Rheology of Soft Glassy Materials

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We attribute similarities in the rheology of many soft materials (foams, emulsions, slurries, etc.) to the shared features of structural disorder and metastability. A generic model for the mesoscopic dynamics of "soft glassy matter" is introduced, with interactions represented by a mean-field noise temperature x. We find power law fluid behavior either with ($x < 1$) or without ($1 < x < 2$) a yield stress. For $1 < x < 2$, both storage and loss modulus vary with frequency as ω^{x-1}, becoming flat near a glass transition ($x = 1$). Values of $x \approx 1$ may result from marginal dynamics as seen in some spin glass models.

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Many soft materials, such as foams, emulsions, pastes and slurries, have intriguing rheological properties. Experimentally, there is a well-developed phenomenology for such systems: their nonlinear flow behavior is often fit to the form $\sigma = A + B\dot{\gamma}^n$ where σ is shear stress and $\dot{\gamma}$ strain rate. This is the Herschel-Bulkeley equation [1,2]; or (for $A = 0$) the "power-law fluid" [1–3]. For the same materials, linear or quasi-linear viscoelastic mesurements often reveal storage and loss moduli $G'(\omega)$, $G''(\omega)$ in nearly constant ratio (G''/G' is usually about 0.1) with a frequency dependence that is either a weak power law (clay slurries, paints, microgels) or negligible (tomato paste, dense emulsions, dense multilayer vesicles, colloidal glasses) [4–10]. This behavior persists down to the lowest accessible frequencies (about 10^{-3}–1 Hz depending on the system), in apparent contradiction to linear response theory [11], which requires that $G''(\omega)$ should be an odd function of ω.

That similar anomalous rheology should be seen in such a wide range of soft materials suggests a common cause. Indeed, the frequency dependence indicated above points strongly to the generic presence of slow "glassy" dynamics persisting to arbitrarily small frequencies. This feature is found in several other contexts [12–14], such as elastic manifold dynamics in random media [15,16]. The latter is suggestive of rheology: charge density waves, vortices, contact lines, etc. can "flow" in response to an imposed "stress". In this Letter we argue that glassy dynamics is a natural consequence of two properties shared by all the soft materials mentioned above: *structural disorder* and *metastability*. In such materials, thermal motion alone is not enough to achieve complete structural relaxation. The system has to cross energy barriers (for example those associated with rearrangement of droplets in an emulsion) that are very large compared to typical thermal energies. Therefore the system adopts a disordered, metastable configuration even when (as in a monodisperse emulsion or foam) the state of least free energy would be ordered [17]. While the importance of disorder has been noted before for specific systems [7,11,18–21], we feel that its unifying role in rheological modelling has not been appreciated.

To test these ideas, we construct a minimal "generic model" for soft glassy matter. For simplicity, we ignore tensorial aspects, restricting our analysis to simple shear strains. Consider first the behavior of a foam or dense emulsion under shear. We focus on a *mesoscopic* region, large enough for a local strain variable l to be defined, but small enough for this to be approximately uniform within the region, whose size we choose as the unit of length. As the system is sheared, droplets in this region will first deform elastically from a local equilibrium configuration, giving rise to a stored elastic energy (due to surface tension, in this example [18]). This continues up to a yield point, characterized by a strain $l_{\rm y}$, whereupon the droplets rearrange to new positions in which they are less deformed, thus relaxing stress. The mesoscopic strain l *measured from the nearest equilibrium position* (i.e., the one which can be reached by purely elastic deformation) therefore executes a saw-tooth motion as the macroscopic strain γ is increased [22]. Neglecting nonlinearities before yielding, the local shear stress is given by kl, with k an elastic constant; the yield point defines a maximal elastic energy $E = \frac{1}{2}k{l_{\rm y}}^2$. A similar description obviously extends to many others of the soft materials discussed above.

