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COURSE 1

MECHANICAL AGING AND NON-LINEAR RHEOLOGY OF CONCENTRATED COLLOIDAL SUSPENSIONS: EXPERIMENTAL FACTS AND SIMPLE MODELS.

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MECHANICAL AGING AND NON-LINEAR RHEOLOGY OF CONCENTRATED COLLOIDAL SUSPENSIONS: EXPERIMENTAL FACTS AND SIMPLE MODELS.

Armand Ajdari

Abstract

Many colloidal systems display very non-Newtonian and solid-like behaviour when concentrated, a striking feature being the apparition of a yield stress. After recalling some basics about the interactions between colloidal particles, I present a few experimental facts commonly observed in these systems: aging and non-linear rheology. A simple phenomenological model is then introduced, in which the local state of the system is described by a single scalar parameter, the fluidity. I proceed with comments on heterogeneous flows in some of these systems. These notes are not intended to be a comprehensive review, and the reader is directed to the references for further reading.

Notes for lectures in les Houches 2002

1 Introduction

1.1 Colloidal glasses ?

In the last years many works [Sollich97, Liu00, Cloitre00, Derec99, Trappe01, Berthier00] have suggested possible cross-interests between (i) research on the glass transition (statistical mechanics, structural glasses, solid polymers), (ii) studies on colloidal "soft" systems . Such cross-interests are based on the two following hopes.

First, colloidal systems could be ideal systems to understand fundamental aspects of the glass transition: they are *tunable* "equivalents" of atomic or molecular systems with controllable interactions, that also sometimes freeze into amorphous disordered phases with solid-like behaviour ("glasses"). The spatial scale is advantageously roughly a thousand times

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larger than in atomic systems, which could permit easier experimental investigation. In addition, playing with the viscosity of the solvents, one can hope to tune the temporal scales, allowing an easier span of the huge range of accessible time scales required for the study of the glass transition.

Second, many common colloidal systems (gels, foams, creams, emulsions) are actually used in this soft solid form that may bear similarities with glasses. Mayonnaise for example is a disordered arrangement of oil drops that behave as an amorphous elastic solid under a weak constraint, and flows plastically under larger stress. Some of the mechanical features of these amorphous colloidal systems may be better apprehended if they are considered as glasses.

1.2 Model and real colloids: interactions

A first step toward the understanding of the behaviour of a colloidal system is the examination of the interactions between its constituents. Without aiming at an exhaustive review, I describe below a set of commonly encountered attractions and repulsions between colloidal particles embedded in a fluid solvent (thorough reviews are provided by textbooks such as [Russell89, Israelachvili85]). The term "colloid" is often coined to particles of size smaller than a few microns dispersed in a solvent, so that gravity has a limited effect on a *single* particle (the exact limit depending on the experiment or application considered). This allows the dispersion of the particles by simple thermal agitation.

1.2.1 Interactions between model colloids

Attractions and Repulsions - I consider here two identical colloidal spheres of radius R in a solvent, separated by a distance d (Figure 1). They induce on each other both attractions (A) and repulsions (R):

A1- The van der Waals attraction, due to the difference in dielectric properties of the solvent and the particles. This leads to a long-range attractive potential $U_{\rm vdw}(d)$, that, in a simple picture neglecting retarded interactions, behaves as $\sim -Hd/R$ for $d \ll R$ and $\sim -H(d/R)^6$ for $d \gg R$. The Hamaker constant H is roughly proportional to the square of the difference in dielectric constant (or in optical index) and of order k_BT. By fine-tuning solvent mixtures it is sometimes possible to diminish the contrast and significantly reduce this attraction.

A2 - Depletion forces, that can for example be induced by dissolving in the solvent polymers that do not adsorb on the surface. The dissolved polymer coils behave as impenetrable objects of typical size say b, which are sterically excluded (depleted) from a corona around the colloidal particles of a thickness of order b. Bringing particles together induces overlap of these depletion coronas, and thus increases the volume accessible to the polymers

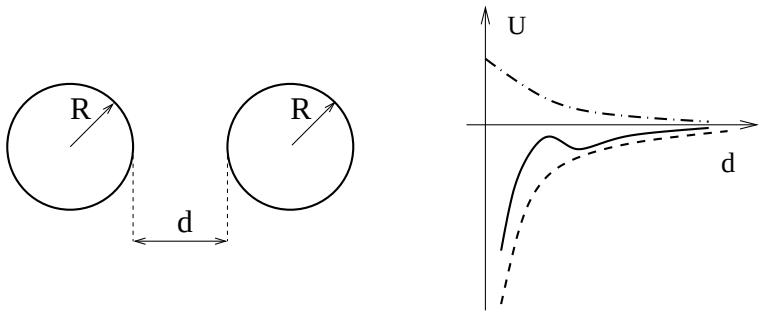

Fig. 1. *Left :* Two model spherical colloids. *Right :* Typical pair potentials in the DLVO theory: the van der Waals attraction (dashed line) and the electrostatic repulsion (dot-dashed line) result in an overall interaction potential (solid line) with a secondary minimum at a a finite distance d.

and consequently the configurational entropy of the system. This induces *a short-range "depletion" attraction* of entropic origin. Its range is of order b and its amplitude controlled by the polymer concentration.

R1 - Core steric repulsion: the particles cannot interpenetrate which results in a very strong and very short-ranged repulsion (a few Angstroms).

R2 - Screened electrostatic repulsion: similarly charged particles dispersed in an electrolyte solvent (e.g. water) repel each other. Electrostatic effects are screened over the Debye length λ_D (a few nm to a few tens of nm typically), due to the presence of dissociated counter-ions and salt. The resulting repulsion potential $U_{\rm el}(r)$ decreases as $\sim \exp(-d/\lambda_D)$ for large separations. Increasing the ionic strength of the solution (e.g. by adding salt) induces a drop of both the amplitude and range λ_D of this repulsion.

R3- (Steric) protection by polymer layers. A classical way to avoid aggregation of the particles is to sterically "protect" the colloids with a polymer layer of thickness δ (grafted or adsorbed). Such layers swollen by the solvent repel each other for entropic reasons and thus provide a rather strong wall potential at $d \simeq 2\delta$. In addition, the dielectric properties of these layers of low polymer concentration are close to that of the solvent, so that they do not induce unfavorable additional van der Waals attractions.

Resulting pair potentials - In general many interactions act concurrently. The classical DLVO theory describes the behaviour of simple charged colloidal spheres in a salty solution under the action of van der Waals attraction and electrostatic repulsions (A1, R1 and R2). The attraction always dominate at very long and very short separations, and the electrostatic repulsion if strong enough can induce a "secondary" potential minimum (see Figure 1). The overall behaviour of a suspension of such particles then depends on

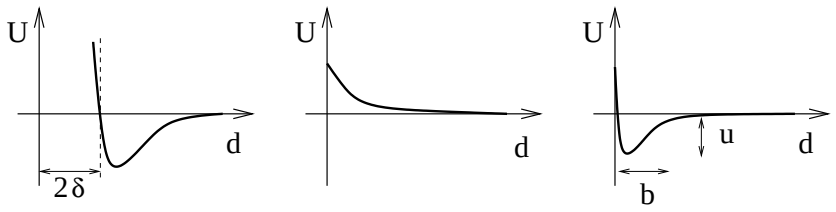

Fig. 2. Examples of pair interaction potentials achievable with model systems.

the depth of this minimum and on the amplitude of the barrier that separates it from the "primary" minimum (which corresponds to quasi-contact). If particles reach this quasi-contact state, very short range interactions and chemistry often take over that result in an irreversible binding.

If the attraction wins, for example upon addition of salt to the system, the particles tend to aggregate into big lumps that sediment or cream (gravity is far from negligible for large aggregates), leading to the "destabilization" of the suspension, an effect often fought against (for example in paints, inks, etc ..). Protection techniques have often been used to strengthen repulsion (R3) and prevent actual contact.

From a fundamental point of view, playing with the set of interactions mentioned above, one can to some extent tailor the interparticle potential, with control of both amplitude and range (see e.g Figure 2b,c,d), and thus prepare in the lab model colloidal systems. In particular the Edinburgh group has managed in the 80s to prepare colloidal suspensions that behave as genuine hard spheres solutions [vanMegen87]. As such this substantiates the claim that model colloidal systems constitute a rich tool-box for the study of the collective behaviour that leads to crystallization or to the glass transition. The reader is however warned that the mastering of the "tunability" of the interaction requires a significant expertise, especially in the chemistry and surface chemistry involved in the preparation of the particles.

1.2.2 More common colloidal systems

The somewhat naive textbook picture for model colloids given above must rapidly be supplemented by corrections that are often relevant:

- *Colloidal particles are not always rigid.* As such they can elastically deform under internal or external forces, which renders the description of their interactions more complex. This in particular the case for emulsions and foams, where the dispersed phase (the particles) is liquid or gaseous. When the system is concentrated the particles pushed against one-another tend to facet at the cost of an elastically stored surface energy. In other systems the elementary particles are elastic and compressible in

their bulk. This is for example the case for small gel beads [Borrega99] or multi-lamellar vesicles (onions) that can expel solvent and deform upon compression [Diat93, Ramos01].

