel, right to left in right panel). From Fielding et al.¹⁹. Copyright The Society of Rheology.

fraction ϵ of its initial value $G(0, t_w) = 1$, for example), then the results will become t_w -independent for sufficiently large t_w .

For $x < 1$, on the other hand, one has aging proper as illustrated in the right panel of Fig. 1.3: the major part of the decay of G occurs on a timescale of order t_w itself, with unimportant corrections to this scaling at early times. We note that in this regime, the SGR model shows the simplest kind of aging, with only a single aging timescale that is directly proportional to t_w , and no separate TTI part of the stress relaxation which would take place for $t - t_w$ of $O(1)$.

Next we consider **oscillatory strain**, for which the stress response is determined by the spectrum (2.9). In principle, this quantity depends on t_s , the time when the oscillatory strain was started. However, when the experimental timescales become large, one finds¹⁹ that this dependence on t_s is weak. In fact, within the SGR model, the conditions needed to make G^* negligibly dependent on t_s (for low frequencies, $\omega \ll 1$) are that $\omega(t - t_s) \gg 1$ and $\omega t_s \gg 1$. The first signifies merely that many cycles of oscillatory strain are performed before the stress is measured; the second ensures that transient contributions from the initial sample preparation stage (the quench at $t = 0$) are negligible. The fact that these crite-

ria are sufficient even in the glass phase is far from obvious physically, and requires a careful discussion.¹⁹ Broadly speaking, they are satisfied in any experiment that would reliably measure a conventional $G^*(\omega)$ spectrum for systems with TTI.

For the purposes of such experiments, we can therefore drop the t_s argument and define a time-dependent spectrum $G^*(\omega, t)$. For long times ($t \gg 1$) this is found to behave as¹⁹

$$\begin{aligned} G^*(\omega, t) &\sim (i\omega)^{x-1} && \text{for } 1 < x < 2 \\ G^*(\omega, t) &\approx 1 - (i\omega t)^{x-1} && \text{for } x < 1 \end{aligned} \tag{4.4}$$

These results are easily understood: by measuring $G^*(\omega, t)$ we are directly probing the properties of the system at the time of measurement, t . In the ergodic phase ($x > 1$), $G^*(\omega, t)$ will reach a t -independent value within a time of $O(1/\omega)$ after the quench, as the relevant traps will then have attained their equilibrium population. The relaxation time is then also of $O(1)$ and the response $G^*(\omega, t)$ is a function only of ω . In contrast, below the glass point the characteristic relaxation time at the epoch of measurement is of order t , and the response is a function only of the product ωt . Since the losses in an oscillatory measurement arise from traps with lifetimes less than about $1/\omega$ (elements in deeper traps respond elastically), the overall response becomes more elastic as the system ages into traps with $\tau > 1/\omega$.

Numerical results for the viscoelastic spectrum $G^*(\omega, t)$ are shown in Fig. 1.4. The spectra become increasingly flat as the glass point $x = 1$ is approached from above, with G' and G'' being of comparable order of magnitude; such flat spectra are seen experimentally in many materials (compare the discussion in the introduction). In the glass phase, the storage modulus at low frequencies evolves upwards, and the loss modulus downwards as expected.^{11,12} If plotted against ω rather than ωt , the data for $x = 0.7$ would resemble Fig. 1.1. Each spectrum terminates at frequencies of order $\omega t \simeq 1$. This is because one cannot measure a true oscillatory response for periods *beyond* the age of the system. Therefore, the rise at low frequencies in G'' -spectra like Fig. 1.1 represents the ultimate rheological behaviour. (The middle rows of Fig. 1.4 illustrate that at $x = 1$ itself, logarithmic corrections cause G' and G'' to scale neither with ω nor with ωt .)