We now ascribe to each mesoscopic region not only its own strain variable l, but also its own maximal yield elastic energy, $E > 0$. We model the effects of structural disorder by assuming a *distribution* of such yield energies E, rather than a single value common to all regions. The state of a macroscopic sample is then characterized by a probability distribution $P(l, E; t)$. We propose the following dynamics for the time evolution of P:

$$\frac{\partial}{\partial t}P = -\dot{\gamma}\frac{\partial}{\partial l}P - \Gamma_0 e^{-(E-\frac{1}{2}kl^2)/x}\, P + \Gamma(t)\,\rho(E)\delta(l) \quad (1)$$

The first term on the r.h.s. arises from the elastic deformation of the regions. This embodies a mean field assumption, that between successive local yield events, changes in local strain follow those of the macroscopic deformation: $\dot{l} = \dot{\gamma}$. Note, however, that due to stochastic yielding events the stress kl is spatially inhomogeneous (as is the local strain l). The macroscopic stress is defined as an average over regions

$$\sigma(t) = k\,\langle l\rangle \equiv k \int l\, P(l,E;t)\, dl\, dE \ . \qquad (2)$$

The second term on the r.h.s. of (1) describes the yielding of our mesoscopic regions. We have written the yielding rate as the product of an "attempt frequency" Γ_0, and an exponential probability for activation over an energy barrier $E - \frac{1}{2}kl^2$ (the excess of the yield energy over that stored elastically). However, the resemblance to thermal activation is formal: we expect these "activated" yield processes to arise primarily by coupling to structural rearrangements elsewhere in the system. In a mean-field spirit, all such interactions between regions are subsumed into an effective "noise temperature", x. We first regard Γ_0, x as arbitrary constants, but later discuss their meaning and their possible dependences on other quantities.

Finally, the third term on the r.h.s. of (1) describes the relaxation of regions to new local equilibrium positions after yielding, which we treat as effectively instantaneous. The first factor in this term is simply the total yielding rate $\Gamma(t) = \Gamma_0\, \left\langle \exp[-(E-\frac{1}{2}kl^2)/x]\right\rangle_P$. The remaining two factors incorporate further mean-field assumptions, as follows. First, the yield energy E for distortions about any equilibrium configuration is uncorrelated with the previous one for this region; it is drawn randomly from the prior distribution ("density of states") $\rho(E)$ which we assume to be time-independent. Second, immediately after yielding, a region always finds itself in a completely unstressed state of local equilibrium with $l = 0$ (hence the Dirac delta function, $\delta(l)$). This latter simplification is not essential, as shown elsewhere [23].

In the absence of flow ($\gamma(t) = 0$), the model (1) describes activated hopping between "traps" of depth $E' = E - \frac{1}{2}kl^2$ with density $\rho(E')$. This corresponds to Bouchaud's model for glassy dynamics [12–14], whose predictions we briefly recall. For high (noise) temperatures x the system evolves towards the Boltzmann distribution $P_{\rm eq}(E') \sim \rho(E')\exp(E'/x)$. As x is lowered, this distribution may cease to be normalizable, leading to a glass transition at $x_{\rm g}^{-1} = -\lim_{E\to\infty}(\partial/\partial E)\ln\rho(E)$. For $x < x_{\rm g}$, no equilibrium state exists, and the system shows "weak ergodicity breaking" and various aging phenomena. A finite value of $x_{\rm g}$ implies an exponential tail in the density of states, $\rho \sim \exp(-E/x_{\rm g})$, which corresponds to a Gaussian distribution of yield strains $l_{\rm y} = (2E/k)^{1/2}$.

A major attraction of the model defined by (1) and (2) is that an exact constitutive equation, relating the stress $\sigma(t)$ to the strain-rate history $[\dot\gamma(t' < t)]$, can be obtained [23]. Since this is quite complicated, we restrict ourselves here to two standard rheological tests, for which the full form is not required. We use non-dimensional units for time and energy by setting $\Gamma_0 = x_{\rm g} = 1$; we also rescale our strain variables (l,γ) so that $k = 1$. In these units, $\rho(E) = \exp[-E(1+f(E))]$ with $f(E) \to 0$ for $E \to \infty$. Up to sub-power-law factors such as logarithms, all power laws reported below are valid for any $f(E)$; numerical examples use $f \equiv 0$. Analytical and numerical support for our results will be detailed elsewhere [23].