- *Colloidal particles are not necessarily spherical.* Rods or needle-shape objects are rather common, as well as plate-like or disk-like particles. Such objects start to interact and produce collective behaviour at volume fractions much weaker than their spherical counterpart. For example laponite systems are made of disk-like particles of a few nm thickness and about 100 nm in diameter, that deviate form dilute behaviour at very low volume fractions [Bonn99a].

- *Colloidal particles are seldom/never uniform.* This is in particular true for the surface charge: heterogeneities in surface charge can lead to very anisotropic electrostatic interactions, and even to attractions between particles of same *average* charge. For example, laponite particles are said to have a different charge density on their perimeter and on their faces for some pH and salt values, allowing for the building of "house of cards" structures.

- *Colloidal particles are seldom/never perfectly smooth*, in line with the two previous points. Their roughness can affect their interactions as short distances, control the apparition of capillary bridges in mixed solvents, and render the link between two particles in the primary minimum rigid [Russell89].

- *Colloidal systems are seldom/never monodisperse.* Large variations in size, shape factor, etc.. is the rule for many practical systems.

- *There is rarely a single kind of particle in a colloidal system.* One extreme, industrial systems (creams, paints, etc ..), are often made of at least 5 or 6 different main ingredients aimed at fulfilling different (and often conflicting) tasks (see the notes of B. Cabane).

Eventually, while we are later in these notes going to discuss physical aging and a mild form of history dependence in these systems, a much more stringent one is that the physico-chemical state of the system, even at small scales, can in general not be anticipated from its sole composition. For example polymers adsorbing on the particles surface can lead to protected colloids if added in a dilute suspension (a complete protecting layer forming around each particle), but can induced bridging and thus promote aggregation if added when the particles are close to one another. Similarly any earlier stage at which the particles have been in contact can induce chemical reactions and irreversible sticking between the particles that will resist later attempts to re-disperse the system.

At this stage, the second point of subsection 1.1. appears rather a matter of trust: although clean model colloidal systems can be prepared, many common colloidal systems rely on very varied and uncontrolled interactions. As such it is not clear that such various and complex systems should obey rather universal features. However we will see below that they share some

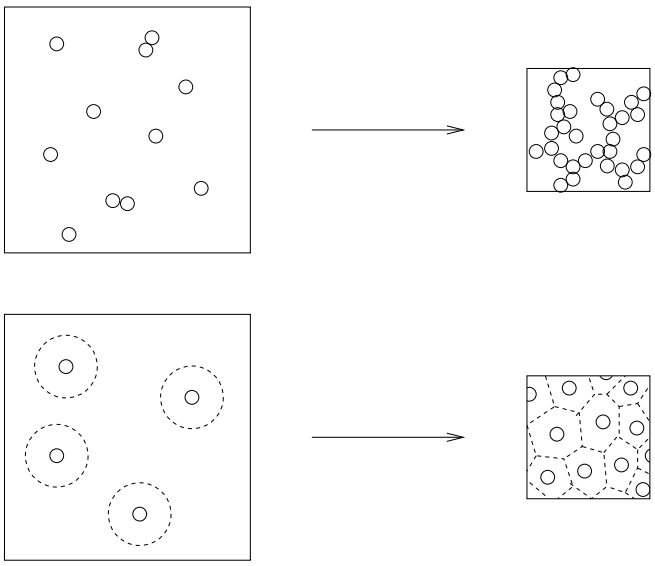

Fig. 3. Two scenarios for the formation of soft solids upon concentration. Top: sticky particles forming aggregates. Bottom: soft repelling particles under osmotic compression (the dashed lines represents the range of the repulsive potential).

similarity in terms of mechanical behaviour, which suggests that it is worth digging further, if only to clarify in what sense "glassy" dirty colloidal systems differ from "model glasses".

1.3 Gels or glasses: various kinds of soft solids ?

Eventually let me stress that since the "soft glass/concentrated colloid" analogy has developed, some confusion has invaded the community working on colloidal systems, that is often mirrored in the terminology used to describe the soft solids that these systems form when concentrated. The terms "gel", "physical gel", "glass", "paste", "jammed system" and others are often used interchangeably, with various authors obviously having different definitions of these terms in mind. There is a great need for a clearer classification (either from the point of view of underlying interactions or resulting behaviour) and for a more systematic terminology, that hopefully the years to come could provide.

Schematically, there are two extreme pictures along which colloidal systems behave when concentrated, corresponding to very different underlying interactions (see Figure 3).

The first one is that of rigid spheres that stick to one another upon contact, with a rather strong and rigid binding (e.g. due to local chemical

binding, or because the roughness of the surface prevents any further rotation). Such particles diffusing in solution tend to form fractal aggregates that also diffuse and aggregate, so that if the concentration is large enough, one ends with a (history dependent) network made of rigidly interconnected aggregates. The volume fraction of such a physical "gel" may be rather weak (sometimes only a few percent), with solvent filling the many voids in the aggregates structure (cite see e.g. [Lewis00] and references therein).

The second image is that of particles that repel through a soft potential (either rigid particles with a repulsive potential of some range or deformable particles with a short range repulsion) . As concentration is increased (typically beyond roughly 50 percent), the particles are "pushed" into one another, the energy of the system increases and it is trapped in a metastable situation of disorderedly crowded particles [Cloitre00,Derec00]. This is what many authors call a soft glass. In contrast with the previous rigidly connected "gel", such a "glass" has a positive osmotic pressure and should swell noticeably and unlimitedly upon addition of solvent.

Given the discussion in the previous subsection, it should be clear that there is potentially a continuum of colloidal systems that connect these two limiting cases (see for example the studies of the Weitz group in the last decade where the attraction energy is systematically varied [Trappe01], and e.g. [Moussaid02, DelGado02] and references therein). In most systems there are both attractions and repulsions, the intensity of which is often comparable (and of order a few k_bT). A systematic "gel or glass" distinction according to the interactions is difficult, since it is not clear that the elementary object at the scale of which such a "gel or glass" distinction should/could be made is the individual colloidal particle rather than some kind of aggregate. Eventually, the rheological properties of such systems are usually probed through dynamical schemes, so that a static picture may not be sufficient to anticipate the response: in some systems the weak aggregation of soft particles can lead to the formation of transient rigid aggregates that can resist a finite force (for a certain amount of time).

1.4 Wrapping up the Introduction

To conclude, colloidal systems are very diverse. Model systems can be produced in the lab that may be used to study fundamental issues regarding the glass state and the glass transition. Most practical systems behave when concentrated as soft and weak solids that can be forced to flow under mechanical constraint. These solids are in general *soft* as their elastic modulus is low (down to a few Pascal in some cases), and *weak* because they flow plastically under weak stresses (also a few Pascal for some systems). The behaviour of these soft-solids is however likely to be somewhat system-dependent, and a systematic classification of their behaviour in relation to their microscopic nature would be welcomed.

The remainder of theses notes is devoted to experimental studies and modelisation of these soft and weak solids, with an emphasis (especially in section 2) on systems with little attractions (i.e. away from the strong gel picture). I will from now on very non-specifically refer to those as "soft-solids", rather than using more specific names that could bear undesired meanings (paste, gel, glass, yield stress fluid).

2 Experimental facts 1: soft solids that flow and age

2.1 Concentrating colloidal suspensions: from a "viscous liquid" to a "soft-solid" behaviour

At low concentrations, colloidal suspensions tend to flow in a Newtonian way under weak stresses. In particular at steady-state the shear stress σ is linear in the shear rate $\dot{\gamma}$: $\sigma = \eta\dot{\gamma}$ where η is the viscosity of the suspension. Often a shear-thinning regime takes over for stronger shear as evidenced by a bending in the stress-shear rate curve. The onset of non-linearities $\dot{\gamma}_{NL}$ is often identified with $1/\tau$ the inverse of the longest relaxation time of structures in the suspension. In a related way, when probed through oscillatory rheology (see definitions in the lectures of M. Cates), the system behaves as a viscous liquid $G''(\omega) \gg G'(\omega)$ at frequencies well below $1/\tau$, and as an elastic solid at larger frequencies.