One can show¹⁹ that the insensitivity of $G^*(\omega, t, t_s)$ to t_s in practical measurements of the viscoelastic spectrum (where an oscillatory strain is maintained over many cycles) arises because the most recently executed strain cycles dominate the stress response at time t . This “forgetfulness” of strain cycles in the distant past also means that, in the SGR model, the

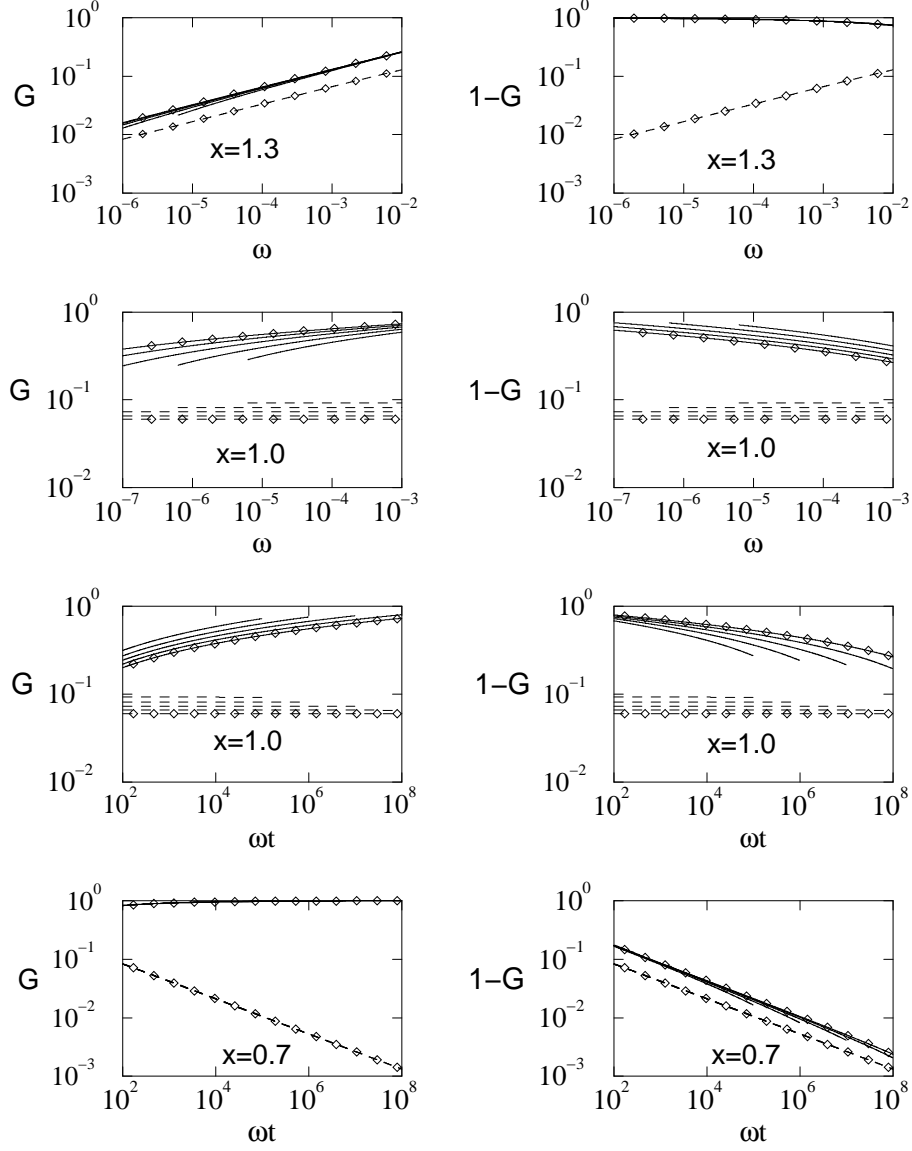


Figure 1.4. Left column: viscoelastic spectra $G'(\omega)$ (solid lines) and $G''(\omega)$ (dashed lines) versus frequency, ω (for $x \geq 1$) or scaled frequency ωt (for $x \leq 1$). Right column: frequency-dependent corrections to Hookean elasticity, $1 - G'$ (solid lines), G'' (dashed lines). Data are shown for systems aged $t = 10^7, 10^8, \dots, 10^{11}$. At any fixed ω the curves lie in order of age; data on the oldest system is marked by the symbols. From Fielding et al.¹⁹. Copyright The Society of Rheology.

Fourier relationship (2.12) between oscillatory and step strain responses is recovered to a good approximation.