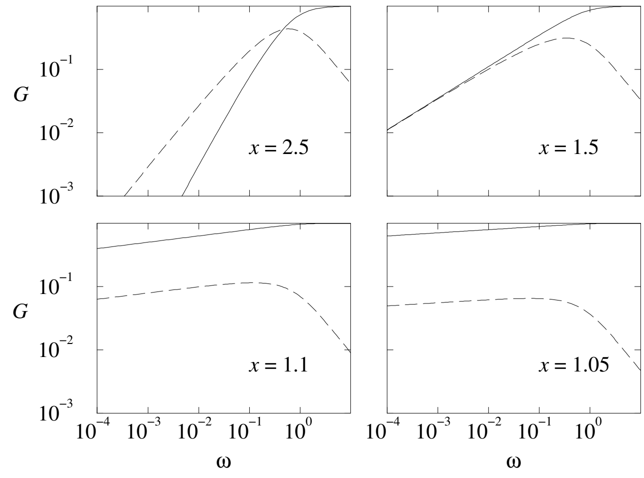

FIG. 1. Linear moduli G' (solid line) and G'' (dashed) vs frequency ω at various noise temperatures.

Consider first the complex dynamic shear modulus $G^*(\omega) = G' + iG''$, which describes the stress response to small shear strain perturbations around the equilibrium state. As such, it is well defined (i.e., time-independent) only above the glass transition, $x > 1$. Expanding (1) to first order in the amplitude γ of an oscillatory strain $\gamma(t) = \gamma\cos\omega t$, we find $G^*(\omega) = \langle i\omega\tau/(i\omega\tau+1)\rangle_{\rm eq}$. This corresponds to a distribution of Maxwell modes whose spectrum of relaxation times $\tau = \exp(E/x)$ is given by the equilibrium distribution $P_{\rm eq}(E) \sim \exp(E/x)\rho(E)$. The relaxation time spectrum thus exhibits power law behavior for large τ: $P(\tau) \sim \tau^{-x}$. This leads to power laws for G^* in the low frequency range (Fig. 1):

$$\begin{array}{llll} G'' \sim \omega & \text{for } 2 < x, & \sim \omega^{x-1} & \text{for } 1 < x < 2 \\ G' \sim \omega^2 & \text{for } 3 < x, & \sim \omega^{x-1} & \text{for } 1 < x < 3 \end{array} \qquad (3)$$

For $x > 3$ the system is Maxwell-like at low frequencies, whereas for $2 < x < 3$ there is an anomalous power law in the elastic modulus. Most interesting is the regime $1 < x < 2$, where G' and G'' have constant ratio; both vary as ω^{x-1}. Behavior like this is observed in a number of soft materials [4–7,10]. Moreover, the frequency exponent approaches zero as $x \to 1$, resulting in essentially constant values of G'' and G', as reported in dense emulsions, foams, and onion phases [6–8]. Note, however, that the ratio $G''/G' \sim x - 1$ becomes small as the glass transition is approached. This increasing dominance of the elastic response G' prefigures the onset of a yield stress for $x < 1$ (discussed below) [24]. If a high energy cutoff $E_{\rm max}$ is imposed on $\rho(E)$ (giving an upper limit on local yield strains), the above results remain valid down to $\omega_{\rm min} = \exp(-E_{\rm max}/x)$. Well-defined equilibrium values