Increasing the volume fraction, the viscosity of the system rises and the range of linear behaviour decreases. At even higher concentrations, the steady-state flow curve looks altogether different. An often encountered situation is schematized in Figure 4: for low shear rates $\dot{\gamma}$, the stress tends to a finite value, the yield stress, often denoted σ_Y [Mason96,Derec00,Cloitre00]. At higher shear rates (in the non linear domain) the behaviour is however not much different from what it looks like at weaker concentrations. It is important to note that what happens at low $\dot{\gamma}$ is not easy to ascertain experimentally. Rheometers allow reliable measurements only down to a finite value of $\dot{\gamma}$, so it is usually impossible to discriminate between a power-law fluid with a weak exponent and an actual finite limit σ_Y. A common engineer's formula to encompass both is the Hershel-Buckley one: $\sigma \to \sigma_Y + A\dot{\gamma}^{\alpha}$ for $\dot{\gamma} \to 0$. In addition it may also be difficult to guarantee that a steady-state is indeed reached in such conditions. [1]

Under oscillatory rheology the response becomes that of a *soft solid* $G' \gg G''$ even at low frequencies. Various frequency dependence of the moduli have been observed: they can both increase with the same weak

[1] Note that the existence of a finite yield stress σ_Y does not forbid non-steady flow for a fixed weaker stress: creeping flows with a decreasing $\dot{\gamma}(t)$ are allowed.

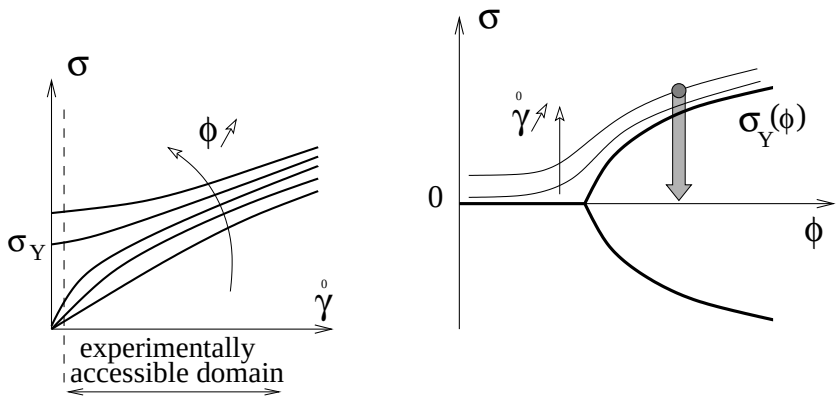

Fig. 4. Sketch of a typical steady-state flow response of a concentrated suspension. Left: steady-state flow curves $\sigma(\dot{\gamma})$ for increasing volume fractions ϕ. Right: steady-state stress as a function of volume fraction ϕ for different imposed shear rates $\dot{\gamma}$ (the thick line corresponds to the limit curve for $\dot{\gamma} \to 0$, i.e. $\sigma = \sigma_Y(\phi)$). The arrow is a schematic representation of a quench from a mechanically fluidized system into the soft-solid region.

power-law, stay both roughly constant, or G' can be roughly constant with G'' displaying a shallow minimum at rather low frequencies.

Obviously some kind of transition occurs upon increase of the concentration, bringing the system from a viscous liquid state to a soft-elastic one. The longest relaxation time-scale and the viscosity increase noticeably (diverge ?) when the transition is approached. Conversely, effective values for the putative yield stress decrease on the solid side when the concentration is decreased. We will from now on deal only with the soft-solid states.

2.2 Probing the system in its "soft-solid" phase

In the solid phase, the system appears as frozen in some region of phase space given that a finite perturbation is required to have it flow. In most cases however, its local structure is disordered and amorphous (only very clean systems crystallize). It is thus likely that such systems lie in a metastable state that is noticeably history dependent. Consequently, to study the mechanical properties of these soft-solids, it is first necessary to define reproducible preparation procedures. In analogy with thermal quenches performed for molecular glasses or magnetic spin glasses, a natural way is to prepare the system in a reproducible fluid initial state, so as to "erase" any history dependence, and then to quench it quickly in the soft-solid phase.

Unfortunately, changing the concentration or other physico-chemical pa-

rameters homogeneously and rapidly throughout the sample is usually very difficult, and temperature is not always very relevant here (unless in the vicinity of some structural thermodynamic transition, see e.g. [Ramos01]). An alternative is to take advantage of the flow induced fluidization of the system to perform a mechanical quench [Derec00, Cloitre00, Viasnoff02a], which is the route represented by the vertical arrow in Figure 4. A steady or oscillatory shear of strong amplitude is applied for some time to the system, with the hope that this leads to a reproducible initial state. Cessation of flow then quenches the system in the soft-solid phase, with the history of the soft-solid starting at this "initial time" that we will call $t = 0$. The validity of such a mechanical quench should of course be asserted by experimental verification of the reproducibility.

2.3 Mechanical aging

An issue which has recently received attention, fed by ideas and concepts coming from the community working on the glass transition, is that of physical aging. In the present context, we focus here on mechanical aging, i.e. the influence of the age t of the system since its quench on its mechanical properties. A measurement usually lasting some time, it is common to introduce the following notations for the time sequence. The quench is at $t = 0$. The system is left at rest until $t = t_w$ (the waiting time), time at which a measurement is started. If the system is not ergodic on experimental time scales, the instantaneous outcome of the measurement at time t depends on the time $t' = t - t_w$ elapsed since the onset of the measurement (as is common), but also in a systematic way on the waiting time t_w.

Recent systematic experiments on microscopically very different colloidal soft-solids have indeed shown a strong dependence of the mechanical relaxation time or time-scale τ of the system, on its "age" t_w (see e.g. fig. 5). Remarkably a clean power law relation is found in many cases $\tau \sim t_w^{\mu} \tau_0^{1-\mu}$, with τ_0 a system dependent time. The exponent μ is called the *aging exponent* in the glass community [Struick78,Bouchaud97]. Let us cite a few examples to emphasize the great disparity of systems: such a law has been found through stress relaxation measurement (i) in a solution of PEO-protected spherical silica particles [Derec00] with $\mu \sim 0.5 - 0.7$, (ii) in a dense suspensions of onions made of surfactant bilayers "doped" with copolymers [Ramos01] with $\mu \sim 0.7 - 0.8$, and through creep measurements (iii) in dense suspensions of swollen micro-beads of polyelectrolyte gel [Cloitre00] with μ close to 1. For other systems the dependence on the age of the system can be even stronger: the effective oscillatory viscosity of laponite solutions was found in [Bonn02] to increase exponentially with t_w which suggests $\tau \sim \exp(t_w/\tau_0)$ (i.e. $\mu \to \infty$).

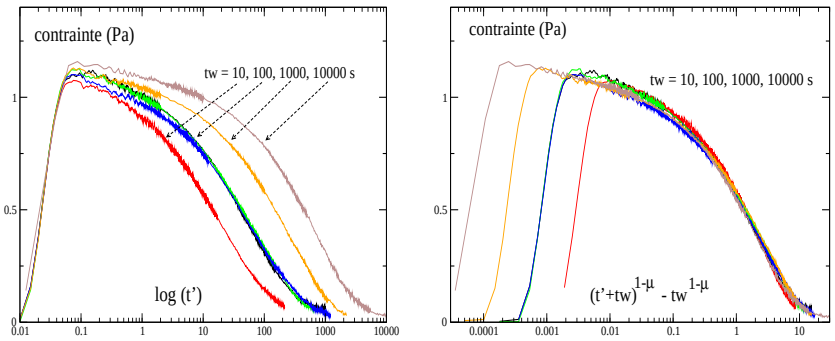

Fig. 5. Experimental stress relaxation measurements after different waiting times (linear-log plot) for a solution of PEO-protected silica particles [Derec01b]: (left) as a function of time t' elapsed since onset of the deformation, (right) as a function of the rescaled variable $(t'+t_w)^{1-\mu} - t_w^{1-\mu}$, which is roughly $\simeq t'/t_w^{\mu}$ at times t' shorter than t_w

This demonstrates physical aging through a systematic route in these systems: the dynamics of the system gets slower and slower as time goes on, with less stable arrangements more rapidly disappearing leaving the system in deeper and deeper metastable states. This slow drift can in principle be driven by energy stored in the system, by experimental mechanical agitation or noise, or by genuine thermal agitation. The description of the mechanisms at work in this slow evolution of the system are clearly the clue to a proper and complete understanding of the physics of aging. In the following we bypass this question for the moment and report on a recent attempt to build a simple phenomenological model able to account for the observations quoted in this section. A more explicit and sophisticated but still phenomenological set of equations, the SGR model, is presented in the lectures of M.E. Cates.

3 A class of simple models

3.1 A Maxwell model with one scalar internal variable

Essentially the aim is here to write down the simplest model that accounts for the observations reported above for the "soft-solid state": (i) there is no obvious intrinsic rheological relaxation time, so that the instantaneous relaxation spectrum ages progressively, (ii) shear is able to fluidize the system and to bring it to a flowing steady-state with a finite instantaneous relaxation spectrum. We implement these features in a model that neglects for the moment heterogeneities.