We mention briefly at this stage that the SGR model has recently also been used to analyse so-called “over-aging” effects.^{16,17} These occur experimentally if one applies a large-amplitude oscillatory strain to an aging system, for some finite duration, then lets the system evolve and eventually measures its viscoelastic spectrum with a small oscillatory probe-strain. Naively, one might suspect that the large-amplitude oscillatory strain would tend to “reset” the aging process, reducing the effective age t . However, the situation is more subtle: Viasnoff and Lequeux¹⁶, Viasnoff et al.¹⁷ the large-amplitude strain leaves elements with large yield energies E unaffected. Elements with moderate E are forced to yield, and will be reborn with small E (as directly after a quench). The population of yield energies is thus depleted in an intermediate range of E , and increased for small E . During the subsequent evolution and continued aging, the new population of small- E elements yields quickly and acquires progressively larger E . The depletion of the intermediate E -values then eventually becomes important, and the viscoelastic spectrum has a *larger* contribution from deep traps. The overall effect is that the sample can behave as if it the large oscillatory strain had made it *older* (hence the name over-aging) rather than younger.

Finally, consider a **startup** experiment in which a steady shear of rate $\dot{\gamma} \ll 1$ begins at time t_w . So long as we restrict attention to times short enough that the total strain remains small ($\dot{\gamma}(t - t_w) \ll 1$) the system exhibits linear response; the crossover to the nonlinear regime is discussed in Sec. 1.4.2 below. One finds¹⁹ for long times and in the linear response regime that $\sigma(t) \sim \dot{\gamma}(t - t_w)$ for $x < 1$ (which is purely elastic behaviour), $\sigma(t) \sim \dot{\gamma}(t - t_w)^{2-x}$ for $1 < x < 2$ (which is an anomalous power law), and $\sigma(x) \sim \dot{\gamma}$ for $x > 2$. Except for prefactors, these scalings are independent of whether $t - t_w \ll t_w$ or $\gg t_w$, so that *linear* startup experiments are not a useful probe of aging dynamics.

1.4.2 Nonlinear response

We now turn to the nonlinear behaviour of the SGR model under imposed strain. For **step strain** of amplitude γ_0 , the effective time interval $Z(t, t')$ is increased by a factor $\exp(\gamma_0^2/2x)$ for times above t_w , and this translates into the simple relation

$$G(t - t_w, t_w; \gamma_0) = G\left((t - t_w) \exp\left(\gamma_0^2/2x\right), t_w\right) \quad (4.5)$$

This result generalizes that of Sollich¹² for the non-aging case ($x > 1$). It can be understood as follows. Within the SGR model, instantaneous

response to a step strain at t_w is always elastic (that is, $G(0, t_w, \gamma_0) = 1$); the fraction of stress remaining at time $t > t_w$ is the fraction of elements which have survived from t_w to t without yielding (see above). The stress decay is therefore determined entirely by the distribution of relaxation times in the system just after the strain is applied at time t_w . The effect of a finite strain is solely to modify the distribution of barrier heights, and hence to modify this distribution of relaxation times τ ; in fact (within the scalar model) nonlinear strain reduces the yield time of every element by an identical factor of $\exp(\gamma_0^2/2x)$.¹²

In Sec. 1.4.1 above we discussed the response to **startup of steady shear** (with $\dot{\gamma} \ll 1$) at time t_w , assuming linear response. Now consider the effect of strain-induced yield events, which cause nonlinearity. For $x > 2$ (where the SGR model predicts Newtonian fluid behaviour for $\dot{\gamma} \ll 1$), one can show that the stress response remains linear at all times, including the steady state limit.¹⁹ For $x < 2$, on the other hand, one finds¹⁹ that the linear period ends at $t \simeq \dot{\gamma}^{-1}$ (within logarithmic terms, discussed below); at later times, the main stress-bearing elements will, during their lifetimes, become strongly strained. Indeed, at strain rate $\dot{\gamma}$, an element with yield energy E will be strained to the top of its yield barrier in a time $t_{\text{int}} \simeq E^{1/2}/\dot{\gamma} \simeq (\ln \tau)^{1/2}/\dot{\gamma}$. The tendency of the distribution of local stresses to evolve toward deeper and deeper traps is thereby *interrupted*: the lifetime of a deep trap is converted from τ to a much smaller value, of order $(\ln \tau)^{1/2}/\dot{\gamma}$.^{11,12} This truncation of the lifetime distribution is enough to ensure that these distributions are never dominated by the deep traps, and a steady state is recovered; accordingly, there are no aging effects at late enough times. Aging is also absent during the initial linear regime (Sec. 1.4.1), so any nontrivial effects must be confined to an intermediate time regime. There, at the end of the linear regime the stress can be *higher* than the steady state value, leading to an overshoot in the startup curve.¹² This overshoot region, unlike the two asymptotes, shows a significant dependence on the system age t_w , as shown in Fig. 1.5. The physics of this is clear: the extent of the linear regime gets progressively larger as t_w is increased, because the system has aged into deeper traps (and because the scalar SGR model assumes that within each trap the relation between stress and strain is linear). Thus the strain at which strong yielding sets in increases (roughly logarithmically) with t_w ; the height of the overshoot is accordingly increased before dropping onto the same, t_w -independent, steady-shear plateau.