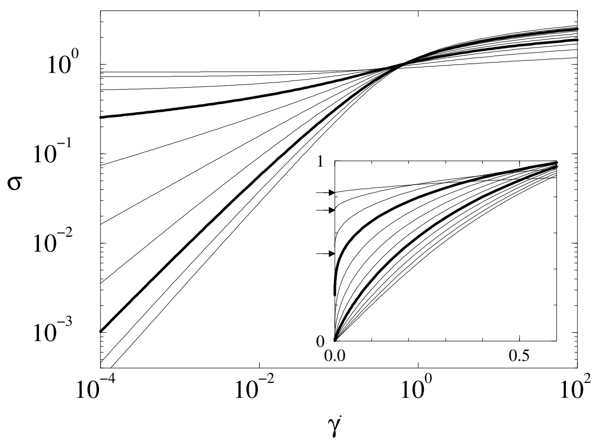

FIG. 2. Shear stress σ vs shear rate $\dot\gamma$, for $x = 0.25, 0.5, \ldots, 2.5$ (top to bottom on left); $x = 1, 2$ are shown in bold. Inset: small $\dot\gamma$ behavior, with yield stresses for $x < 1$ shown by arrows.

of the linear moduli then exist also for $x < 1$; one still finds $G'' \sim \omega^{x-1}$ for $\omega_{\rm min} \ll \omega \ll 1$. For x just below $x_{\rm g} = 1$, a log-log plot of $G''(\omega)$ therefore exhibits a small *negative* slope (whereas G' is constant). This may again be compatible with recent experimental data [7–10].

We now turn to the case of steady shear flow, $\dot\gamma =$ const, for which the steady state distribution $P_{\rm ss}(l, E)$ can be obtained analytically. After integrating over E, one finds $P_{\rm ss}(l) \sim \Theta(l) g(z(l))$ with

$$z(l) = \frac{1}{\dot\gamma}\int_0^l e^{\gamma^2/2x} d\gamma \quad g(z) = \int \rho(E) \exp(-z e^{-E/x})\, dE$$

In the large z limit, $g(z) \sim z^{-x}$. Figure 2 shows that for large shear rates, $\dot\gamma \geq 1$, σ increases very slowly for all x ($\sigma \sim (x \ln \dot\gamma)^{1/2}$). More interesting is the small $\dot\gamma$ behavior, where we find three regimes: (i) For $x > 2$, the system is Newtonian, $\sigma = \eta\dot\gamma$. The viscosity is simply the average relaxation time $\eta = \langle \exp(E/x) \rangle_{\rm eq} = \langle \tau \rangle_{\rm eq}$ taken over the equilibrium distribution of energies, $P_{\rm eq}(E) \sim \exp(E/x)\rho(E)$. Hence $\eta \sim \langle \exp(2E/x) \rangle_\rho$, which diverges at $x = 2$. (ii) For $1 < x < 2$ one finds power law fluid behavior, $\sigma \sim \dot\gamma^{x-1}$. (iii) For $x < 1$, the system shows a yield stress: $\sigma(\dot\gamma \to 0) = \sigma_{\rm y} > 0$. (This has a linear onset near the glass transition, $\sigma_{\rm y} \sim 1 - x$.) Beyond yield, the stress again increases as a power law of shear rate, $\sigma - \sigma_{\rm y} \sim \dot\gamma^{1-x}$ (for $\dot\gamma \ll 1$). The behavior of our model in regimes (ii) and (iii) therefore matches respectively the power-law fluid [1–3] and Herschel-Bulkeley [1,2] scenarios as used to fit the nonlinear rheology of pastes, emulsions, slurries, etc.

We now speculate on the origin and magnitude of the "attempt frequency" Γ_0 and the "noise temperature" x. First note that the parameter Γ_0 is the only source of a characteristic timescale (chosen as the time unit above). We have approximated it by a constant value: $\Gamma_0(\dot\gamma) = \Gamma_0(0)$. One possibility is that the intrinsic rate constant Γ_0 arises from *true* thermal processes. If so it can be estimated as $\Gamma_{\rm loc} k_{\rm B} T P_{\rm eq}(0) Q$ with $\Gamma_{\rm loc}$ a local diffusive attempt rate (for 1 μm emulsions this might be 0.01s); $k_{\rm B} T P_{\rm eq}(0)$ is the (small) fraction of regions in which true thermal activation can surmount the yield barrier. The factor Q denotes the number of neighboring regions perturbed as a result of one such thermal event. A more detailed analysis (involving an extension to our model [23]) then shows that $k_{\rm B} T P_{\rm eq}(0) Q$ must be large enough (at least of order unity) to avoid depletion of the low energy part ($E \leq k_{\rm B} T$) part of the barrier distribution. This mechanism may arise in systems (such as foams) in which one local rearrangement can trigger a long sequence of others [20,21]. If so, the resulting intrinsic rate $\Gamma_0 \sim \Gamma_{\rm loc}$ provides a plausible rheological timescale. (If Q is too small, Γ_0 will instead be of order $\Gamma_{\rm loc} e^{-\bar E/k_{\rm B}T}$, which for typical barrier energies $\bar E = \langle E \rangle_\rho$ is unfeasibly slow.)