This can be achieved through a simple adaptation of the Maxwell model, which is the simplest visco-elastic model, with a single time scale τ, cor-

responding to an elastic element in series with purely viscous one. The resulting equation for a scalar description of shear linking the stress σ to the applied shear rate $\dot{\gamma}$ is then: $\partial_t \sigma = -\sigma/\tau + G_0\dot{\gamma}$, with G_0 the elastic modulus and $\eta = G_0\tau$ the viscosity. For the soft-solids that we aim to describe there is no intrinsic time scale, but an instantaneous one that drifts towards infinity spontaneously, unless an applied shear fluidizes the system. We thus chose to take the mechanical relaxation time scale as a variable describing the instantaneous state of the system, the evolution of which is ruled by the competition of spontaneous aging and flow induced fluidization. We use equivalently $a = 1/\tau$, which we call the "fluidity"of the system. The resulting set of equations read:

$$\partial_t \sigma = -a(t)\sigma + G_0\dot{\gamma} \tag{3.1}$$

$$\partial_t a = -f(a) + g(a, \sigma, \dot{\gamma}) \tag{3.2}$$

where f (spontaneous aging) and g (shear-induced fluidization) are positive functions. Aging requires that under the sole action of f, a tends towards 0 as time goes on. G_0 is taken constant in the simplest picture.

For long waiting times and weak shear the fluidity is expected to be small (the relaxation time is very long), so what will matter is the behaviour of functions f and g in the vicinity of $a \simeq 0$. Using rather formal expansions we write:

$$f(a)_{a\to 0^+} \simeq r_1 a^{\alpha} + r_2 a^{\alpha+\beta} + ... \tag{3.3}$$

$$g(a, \sigma, \dot{\gamma})_{a\to 0^+} \simeq u_1 a^{n_1}\sigma^{m_1}\dot{\gamma}^{p_1} + u_2 a^{n_2}\sigma^{m_2}\dot{\gamma}^{p_2} + ... \tag{3.4}$$

It is expected that g should be even in $(\sigma,\dot{\gamma})$, so that if g is analytic then $m_1 + p_1$ and $m_2 + p_2$ should be even. If g is not analytic, then σ and $\dot{\gamma}$ in the above equation should be replaced by their absolute values.

In our earliest attempts we proposed in an analogy with a Landau description of a transition where a would be the order parameter, to consider that r_1 increases with concentration from a negative value in the viscous-liquid state to a positive one in the soft-solid one: $r_1 \sim (\phi - \phi_c)$. We will not pursue this any further here (see [Derec01a, Derec01b] for related discussions) and instead focus on the properties of the soft-solid phase, taking r_1 and u_1 as positive constants.

3.2 Relation to other models in the literature

3.2.1 Bond models for gels

Given that it is the simplest approach, the use of a single scalar parameter to describe the state of the system has been pursued in many works.

For example an empirical model for particles that stick to one another describes the instantaneous state of the system by an average number of

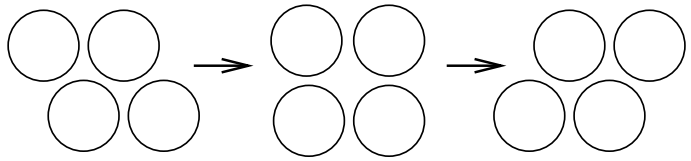

Fig. 6. Elastic deformation and rearrangement under shear of a set of particles

bonds per particle Λ. This number tends to increase spontaneously, but is reduced by the action of shear breaking some bonds. A set of equations proposed by Coussot et al. in [Coussot02a] is $\partial_t \Lambda = 1/\tau - A\Lambda\dot{\gamma}$, complemented with the phenomenological rheological law $\sigma/\dot{\gamma} = \eta = \eta_0(1+\Lambda^n)$, with τ and A constants, and n an exponent.

Taking the rheological law to be roughly equivalent to the Maxwell equation (3.1) if stress relaxes faster than Λ, this model can be more or less recast into (3.1)(3.2) with $a = (G_0/\eta_0)(1+\Lambda^n)^{-1}$. In that case, the exponents proposed in (3.3)(3.4) read: $\alpha = 1 + 1/n$, $n_1 = 1$, $m_1 = 0$, $p_1 = 1$.

3.2.2 Activated hopping

In many models for plastic flows of amorphous solids, flow is thought to occur by the elastic distortion of "elements" up to a point where they become unstable to a rearrangement of the local structure (see e.g. [Tewari99, Debregeas02, Sollich97]), rearrangement that yields a reorganization of the stress field on other elements (Figure 6).

For these plastic events to occur, an activated state must thus be reached, which is usually a conformation of higher energy and lower density (to allow the particles to pass each other). It is often chosen to describe the rates for such events as the exponential of an activation factor $\mathcal{E}$ that is often conceptualized as $\Delta E/T_{\text{eff}}$ with ΔE the barrier to overcome and T_{eff} the effective temperature in the system [Sollich97]. The rheological equation is then $\dot{\gamma} = \dot{\gamma}_{\text{elastic}} + \dot{\gamma}_{\text{plastic}}$, with $\dot{\gamma}_{\text{elastic}} = \partial_t \sigma / G_0$ and in a linearized version $\dot{\gamma}_{\text{plastic}} \simeq \tau_0^{-1} e^{-\mathcal{E}}(\sigma/\sigma_0)$ as in the Eyring model (τ_0 and σ_0 are constants).

This is very similar to our adaptation of the Maxwell model with $a = (\sigma_0\tau_0)^{-1}e^{-\mathcal{E}}$. If the effective temperature of the system decreases as the system ages, or conversely if the typical barrier for rearrangement increases then this should be described by an evolution equation for $\mathcal{E}$. This spontaneous evolution itself is likely to occur through activated rearrangements that may or may not be identical to those probed by the shearing. This yields for the spontaneous evolution of $\mathcal{E}$ a law of the kind $\partial_t \mathcal{E} \sim K e^{-n\mathcal{E}}$ with K a constant and n the ratio between the activation factor for these rearrangements and those corresponding to the plastic shear deformation (if those are identical, as e.g. in the SGR model [Sollich97] then $n = 1$).

The above mentioned dynamics for $\mathcal{E}$ corresponds to an exponent $\alpha = 1+n$ in (3.3).

In a similar description inspired by a "free-volume" picture for activated rearrangements, where $\mathcal{E} = \Delta v/v_{\rm free}$ and the free-volume $v_{\rm free}$ measures the compaction of the system and controls the statistical likelihood of an activation volume Δv, Lemaitre [Lemaitre02] has recently proposed a model that in its linearized isotropic version boils down to something very close to equations (3.1-3.4) (with additional logarithms) with $\alpha = 1+n$, $n_1 = 2$, $m_1 = 2$, $p_1 = 0$.

3.2.3 a 4-state model

Eventually let me briefly mention a model that we proposed a few years ago inspired by the same physics than in the previous subsection 3.2.1 [Derec99]. In this model each element is supposed to be in one of the four following state of stress $-3, -1, +1$ and $+3$. The dynamics of the system (the evolution of the probability for an element to be in a given state of stress) is ruled by three processes: (i) a positive shear rate $\dot\gamma$ tends to shift the elements to states of higher stress, (ii) the states -3 and $+3$ are unstable, so that they rearrange and relax with a decay rate $1/\tau_0$ to either of -1 or $+1$, (iii) these rearrangements trigger a random re-shuffling of the stresses of other elements modeled by an effective diffusion of the stress value at a rate D proportional to the instantaneous number of rearrangements. The dynamics of this system was shown to be similar to (3.1-3.4) in the vicinity of the liquid/soft-solid transition observed, with D proportional to the fluidity a, and $\alpha = 1$, $\beta = 1$, $n_1 = 0$, $m_1 = 0$, $p_1 = 1$.

3.2.4 a concluding remark

In conclusion, the simple class of models described by equations (3.1-3.4) roughly encompass various models in the literature corresponding to specific choices for the phenomenological exponents describing the behaviour of f and g at low fluidity. We will consequently pursue without much restrictions on the latter to examine the behaviours described by these models. In particular, α need not be an integer. Let us however point out that in all the models quoted here $\alpha \geq 1$, which simply states that at long waiting times (low values of a), the instantaneous rate of decrease of a, which reads $r_1 a^{\alpha-1}$, decreases with time (in line with the picture of physical aging). We thus restrict ourselves to $\alpha \geq 1$ in the following.

We will now examine in some detail the predictions of this model, leaving a discussion of its virtues and shortcomings to section 5.

3.3 Predictions

Let us now briefly span some of the predictions of the model for various mechanical probing. We refer the reader to [Derec01a, Derec01b] for a more thorough presentation. In all cases the system has been quenched at $t = 0$, and the measurement starts at t_w.

3.3.1 Mechanical aging

An immediate remark is that during the spontaneous relaxation before the onset of the measurement, a decreases with time. More precisely $a(t) \sim 1/(r_1 t_w)^\mu$ for long times with an aging exponent:

$$\mu = 1/(\alpha - 1) \tag{3.5}$$

This holds for $\alpha > 1$, with for the marginal case $\alpha = 1$, $a(t) \sim \exp(-r_1 t_w)$.

We show below that μ indeed coincides with the definition given in 2.3: the characteristic mechanical time scale of the system τ is the inverse of the fluidity at the onset of this measurement, and $\tau \simeq \tau_0^{1-\mu} t_w^\mu$ (with the microscopic time $\tau_0 = r_1^{\frac{\mu}{1-\mu}}$).