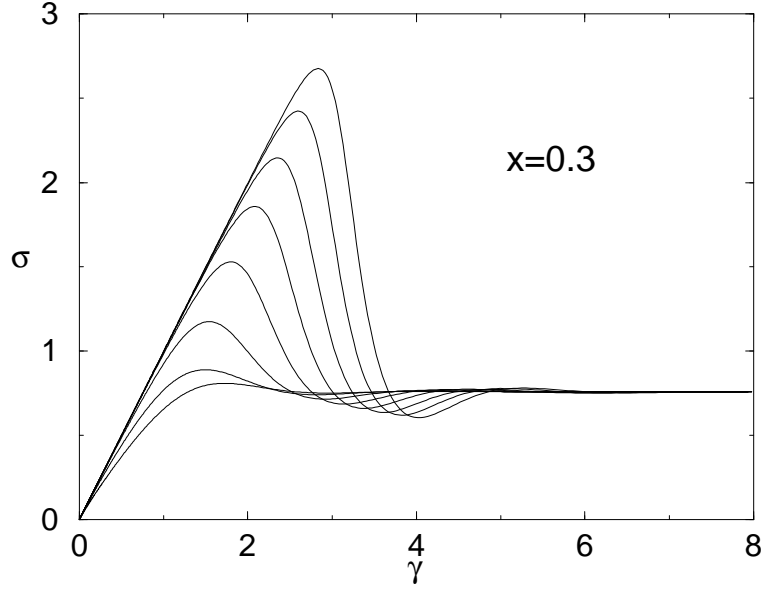


Figure 1.5. Stress response σ , in shear startup, vs strain γ at noise temperature $x = 0.3$ and strain rate $\dot{\gamma} = 0.001$. Curves from bottom to top correspond to increasing ages $t_w = 10^2, 10^3 \dots 10^9$ at time of startup. From Fielding et al.¹⁹. Copyright The Society of Rheology.

1.5 Rheological aging: Imposed stress

We now review the SGR model's predictions for various stress-controlled rheological experiments; these are mostly obtained by numerical solution of the constitutive equations.¹⁹

1.5.1 Linear response

In **step stress**, the SGR model predicts that there will be an instantaneously elastic response. Elements then progressively yield and reset their local stresses to zero; thus we must apply progressively more strain to maintain the macroscopic stress at a constant value. Potentially therefore, individual elements can acquire large local strains and linearity of the response need not be maintained at late times. As for shear startup, it is therefore sensible to first assume that the response *is* linear and then to consider *a posteriori* up to what time t the linear results remain valid.

In the linear regime the step stress response is described by the creep compliance $J(t - t_w, t_w)$, defined in Sec. 1.2.5. One finds that J scales as $t - t_w$ for $x > 2$ and as $(t - t_w)^{x-1}$ for $1 < x < 2$. These results apply