We emphasize, however, that Γ_0 may be strongly system dependent, and any specific interpretation of it remains speculative. Nonetheless we may view the activation factor in Eq.(1) as the probability that a perturbative "kick" to a given mesoscopic region (from events elsewhere) causes it to yield. We believe this activation factor should be primarily geometric in origin and hence depend on the disorder, but not on any intrinsic energy scale. Accordingly (in our units) x values generically of order unity can be expected. We argue next that x values *close to* unity may be normal.

Consider first a steady shear experiment. For soft metastable materials, the rheological properties of a sample freshly loaded into a rheometer are usually not reproducible; they become so only after a period of shearing to eliminate memory of the loading procedure. In the process of loading one expects a large degree of disorder to be introduced; the initial dynamics under flow should therefore involve a high noise temperature $x \gg 1$. As the sample approaches the steady state, the flow will (in many cases) tend to eliminate much of this macroscopic disorder [25] so that x will decrease. But, as this occurs, the noise-activated processes will slow down; as $x \to 1$, they become negligible. Assuming that, in their absence, the disorder cannot be reduced further, x is then "pinned" at a steady-state value at or close to the glass transition. This scenario, although extremely speculative, is strongly reminiscent of the "marginal dynamics" seen in some mean-field spin glass models [26].

There remains several ambiguities within this picture, for example whether the steady state value of x should depend on $\dot\gamma$; if it does so strongly, our results for steady flow curves will of course be changed. If a steady flow is stopped and a linear viscoelastic spectrum measured, the behavior observed should presumably pertain to the x characterizing the preceding steady flow (assuming that x reflects structure only). But unless the strain amplitude is extremely small the x-value obtained in steady state could be affected by the oscillatory flow itself [27].

Also uncertain is to what extent a steady energy input is needed to sustain the nonlinear dynamics. Although not represented in the model, a small finite strain rate amplitude might be needed to balance the gradual dissipation of energy in yield events. In its absence, one might expect the sample to show aging (i.e., $P(l, E; t)$ nonstationary in time). Within the model, aging in fact only occurs for $x < 1$ [14] (the regime for which we predict a yield stress). Conversely we saw above that, even in this regime, for finite $\dot{\gamma}$ a well-defined steady state distribution is recovered: *flow interrupts aging* [13]. This can be understood by considering the distribution of energies. Without flow, one obtains a Boltzmann distribution $P(E) \sim \rho(E)e^{E/x}$ up to (for $x < 1$) a cutoff which shifts to higher and higher energies as the system ages [12]. This cutoff, and hence the most long-lived traps visited (which have a lifetime comparable to the age of the system), dominate the aging behavior [14]. The presence of flow leads to a steady state value of this cutoff of $E \sim x\ln(\dot{\gamma}^{-1}x^{1/2})$, while for higher energies one has $P_{\rm ss}(E) \sim \rho(E)E^{1/2}$. Hence flow prevents regions from getting stuck in progressively deeper traps and the aging process is truncated after a finite time.

We are currently investigating more complicated nonlinear strain histories [23]. In future work, explicit spatial structure and interactions between regions must be added so as to understand better the mutual dynamical evolution of the attempt rate, the effective noise temperature and the disorder. One issue concerns the relative importance of localized [19,28–33] versus avalanche-like [20,21] events in the relaxation of stress.

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