An important distinction can be obtained by inspection of equation 3.1 to 3.4: if $\alpha > 2$ then a relaxes much slower than the stress σ, whereas if $\alpha < 2$, a relaxes to zero faster which freezes the dynamics and prevents σ to relax down to 0. This distinction matches here the classical one between subaging ($\mu < 1$) and superaging ($\mu > 1$). "Full aging" ($\mu = 1$) here corresponds to the limit case $\alpha = 2$, where the same processes rule the relaxation of a and σ.

Let us now assert these points by examining the linear response to a stress-relaxation measurement performed at t_w: at t_w a weak deformation of amplitude γ_0 is applied to the system and then maintained fixed. This creates an almost instantaneous stress $\sigma = G_0\gamma_0$ that subsequently relaxes as $\sigma(t) = G(t', t_w)\gamma_0$, where $G(t', t_w)$ is the time-dependent modulus that for an aging system depends on both the age of the system at onset of the deformation t_w and of the time elapsed since onset $t' = t - t_w$.

- for $\alpha > 2$ (i.e. sub-aging $\mu < 1$),

$$G(t', t_w) = G_0 \exp\left[-\frac{(t' + t_w)^{1-\mu} - t_w^{1-\mu}}{(1-\mu)\tau_0^{1-\mu}}\right] \tag{3.6}$$

  This kind of scaling variable appears in the description of mean field models for glassy phases in spin-glass systems [Bouchaud97]. For times shorter than the system's age $t' \ll t_w$, $G(t', t_w) \sim \exp[-t'/\tau]$, a simple exponential relaxation with a characteristic time $\tau = \tau_0^{1-\mu} t_w^\mu$. For much longer times $t' \gg t_w$, $G(t', t_w) \sim \exp[-t'^{1-\mu}/((1-\mu)\tau_0^{1-\mu})]$,

the stress decreases to 0 as a stretched exponential [2] with a stretching exponent $1-\mu$ smaller than 1.

- for $\alpha < 2$ (i.e. super-aging $\mu > 1$),

$$G(t', t_w) = G_0 \exp\left[-\frac{\frac{1}{t_w^{\mu-1}} - \frac{1}{(t'+t_w)^{\mu-1}}}{(\mu-1)\tau_0^{1-\mu}}\right] \tag{3.7}$$

At short times $t' \ll t_w$ we have again $G(t', t_w) \sim \exp[-t'/(\tau_0^{1-\mu} t_w^{\mu})]$, whereas at longer times $t' \gg t_w$, relaxation proceeds as $G(t', t_w) \to G_\infty(t_w) = G_0 \exp(-(\tau_0/t_w)^{1-\mu})$, i.e. there remains a non-zero residual stress $\sigma_\infty = G_\infty(t_w)\gamma_0$ that increases with t_w.

- for $\alpha = 2$ (full aging $\mu = 1$), The stress decays algebraically:

$$G(t', t_w) \simeq G_0 \left(\frac{t_w}{t' + t_w}\right)^{1/r_1} \tag{3.8}$$

3.3.2 Non-linear "steady-state" rheology

We now address the most common rheological characterization, namely the steady-state flow curve $\sigma(\dot\gamma)$. With the equations at hand, such a steady-state is always reached if a fixed $\dot\gamma$ is applied, with the history of the system erased (aging suppressed). Using (3.1), the fluidity a in this steady state is set by $f(a) = g(a, G_0\dot\gamma/a, \dot\gamma)$. For low values of $\dot\gamma$, the fluidity remains weak so that using the formal expansions (3.3,3.4), one finds from the competition of spontaneous aging and flow-induced rejuvenation $a \sim \dot\gamma^{\frac{\nu-\epsilon}{\nu}}$, which leads to a power law steady-state relation $\sigma(\dot\gamma \to 0) \sim \dot\gamma^{\frac{\epsilon}{\nu}}$, where $\nu = \alpha - n_1 + m_1$ and $\epsilon = \alpha - n_1 - p_1$. Note that $\nu - \epsilon = m_1 + p_1$ is likely to be a positive number if shear is to enhance fluidity in (2)-(4).

So the low shear steady-state behaviour leads us to the following distinction according to $\epsilon = \alpha - n_1 - p_1$ (see Figure 7):

- for $\epsilon > 0$, at low shear rates the fluid behaves as a power law fluid $\sigma(\dot\gamma \to 0) \sim \dot\gamma^{\frac{\epsilon}{\nu}}$ (full line in Fig. 7),
- for $\epsilon = 0$, stress tends to a finite value $\sigma_y = G_0^{\frac{p_1}{\nu}} (r_1/u_1)^{\frac{1}{\nu}}$ (dashed line in Fig. 7),
- $\epsilon < 0$ corresponds to a stress diverging as $\dot\gamma$ goes to zero which is unphysical for the local flow rule of a realistic system, which has clearly finite stress limits for yield to occur.

[2] Note that the stretched exponential here stems from the non-linear equation, in contrast to the classical picture for glassy systems of a convolution of single exponential processes with a distribution of time scales.

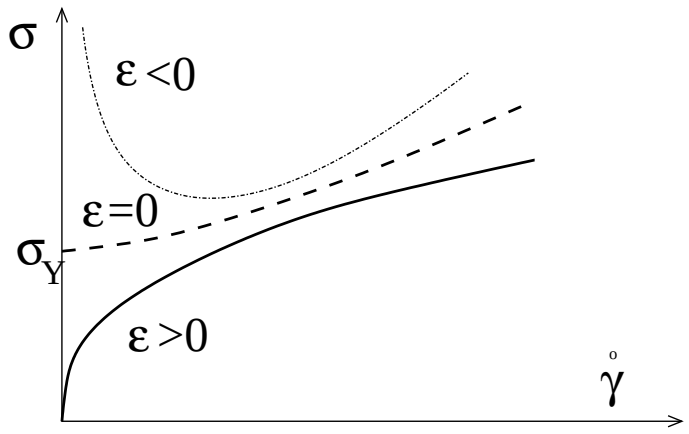

Fig. 7. Steady-state rheology as a function of the exponent $\epsilon = \alpha - n_1 - p_1$. The case $\epsilon < 0$ is unphysical (see text).

For larger values of the shear, the next terms in the expansion of both f and g start to play a role, modifying the effective stress-strain rate behaviour (see e.g. [Derec01a]). This can lead to some subtleties for the case $\epsilon = 0$ as we will see later.

3.3.3 More complex topics: oscillating rheology and transients

This subsection deals with more intricate points that the reader may want to skip in a first reading, if only to secure that it does not become the last reading too ...

"Steady state" oscillatory rheology - An oscillatory measurement is performed on the pasty phase, e.g. a deformation $\gamma = \gamma_0 \cos(\omega t + \psi)$ is applied from t_w on. No matter how small γ_0, at long times it is this shear that will control the oscillating value of the fluidity through equation (3.2) (this is for example in contrast with the SGR model where the effective temperature is fixed to a finite value, which guarantees an intrinsic linear domain). As a consequence the long-time response is intrinsically non-linear with many harmonics in the stress response.

Although there are consequently no linear moduli $G'(\omega)$ and $G''(\omega)$, we can still discuss the outcome of a rheometer measuring the in-phase and out-of-phase first harmonic of the stress divided by γ_0, and call these numbers $G'_\infty(\omega, \gamma_0)$ and $G''_\infty(\omega, \gamma_0)$ by extension (the ∞ subscript is to emphasize that these are asymptotic long-time values). A qualitative analysis developed in [Derec01a,Derec01b] shows that one expect a frequency dependence reminiscent of the Maxwell model in gross features but with different slopes

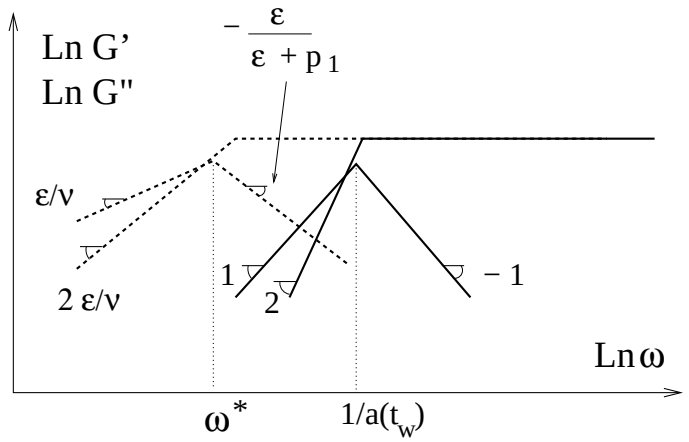

Fig. 8. Oscillatory rheology: $\gamma = \gamma_0 \cos(\omega t)$. Left (dashed lines): effective moduli in the asymptotic long-time regime (non-linear). Right (full lines): linear response at short times ($t - t_w \ll t_w$). As time goes on, the measured moduli drift from the latter to the former. $\omega^* \sim \gamma_0^{\nu/(\nu-\epsilon)}$ depends on the measurement amplitude

for $\epsilon > 0$ (see dashed lines in Figure 8). The cross-over frequency ω^* in this non-linear situation is amplitude dependent and weak if γ_0 is small. Therefore experimental observations may well be restricted to the $\omega > \omega^*$ domain. [3]

Transients and thresholds for non-linear behaviour

The results mentioned above, both for steady and oscillatory rheology, correspond to the long-time behaviour in measurement processes by which energy is constantly fed into the system (in contrast to stress relaxation measurement - see 3.3.1 -, where a finite perturbation is made on a system of initially non-zero fluidity).