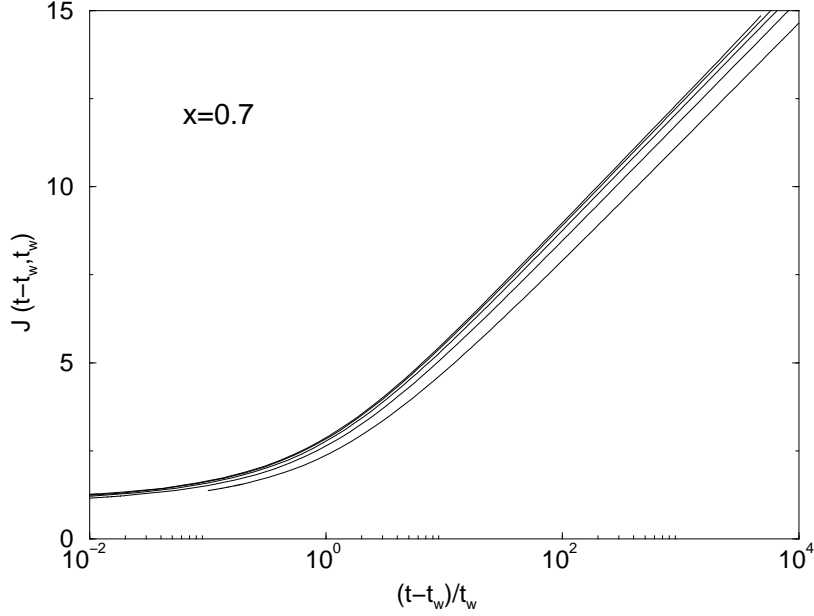


Figure 1.6. Linear creep compliance $J(t - t_w, t_w)$ against scaled time interval $(t - t_w)/t_w$ for noise temperature $x = 0.7$. Curves from bottom to top correspond to increasing times $t_w = 10^2, 10^3 \dots 10^6$ of stress onset. Note the approach to a limiting scaling form as t_w becomes very large compared with the microscopic time $\tau_0 = 1$. From Fielding et al.¹⁹. Copyright The Society of Rheology.

both for $t - t_w \ll t_w$ and $t - t_w \gg t_w$, though with different prefactors. The non-Newtonian behaviour for $1 < x < 2$ reflects the low-shear rate power-law behaviour of the flow curve. In the glass phase ($x < 1$), finally, one finds $J \sim \ln(t - t_w/t_w)$ for $t - t_w \gg t_w$. This exhibits the expected aging effects, but being logarithmic these are rather weak; see Fig. 1.6. Such behaviour is intuitively reasonable: the strain response at time t to step stress is *not* determined purely by the relaxation spectrum at t_w (as was the case in step strain), but by the dynamics of the system over the entire interval between t_w and t . This decreases the sensitivity to the time t_w at which the perturbation was switched on.

For **oscillatory stress**, one finds results very similar to those for the case of oscillatory strain (Sec. 1.4.1). Although unsurprising, this does require explicit confirmation in a system exhibiting rheological aging; see Sec. 1.2.6. One confirms numerically that the reciprocity relation $J^*(\omega, t) = 1/G^*(\omega, t)$ is obeyed to good accuracy, so that the linear responses to imposed oscillatory strain and stress contain essentially the same information.

1.5.2 Nonlinear response

Within the SGR model, application of a **step stress** of size $\sigma_0 \ll 1$ induces a strain response $\gamma(t)$ which increases over time, but remains linear in σ_0 for at least as long as the linearized constitutive equations predict $\gamma(t) \ll 1$. This is because $\gamma(t)$ provides an upper bound on the local strain of each element. Although sufficient to ensure linearity, this is not always necessary; one requires only that the characteristic strain *of those elements which dominate the stress* is small. For $x > 2$ (the Newtonian regime) the dominant elements have lifetimes $O(1)$ and so the response is linear to indefinite times so long as $\sigma_0 \ll 1$ (ensuring $\dot{\gamma}(t) \ll 1$ for all times t). But, whenever $x < 2$, the linear analysis sketched above¹⁹ indicates that the dominant elements have lifetimes of order $t - t_w$; so a self-consistently linear response is maintained only provided that $\dot{\gamma}(t)(t - t_w) \ll 1$, just as in startup of steady shear (see Sec. 1.4.2. For $1 < x < 2$ this condition translates into $t - t_w \ll (1/\sigma_0)^{1/(x-1)}$.¹⁹ Fig. 1.7 indeed shows a linear regime of the expected temporal extent, followed by a crossover into a nonlinear steady-state flow regime, in which $\gamma(t) \propto \sigma_0^{1/(x-1)} t$. The latter is in agreement with the flow curve (3.10).