However, when the measurement (applied constant shear rate or oscillatory shear) starts at t_w the system initially responds as a Maxwell fluid of characteristic time $1/a(t_w) \sim t_w^{\mu}$. There is thus in the two experiments a cross-over in time from the linear response at short times to the non-linear "steady" response at long times. The duration of the linear response decreases if the amplitude $\dot{\gamma}$ or γ_0 increases, but also if the waiting time t_w increases [Derec01a].

Following the response in time, one thus anticipates in the steady shear experiment an instantaneous viscosity that decreases from $\eta(t_w) \sim 1/a(t_w)$

[3] The case $\epsilon = 0$ yields non-linear constants $G'_\infty(\omega, \gamma_0) = G_0$ and $G''_\infty(\omega, \gamma_0) \sim G_0 \gamma_0^{\frac{\nu}{p1}}$.

to its asymptotic value $\eta_\infty \sim \dot{\gamma}^{\frac{\epsilon-\nu}{\nu}}$ for very weak applied shear rate $\dot{\gamma}$. [4]

Similarly, if one follows the first harmonic of the stress in an oscillatory experiment, one expects that the hump in G'' slides progressively to lower frequencies before saturating at ω^* with the slopes of the moduli becoming progressively weaker (Figure 8).

3.4 Intermediary conclusion

The class of models described by the simple equations (3.1-3.4) generates a rich physics not dissimilar to experimental observations quoted in section 2. For systems under weak shear, the response is dictated by the behaviour for small fluidities of the functions f and g describing spontaneous aging and flow induced rejuvenation in (3.2). If these behaviour are power-law like ($f \simeq r_1 a^\alpha$, $g \simeq u_1 a^{\alpha-\epsilon}\sigma^{\nu-\epsilon}(\dot{\gamma}/a\sigma)^{p_1}$), then (i) physical aging is characterized by the exponent $\mu = (\alpha-1)^{-1}$ (see 3.3.1) and (ii) the low shear steady-state rheology is that of a power-law fluid for $\epsilon > 0$ and of a yield stress fluid for the smallest acceptable value $\epsilon = 0$. We will see later that this last case deserves more careful attention.

4 Experimental facts 2: soft solids that flow in a strange way

4.1 Avalanches and "viscosity bifurcation"

The rheological behaviour of colloidal soft-solids is sometimes less smooth than suggested by the flow curves discussed in the previous section. A spectacular manifestation is that of surface avalanches as reported in a recent letter [Coussot02a]: a plane covered by a layer of soft-solid is progressively inclined with respect to horizontal. For a power-law fluid (e.g. flow curve akin to the lower curve in Figure 7) one expects a progressively increasing downhill sliding as the slope is increased. For a yield-stress fluid (e.g. steady flow curve as the middle one in Figure 7), one expects no flow before the tangential component of the stress reaches the yield stress value σ_Y, and a progressive flow thereafter. What is in contrast sometimes observed, for a wide variety of soft solids of very different chemical nature, is the sudden onset of an "avalanche" for a stress σ_c, with some material spontaneously accelerating [Coussot02a].

In more conventional rheometry, a related experiment is as follows [Coussot02a]: for a given reproducible preparation scheme, apply at time t_w a fixed stress

[4] If the measurement is so strong that it "immediately" leads the system into non-linearity, other features can be observed such as a peak (overshoot) in the stress response to a fixed applied $\dot{\gamma}$. The value of this peak drifts with the age of the sample, providing a simple way to assess physical aging in the system (see [Derec01b] for a related discussion).

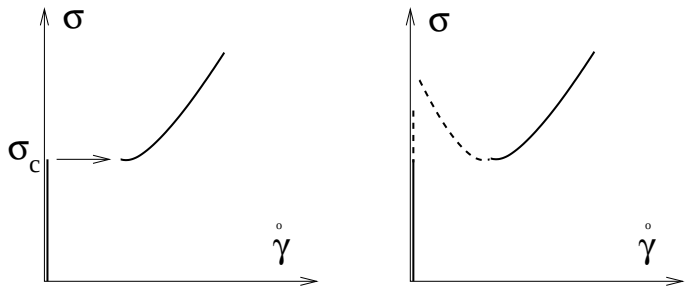

Fig. 9. Scheme for the observed viscosity bifurcation

σ and subsequently measure the instantaneous flow rate $\dot{\gamma}(t)$ or equivalently an instantaneous viscosity $\eta(t) = \dot{\gamma}(t)/\sigma$. The observation, again for many complex systems of different microscopic nature, is that for σ smaller than a value σ_c, the viscosity $\eta(t)$ tends to infinity with time (in the model terms the fluidity tends to 0, the system freezes), whereas for σ larger than σ_c, the viscosity tends at long times to a finite value. The long time viscosity $\eta(t \to \infty)$ actually jumps from ∞ to a finite value at σ_c, hence the term "viscosity bifurcation" coined for this jump.

Such a phenomenon suggests a jump between two branches in the steady-state flow diagram (Figure 9 left), which in a simple picture can be the outcome of an underlying flow curve with a decreasing branch (Figure 9 right) .

4.2 Parallel with flow induced transitions: heterogeneous "banded" flows

In many complex fluids, non monotonic local flow curves are taken to be often responsible for transitions between a high viscosity branch and a low viscosity one. Such a decreasing branch is notoriously unstable when inertial effects are taken into account. As a result the system can separate into domains (bands) of material corresponding to each of the stable branches. Many studies have recently explored these flow induced transitions and started to shine some light on these complex far from thermal equilibrium problems [Olmsted97, Olmsted99, Radulescu99, Dhont99, Britton97, Ramos00, Berret97, Diat95]. The resulting macroscopic flow behaviour, relating the macroscopic stress Σ to the macroscopic or effective shear rate $\dot{\Gamma}$, can be rather complex, with selection rules in the banded regime very sensitive to gradient terms in the equation that decide of the stability of the interfaces between bands [Lu00].

Direct observation of banding in the slow flows of some soft-solids have been reported [Pignon96,Coussot02b,Cloitre01,Debregeas02] and also shows up in some numerical simulations [Debregeas02, Varnik02]. In both experiments and numerical work, boundaries where sometimes shown to affect the

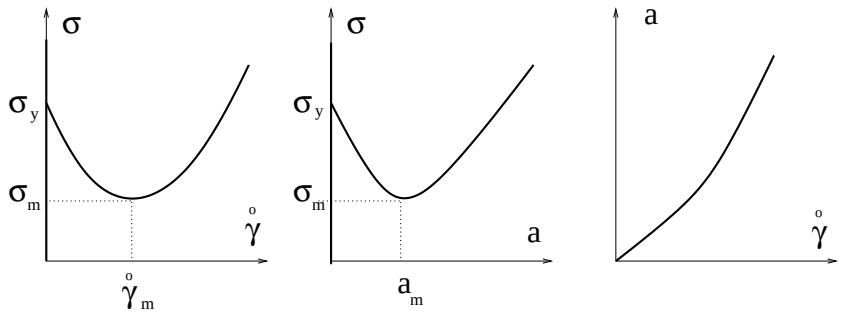

Fig. 10. Steady-state solutions of equations (3.1-3.2) for $\epsilon = 0$ and a non-monotonic $\sigma(\dot{\gamma})$.

banding phenomena. One in principle expects all the complexity revealed by former studies on "flowing" complex fluids to be potentially present here, with in addition the specificities linked to having one of the "phases" being a non-ergodic aging soft-solid.

4.3 Description within the simple class of models

Given this potential complexity it is tempting to investigate such behaviour within our simple model by considering situations where the competition between aging and flow induced fluidization results in a local flow curve similar to Figure 9b . A necessary condition within our model is that $\epsilon = 0$. For example if $n_2 + p_2 > \alpha + \beta$ and if r_2 and u_2 are positive, then $\sigma_{\dot{\gamma}\to 0^+} \simeq \sigma_y[1 - (..)\dot{\gamma}^{n_2+p_2-\alpha}]$. In such a case, both the $\sigma(a)$ and $\sigma(\dot{\gamma})$ plots present a decreasing section down to a value σ_m, before increasing monotonically again (Figure 10).

4.3.1 Adapting the model

We have investigated the behaviour of the system in this situation for the simplest geometry where heterogeneity is allowed only in the direction of the velocity gradient (gradient banding): the fields σ, a and $\dot{\gamma}$ vary along a single direction z normal to the two boundaries in relative motion. We then add a diffusion like term for the equation describing the evolution of the local fluidity. I will not enter here the detailed description of the model (the reader is referred to [Picard02]) but rather focus on a few remarks before presenting the resulting macroscopic behaviour under steady driving, either at fixed stress Σ or at fixed strain rate $\dot{\Gamma}$.

- There is now an absolute need for boundary conditions on the walls, not only for the fluid velocity but also for the internal variables, here the fluidity a. How the wall affects the density, degree of order and mobility of a

colloidal fluid in their neighborhood is a difficult question, that will be shown to have important consequences on the overall macroscopic behaviour.

- The choice of a diffusion term in the equation for the evolution of a is debatable, and used here as a simple choice involving gradients. Obviously the corresponding diffusion coefficient D may itself depend on a. As a result the thickness ℓ of the interface between frozen ($a \sim 0$) and fluidized regions (a finite) in a banded flow, is fixed on the frozen side by the competition between $f(a) \sim -r_1 a^\alpha$ and the diffusion term scaling as $D(a)a/\ell^2$, which yields $\ell \sim (D(a)a^{1-\alpha})^{1/2}$ indicating an algebraic decay unless D scales as $a^{\alpha-1}$. Thus in contrast with flow induced transitions between two branches of finite viscosity, the interfaces between bands need not have a finite thickness, and the bands can interact through algebraic effective potentials.

4.3.2 Fixed stress Σ

In the case where the macroscopic stress Σ is maintained at a fixed value, within our model the dynamics of the field $a(z)$ is such that the system evolves toward the local minimum of a Σ dependent functional (very similar to a free-energy in a field theory for wetting).

Essentially there are two effective branches: a frozen branch corresponding to a frozen bulk $a \sim 0$ with layers of finite fluidity close to the wall induced by the boundary conditions, and a fluidized branch with the bulk at a value of a corresponding to the stress Σ on the up-rising part of the local flow curve (Figure 11a) with layers of possibly weaker fluidity close to the walls. It is important to point out that σ_i and σ_d in Figure 11a depend sensitively on the boundary conditions for a on the wall, as the walls can act as nucleation centers for either of the frozen and fluidized "phases". [5]

For stress values Σ lower than σ_d only the frozen branch is stable, whereas for values larger than σ_i only the fluidized branch is. For intermediate values of the stress $\sigma_d < \Sigma < \sigma_i$, both branches are possible solutions at long times. *Which branch is selected depends then on the initial conditions.* For a given preparation scheme of the system, and test under increasingly large applied fixed stresses, one thus anticipate a sudden jump from the frozen to the fluid branch at a given value Σ_c that depends on the preparation scheme (with $\sigma_d < \Sigma_c < \sigma_i$). This is in agreement with the experimental picture for the "viscosity bifurcation" (section 4.1), and further suggests that this value increases with the age of the system, the transition occurring later for a weaker initial fluidity.

If the stress is ramped up and down slowly a hysteresis loop is described as indicated by the arrows on Figure 11a. In an avalanche experiment as

[5] A finite amount of noise in the dynamics can also trigger this nucleation in the bulk which would result in the narrowing of the hysteresis loop around a value σ^*.

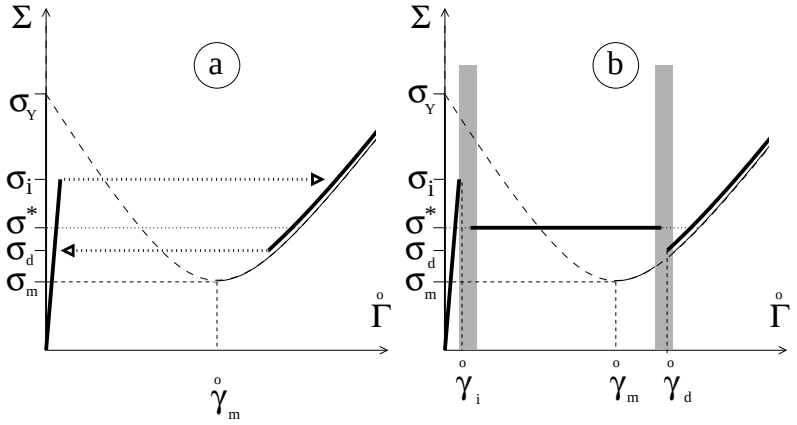

Fig. 11. Flow behaviour (full lines) under steady driving: (a) at fixed stress Σ, (b) at fixed average shear rate $\dot{\Gamma}$. The thin lines are the local steady-state solutions of (3.1-3.2) depicted in Figure 10. Oscillating stress response can be observed in the grey areas.

reported in 4.1 [Coussot02a], σ_i would thus play the role of the critical stress σ_c. Other rheological experiments could conclude that the system has an effective yield stress anywhere between σ_d and σ_i.

4.3.3 Fixed shear rate $\dot{\Gamma}$

The case of an imposed macroscopic constant shear rate $\dot{\Gamma}$ (i.e. the two bounding plates moved at a constant relative velocity), is much more complex as both the field $a(z,t)$ and $\Sigma(t)$ evolve in a coupled way.

The resulting macroscopic picture is represented on Figure 11b. Basically the two branches described in the previous subsection are still present, but for intermediate shear rates, the system can now stabilize in a banded state at a stress very close to σ^*. In these banded situations the system is essentially divided into a fraction of the system at a fluidity close to 0 and a fraction at a fluidity close to $a(\sigma^*)$, the proportion between the two being set by the value of $\dot{\Gamma}$. [6]

Actually the physics is sometimes even richer. For some parameters, usually close to the frozen branch - plateau region (left shaded area in

[6] In the absence of noise, there may be various banding patterns that constitute attainable steady states, corresponding to only imperceptibly different macroscopic stresses. In this banding domain, the transient that lead to one of this or these steady-state solutions essentially consists of two stages. First the fluidity evolves to form domains or bands of frozen ($a \sim 0$) and fluid ($a \sim a(\sigma^*)$) material, then in a second much slower stage these bands coarsen until a steady-state is reached.

Figure 11b), an oscillating situation is reached for both $a(z,t)$ and Σ: there is thus no steady-state ! Looking at the structure of $a(z,t)$, these oscillations correspond to a *localized* oscillation of a in a narrow region, often but not always close to a wall, that alternatively freezes, so that the stress increases beyond σ_Y then fluidizes which induces a release of the stress that drops below σ_m which induces in turn the re-freezing. This localized oscillating fracture, results in a macroscopic stick-slip behaviour.

The overall behaviour is very similar to that observed by Pignon et al. [Pignon96] on a laponite suspension (an oscillating fracture was observed by direct imaging), and by Varnik et al. in their simulations [Varnik02]. It should however be noted that in the situation where macroscopic bands are present these works show some evidence of a value of $\dot{\gamma}$ in the flowing band that changes with $\dot{\Gamma}$ (and thus the size of this flowing region), in contrast to the predictions of the present simple model.

4.3.4 Transients

Of course there are in principle lots of thing that can be analyzed beyond the long-time response to an applied constant stress or shear-rate. Of particular interest could be the analysis of the mechanical aging of a system prepared in a heterogeneous banded state. [7]

4.4 Intermediary conclusion

From experimental observations emerges the picture that for some colloidal soft solids, the structure of slow flows can be complex, both temporally and spatially. To apprehend this complexity various experimental schemes, possibly going beyond the measurement of purely mechanical responses may be necessary. Eventually, experimental, analytic and numerical works emphasize the role of the boundaries, always present in a mechanical measurement .

5 Criticism of the model and perspectives

We end with a brief description of the interests and shortcomings of the models described by equations (3.1) and (3.2), before presenting a few comments as to some perspectives.

[7] For a mechanical quench to study mechanical aging (see 2.2), one should clearly shear the system strongly so that it lies fully on the fluidized branch.

5.1 A classification of the phenomenologies

We have built a very simple class of models, where the main ingredients of the physics at work is hidden in the functions f and g. Analyzing these models a classification has naturally emerged related to the behaviour of these functions at low fluidity.

- A choice for f determines the value of α and thus of of $\mu = (\alpha - 1)^{-1}$.

  - If $\alpha > 2$ the system undergoes spontaneously sub-aging ($\mu < 1$), with the corresponding rescaling of the stress relaxation modulus, in qualitative accordance with some experiments [Derec00, Ramos01].

  - On the contrary $\alpha < 2$ imposes super-aging $\mu > 1$, and stresses that freeze without relaxing to 0. The limit case $\alpha = 1$ corresponds to an exponential temporal increase of the mechanical relaxation time, as observed in [Bonn02].

  - The marginal full-aging case $\alpha = 2, \mu = 1$ is consistent with other observations [Cloitre00, Viasnoff02b].

- The combined choice of f and g sets the value of ϵ. [8]

  - If $\epsilon > 0$, the steady-state flow curve is that of a "gentle" power-law fluid, that flows homogeneously, and can be confused with a yield-stress fluid only due to experimental difficulties to access the weak $\dot{\gamma}$ domain.