In the glass phase, $x < 1$, for which the flow curve shows a finite yield stress, $\sigma_y(x)$, the behaviour is rather more complicated. As expected, the numerical results for step stress of very small amplitude $\sigma_0 \ll \sigma_y$ show no crossover to a steady flow regime at late times. Instead, the system continues to creep logarithmically, according to the linear creep result for $J(t - t_w, t_w)$. When σ_0 is not small but less than the yield stress σ_y the creep is still logarithmic to a good approximation, but now with a nonlinear dependence of its amplitude on stress. Very close to the yield stress, $\gamma(t)$ grows more quickly in time, but with a strain rate $\dot{\gamma}(t)$ that still decreases to zero at long times. Finally, as expected from the flow curve, only for stress amplitudes exceeding the yield stress σ_y does one see an eventual crossover from logarithmic creep to steady flow at long times which recovers numerically the flow-curve result, $\gamma(t) \propto (\sigma_0 - \sigma_y)^{1/(1-x)}(t - t_w)$. Fig. 1.8 illustrates these various behaviours. Comparison of the curves for the two different waiting times for $\sigma_0/\sigma_y = 1.2$ shows that before the crossover into flow, the response scales with $(t - t_w)/t_w$; once ergodicity has been restored and the system flows, on the other hand, scaling with $t - t_w$ is recovered.

1.6 Discussion and conclusion

In this chapter we have reviewed the soft glassy rheology (SGR) model. Taking into account only the shared features of disorder and

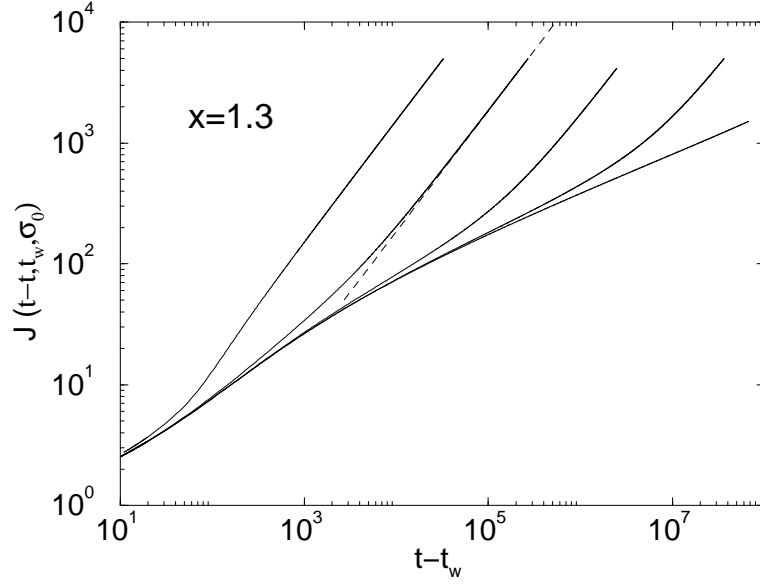


Figure 1.7. Nonlinear creep compliance $J(t-t_w, t_w, \sigma_0)$ as a function of time interval $t-t_w$, for a step stress of size σ_0 applied at time $t_w = 100$. The noise temperature is $x = 1.3$. Solid lines, bottom to top: $\sigma_0 = 10^{-3}, 10^{-2.5}, 10^{-2}, 10^{-1.5}, 10^{-1}$. Over the time intervals shown, the curve for $\sigma_0 = 10^{-3}$ is indistinguishable from the linear compliance (not shown). Dotted line: final flow behaviour predicted from steady state flow curve for $\sigma_0 = 10^{-1.5}$. From Fielding et al.¹⁹. Copyright The Society of Rheology.

metastability that are present in many soft glasses, the model essentially adds strain degrees to Bouchaud's trap model. In the original formulation only shear strain and stress are considered, but we have also outlined a recent generalization which properly accounts for the tensorial nature of stress and strain. In either version, the model can be solved to give an explicit constitutive equation.

One of the hallmarks of glassy systems is the occurrence of aging, where time-translation invariance is lost, and the SGR model indeed predicts such aging effects in the rheology of soft glasses. We outlined in Sec. 1.2 a general formulation of the linear and nonlinear rheological response functions suited to aging materials, and also distinguished aging from ordinary transients that occur during equilibration. This conceptual framework is independent of the SGR model and should be of wider relevance, not least to the analysis of gel rheology.