  - If $\epsilon = 0$, the system has a true yield stress, and a Herschel-Buckley behaviour $\sigma(\dot{\gamma} \to 0) \simeq \sigma_Y + A\dot{\gamma}^n$. If $A \geq 0$ the system again is expected to flow homogeneously, at a steady rate $\dot{\gamma}$ if the stress is larger than σ_Y. However, A can be negative, in which case there is an initial decreasing branch in the flow curve, yielding the viscosity bifurcation, gradient banding and sometimes oscillating phenomenologies described in section 4. [9]

The classifications according to the signs of $\alpha - 2$ and ϵ are a priori not directly related to one another which allows in principle for the existence of various kind of soft-solids from a phenomenological point of view. In both the scalar model of subsection 3.2.1 and in the activated model of Lemaitre (3.2.2), the exponents α and ϵ are related by $\alpha - 2 = \epsilon$, so that the two classifications above boil down to a single one. In the 4-state model presented in 3.2.3, $\alpha = 1$ and $\epsilon = 0$ corresponding to a super-aging yield-stress fluid. The SGR model [Sollich97], which cannot be mapped onto the

[8] Once again, a realistic model according to (3.1-3.4) forbids $\epsilon < 0$, as this would mean resistance of the frozen state ($a = 0, \dot{\gamma} = 0$) to an infinite amount of stress.

[9] There is then another important characteristic state $(a_m, \dot{\gamma}_m, \sigma_m)$ (see Figure 10) that may or not be in the range of small fluidities that allow the expansions of (3.3-3.4).

simple equations (3.1,3.2), yields a phenomenology corresponding to full aging ($\alpha = 2$) and a finite yield stress ($\epsilon = 0$).

This diversity of possible behaviour seems indeed to show up in the spectrum of "soft solids". Very crudely what people often name "gels" typically fall in the super-aging ($\alpha < 2$) and yield-stress behaviour ($\epsilon = 0$) category, whereas "glasses" often display sub-aging or aging behaviour, with a rheology often difficult to discriminate between a power-law behaviour with a weak exponent or a true yield stress-behaviour. I recall however (see section 1) that there is no clear definition of these terms, and that tuning of some parameters (ionic strength, temperature, etc ..) can lead continuously from one category to the other.

5.2 Successes and failures of these models

An potential interest of the models encompassed by equations (3.1,3.2) is their analytical simplicity which could allow to use them to follow or anticipate complex rheological histories.

A more thorough attempt to confront experimental data with a specific set of exponents in equations (3.3,3.4) was performed for suspensions of protected silica particles [Derec01b], with the following set of successes and failures:

Successes: the equations naturally describe mechanical aging with a rescaling variable $S(t', t_w) = \frac{(t'+t_w)^{1-\mu} - t_w^{1-\mu}}{(1-\mu)\tau_0^{1-\mu}}$ naturally showing up in equation (3.6), that is well suited to account for the rescaling of relaxation experiments performed at different waiting times on rather diverse systems [Cloitre00, Derec00, Ramos01]. Also many non-linear features of steady and oscillatory rheology are reasonably captured with rather simple forms for f and g. A nice point is that the model also apprehends semi-quantitatively correctly features of transient regimes [Derec01b], and as such can be of help to anticipate/interpret experiments.

Failures: the use of a single (although evolving) time scale leads to inadequate scaling functions for the mechanical response. For example equation the modulus in (3.6) is a single exponential of the rescaling variable, whereas experiments in [Derec00, Ramos01] suggest a stretched exponential (in $S(t', t_w)$) (see e.g. fig. 5). In addition, in many systems [Borrega00, Derec01b] the value of the elastic plateau, which is a constant G_0 in the model, actually increases slowly with time as $\log(t_w)$. This usually mild feature can in principle be accounted for by a natural modification of the system of equations if one thinks in terms of activation barriers ($G_0 = G_0(\mathcal{E})$ with $\mathcal{E}$ increasing as $\log(t_w)$ in the description of 3.2.2 , see also [Viasnoff02b]), but at the cost of an increased complexity. Eventually the description of the vicinity of the fluid/soft-solid transition using only r_1 as a control parameter was shown to be unsatisfactory again because it

neglects the variations of G_0 with concentration.

So altogether, the main merit of these models is indeed that their simplicity and tractability permits simple estimates for the outcome of an experiment. They also allow one to make qualitative comments on the influence of heterogeneities in banding flow, in a domain where more accurate/complete models may be practically unusable.

A clear drawback at this stage is the total absence of connection of the phenomenological equations and exponents with microscopic mechanisms of some generality, or with coarse-grained versions of the latter. It is at this level that a possible relation between the microscopic interactions and the macroscopic rheological behaviour is to be made.

In the following we comment briefly on direction for possible extensions of these models, very likely at the cost of simplicity.

5.3 Better models: more variables? which collective physics ?

Taking the equations (3.1,3.2) as a starting point, extensions of the number and type of variables are suggested by experimental observations and theoretical considerations:

- The observation of stretched exponentials response functions [Derec00, Ramos01] (in the rescaled variables) suggests the existence of a spectrum of relaxation time rather than a single one. For homogeneous systems this suggests the use of instantaneous distributions or probability distributions for either the local deformation (as e.g. in the SGR) or the local stress (as e.g. in [Hebraud98, Derec99, Debregeas02]), rather than the local averages σ and $\dot{\gamma}$ in the models quoted here.

- Recent experimental observations have shown that an applied moderate shear can in some special conditions lead to an actual increase of the apparent mechanical age of the system [Viasnoff02a, Viasnoff02b]. To account for such a flow induced "overaging" it is tempting to evoke a set of processes operating in parallel, in line with the previous point.

- In the observations of Cloitre et al. [Cloitre00], a logarithmic recovery of the strain is observed when stress is cut down to 0. Such an evolution is forbidden in the Maxwell model which implicitly takes $\dot{\gamma}(t)$ as the driving and $\sigma(t)$ as the response. A way out if one insists on avoiding using whole distributions is to introduce at least a single "tensorial" variable in addition to the stress, which keeps the memory of the direction of past flow (a task which the "scalar" fluidity a is unable to perform). I point out that in related models for the plastic flow of amorphous solids, recent developments by Langer and co-workers actually suggest the use of such local variables to describe the instantaneous state of the system ("shear-transformation-zones" models [Falk98, Langer01, Eastgate03, Lemaitre02]). Of course models involving local distributions of stresses or strains will naturally bear such "tensorial" memory.

- To take into account the banding observed in some cases and the corresponding localization of the deformation, it is necessary to extend whatever is the set of local variables to spatially and temporally dependent fields. Of course this can be performed in the simple fluidity model presented here [Picard02], but should in principle be done for models involving local distributions.

- An eventual point in this list is that the description we have made up to know has neglected the intrinsically tensorial nature of both stress, deformation, and structure or texture factors. There are instances where normal stresses have been shown to play a role in the selection of heterogeneous patterns [Schmitt95], and situations where the convection of fluctuations or structures by the flow is important require a proper tensorial description (see e.g. the recent mode-coupling description of [Fuchs02]).

As a relevant aside, let me emphasize that the respective role of stress and strain (or strain rate) in constitutive mechanical models is far from clear. Most models actually take one or the other as the driving field, the remaining one acting as a state variable. In an experiment, what is actually imposed is in general boundary conditions on one or the other, with the propagation of these tensorial fields in the bulk ruled by mechanical equilibrium and conservation laws, in addition to the constitutive rule chosen.

At the end of this list one expects thus that a general model should consist in a set of coupled non-linear differential equations (or possibly worse integro-differential), describing a large number of spatially and temporally varying fields, with consequently very diverse possible outcomes even under steady driving [Groisman98, Grosso01, Cates02]. Such models could remain rather phenomenological (as e.g. the SGR model) or try to make tighter connections with structural information on the colloidal system (as e.g. in models inspired by mode-coupling theories [Fuchs02]). At a very local scale, one expects very dramatic non-linear events, the "rearrangements", to be the building elements of a more collective macroscopic response.

It is also possible that for some problems involving heterogeneous flows, it could be physically more meaningful to describe the evolution by focusing on a dynamical description of the interfaces between the "dynamical phases" in contact, rather than carrying a complete description of the fields everywhere in the bulk [Olmsted97, Ajdari98, Goveas99, Butler02].

5.4 Back to facts

Given the complexity alluded to above in the construction of models, it seems that the most important thing to do now is, guided by concepts and simple models that have emerged in the last years, to build first sets of experimental data on well controlled systems, where one has grasp on the synthesis of the system and experimental means of investigation of their structure under flow beyond the simple mechanical response (see e.g. the

review [Cipelletti02]). A similar statement holds for numerical simulations [Varnik02, Debregeas02, Tewari99]. From the discussion above, one should obviously not necessarily expect too much universality but rather try to infer classes of behaviour from the analysis of such sets of data.

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