The SGR model and its simple rheological properties were reviewed in Sec. 1.3, while Secs. 1.4 and 1.5 cover the more complicated rheological aging effects. These occur mainly in the glass phase of the model ($x < 1$),

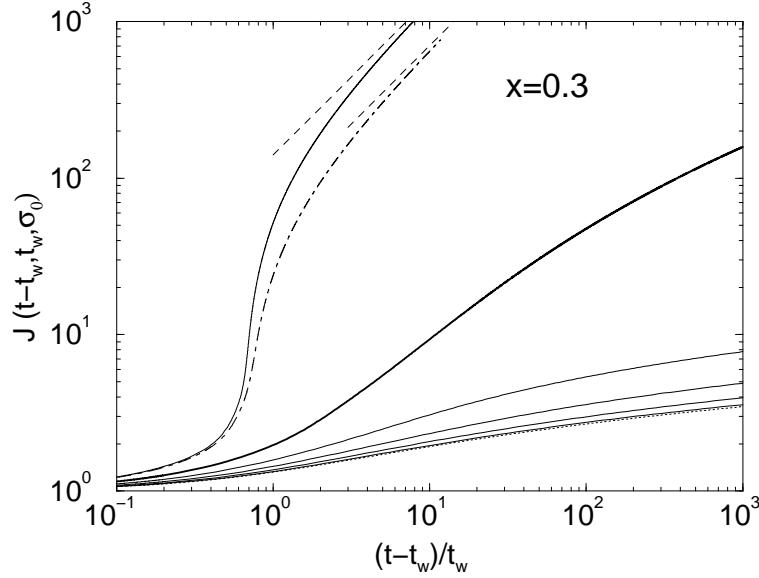


Figure 1.8. Nonlinear creep compliance $J(t - t_w, t_w, \sigma_0)$ as a function of scaled time interval $(t - t_w)/t_w$, for a step stress of size σ_0 applied at time t_w . The noise temperature is $x = 0.3$. Solid curves, bottom to top: $\sigma_0/\sigma_y = 0.2, 0.4, \dots, 1.2$, all for $t_w = 100$. The case $\sigma_0 = \sigma_y$ is shown in bold; the dotted curve is the linear response result ($\sigma_0 \rightarrow 0$). The dot-dashed curve shows the effect of decreasing the waiting time to $t_w = 50$, for $\sigma_0/\sigma_y = 1.2$. The dashed lines are the predictions for final flow behaviour (for the stress above yield) from the steady state flow curve. From Fielding et al.¹⁹. Copyright The Society of Rheology.

where the elastic elements that it describes evolve forever towards higher yield thresholds (deeper traps), causing a progression toward more elastic and less lossy behaviour. Within this glass phase, there is a yield stress σ_y , and genuine aging arises for applied stresses less than this. For step strains and stresses, we showed that the nature of the aging is relatively simple: both the linear stress relaxation function $G(t - t_w, t)$ and the linear creep compliance $J(t - t_w, t_w)$ become functions of the scaled time interval $(t - t_w)/t_w$ only. The time-dependent viscoelastic spectra $G'(\omega, t)$ and $G''(\omega, t)$ have the characteristic aging behaviour shown in Fig. 1.1: a loss modulus that rises as frequency is *lowered*, but falls with age t , in such a way that it always remains less than $G'(\omega, t)$ (which is almost constant by comparison). For $x < 1$ such spectra collapse to a single curve (see Fig. 1.4) if ωt , rather than ω , is used as the independent variable.

Significant aging was also found for nonlinear rheological responses of the SGR model. For example the nonlinear step-strain relaxation follows

the same aging scenario as the linear one, except that all relaxation rates are speeded up by a single strain-dependent factor (Eq. (4.5)). This form of nonlinearity is a characteristic simplification of the SGR model, and extends to its tensorial generalization.²⁰ Another interesting case was startup of steady shear; here there is no significant aging in either the initial (elastic) or the ultimate (steady flow) regime; yet, as shown in Fig. 1.5, the intermediate region shows an overshoot that increases with sample age. Finally we found that the nonlinear creep compliance (Fig. 1.8) shows interesting dependence on both the stress level and the age of the sample. For small stresses one has logarithmic creep. As the yield stress is approached this crosses over to a more rapid creep that nonetheless has zero strain rate in the long time limit, and then finally to steady flow above the yield stress.

There are, of course, many open issues with the model; these are discussed in detail elsewhere.¹² One of these concerns the interpretation of the noise temperature x and whether or not this should depend on flow history: we have assumed throughout that it does not. Also, the rheological aging predictions of the model, though surprisingly rich as we have shown, do not include all those found experimentally.^{13–15} As a model for *gel* rheology, the SGR model has further drawbacks. As explained in the introduction, it was designed for (soft) repulsive glasses, whereas gels are more akin to attractive glasses. It also neglects the possibility of significant structural change during aging, and assumes that the local elastic properties are homogeneous. Nonetheless, the model certainly represents a useful step towards understanding the rheology of soft glassy materials, in particular in regimes where their behaviour is not time-translation invariant.¹⁹

We conclude by mentioning some recent approaches related to the SGR model, which may provide inspiration for the development of improved models in the future. Lequeux and co-workers proposed a model which is not dissimilar from the SGR model but attempts to make explicit that the effective noise in the system arises from yield events.^{38,39} Starting from the SGR picture, their model can be obtained by the following modifications: (1) All elements have the same yield energy E ; (2) the yield rate, rather than being activated, is zero for $kl^2/2 < E$ and a constant $1/\tau_0$ for larger $|l|$; (3) yield events are assumed to lead to random changes and thus to an effective diffusion of the local strain l . The self-consistent nature of the model comes in through the postulate that the relevant diffusion constant D is proportional to the overall yielding rate, $D = \alpha Y$. The constant α governs the behaviour of the model: in the absence of shear ($\dot{\gamma} = 0$), the system has nonzero Y and D only for $\alpha > \alpha_c = 1/2$, while for $\alpha \leq \alpha_c$ it is completely frozen. This occurrence

of a glass-like phase is reflected in the flow curve: for $\alpha < \alpha_c$ there is a nonzero yield stress, while for $\alpha > \alpha_c$ Newtonian behaviour is predicted. Precisely at the transition, a power-law flow curve $\sigma \sim \dot{\gamma}^{1/5}$ is predicted; this also governs the behaviour for α close to α_c and intermediate $\dot{\gamma}$. It is arguable whether such a fixed power-law exponent can be expected to reflect the behaviour of a wide range of soft glasses. The behaviour under small oscillatory strain is also unusual: in the glass phase, the stress response is always nonlinear, with G'' exhibiting a peak at a frequency scaling linearly with the strain amplitude γ_0 . The linear response limit $\gamma_0 \rightarrow 0$ therefore gives purely elastic behaviour.

We mention here that one could similarly make the effective temperature in the SGR model self-consistent, e.g. by assuming that it is proportional to the overall yield rate, $x = \alpha Y$. The consequences of this remain to be fully explored but appear to include interesting effects such as flow curves with metastable and unstable branches.

To simplify their analysis yet further, Derec, Ajdari and Lequeux later suggested a model with only two fundamental variables: the (shear) stress σ and a “mobility” D .^{40,41} The dynamic equation for σ is $d\sigma/dt = -D\sigma + k\dot{\gamma}$ so that for $D = 0$ one gets purely elastic behaviour; viscous effects require $D > 0$. For the time evolution of D , the assumption is that dD/dt can, by loose analogy with a Landau expansion, be expanded in powers of D for small D . The coefficients are then taken to depend on stress σ and the imposed shear rate $\dot{\gamma}$. Depending on whether D evolves to zero in the quiescent state ($\dot{\gamma} = 0$) or not, one then again finds glass and liquid states. An interesting result is that, for appropriate choices of the exponents in the Landau-like expansion, the model predicts sub-aging, where the typical relaxation timescale grows not as t_w but as t_w^μ with $\mu < 1$. Some caveats apply, however: for example, some of the parameter settings considered by Derec *et al.*^{40,41} give a well-defined response to oscillatory strain but produce divergences for step strain. An even simpler one-parameter model involving only the “degree of jamming” (essentially the inverse of D) has also recently been proposed.⁴²

Finally, it is important to mention the so-called shear-transformation zone (STZ) theory, developed by Falk and Langer⁴³ around the same time as the SGR model. Inspired by numerical simulations, STZ theory postulates that plastic deformations in a sheared amorphous material take place in local elements that have bistable configurations. The defining equations of motion then govern the evolution of the populations of the two kinds of configurations as they are transformed into one another, created or destroyed. This model has been very influential, and continues to be developed further.^{44–46}

It will be clear from the above brief survey that there are by now a number of simple models designed to describe the rheology of soft glasses, with the predictions of the SGR and STZ models having been explored in most detail. Much further work needs to be done, in particular in making the models more realistic without losing the important advantage of being able to extract predictions analytically rather than by simulation. There is even more scope in modifying and extending models of this type to make them applicable to gels in particular.

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