Shear-Thickening and Entropy-Driven Reentrance

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We discuss a generic mechanism for shear thickening analogous to entropy-driven phase reentrance. We implement it in the context of nonrelaxational mean-field glassy systems: although very simple, the microscopic models we study present a dynamical phase diagram with second- and first-order stirring-induced jamming transitions leading to intermittency, metastability, and phase coexistence as seen in some experiments. The jammed state is fragile with respect to change in the stirring direction. Our approach provides a direct derivation of a mode-coupling theory of shear thickening.

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When liquids are subjected to strong stirring, in general their viscosity decreases, a phenomenon known as "shear thinning." The opposite ("shear-thickening") behavior when stirring leads to increased jamming is rather exceptional and intriguing [1]. That shear thinning should be generic is quite easy to understand by considering the structure of any system having a large viscosity and long relaxation time scales. From the point of view of the phase-space energy landscape, the long relaxation times are the consequence of directions that are either almost flat, or contain barriers that can only just be crossed. When the system is stirred by nonconservative forces, displacements are easily induced along these directions, and this has the effect of speeding the relaxation. From the real space point of view, slow relaxations are linked to extended dynamically correlated spatial regions [2], and stirring tends to break off these domains, thus making the system more fluid. It is thus no surprise that just about any system (and any model) will naturally exhibit shear thinning.

For shear thickening instead, several explanations have been attempted, and it is at present not clear whether a universal one will apply for all possible systems. There are indications that jamming in particulate suspensions is related to increased disorder [3], and in some cases to the formation of clusters of particles in lubrication contact [4,5]. To the extent that at large densities the strongly jammed state has the appearance of an amorphous, glassy solid, shear thickening may be thought of as a consequence of an underlying glass transition induced by stirring [6]. For such collective behavior one can attempt a theory with less focus on the details but founded on notions that are thought to be generic of glasses: this has suggested, for example, the casting of the problem in a mode-coupling format [6].

In this Letter we attempt a microscopic setting in which glassiness and shear thickening emerge naturally and are simultaneously understood. The basic idea is to exploit the analogy between entropy-driven transitions in which systems freeze upon heating and those in which they jam under the action of stirring. To obtain concrete results, we discuss this idea within the "random first-order" scenario for the glass transition, although it is not restricted to it. In its simplest version, the random first-order scenario applies to models of fully connected degrees of freedom and a complicated set of interactions with or without quenched disorder [7,8]. It allows for a unified description of the (fragile) glass transition, both from the dynamical and from phase-space landscape points of view. The approach contains as a special, high temperature case the mode-coupling theory [9], while in the low temperature regime it provides a theory for aging [8]. As is characteristic of this approach, it has the satisfactory feature that many different aspects of the collective behavior follow without further assumptions, and the weakness that spatial features are not (for the moment) fully incorporated.

Introducing stirring.—Shear thinning appears naturally if one considers the action of "stirring" terms capable of generating permanent currents, i.e., forces that do not derive from a (global, time-independent) potential. A useful, though approximate, way to see the effect of random stirring is the following: consider a system with coordinates x_i evolving according to some form of dynamics (Langevin, Monte Carlo, molecular dynamics) in contact with a heat bath at temperature T and under the action of a potential and of stirring forces $f_i^{\rm stir}$ acting on the ith degree of freedom. Stirring forces are by definition nonconservative; suppose (although this is inessential) they are linear: $f_i^{\rm stir} = J_{ij}^{\rm as} x_j$. If we make the simplifying though rather crude assumption that the $J_{ij}^{\rm as}$ are long range, randomly distributed (so $J_{ij}^{\rm as}$ is asymmetric), and uncorrelated, one can easily show [10,11] that on average $f_i^{\rm stir} = \rho_i(t)$ where $\rho_i(t)$ are Gaussian noises with correlations $\langle \rho_i(t)\rho_j(t')\rangle = \delta_{ij} C(t,t')$ where $C(t,t') = \sum_k \langle x_k(t) x_k(t')\rangle / N$ is the two-time autocorrelation function. The stirring thus provides a random noise unmatched by a friction term: this can be seen as a coupling to an infinite temperature (self-consistent) bath [12]. Just like in any stirring situation, if the system for some reason does not flow, the noise ρ_i becomes time independent and hence does no work.

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The generic situation when the (e.g., Monte Carlo) dynamics is perturbed by a nonconservative force is that the structural α-relaxation time becomes shorter—a shear-thinning effect—and that a two-temperature regime emerges [13] even in the supercooled liquid phase. This scenario has been tested in realistic systems [14] and the agreement is impressive. In contrast to the case of shear thinning, there has as yet been no way to introduce or understand shear thickening in these terms, and a phenomenological construction with a mode-coupling flavor has to be introduced in a somewhat *ad hoc* manner, with no underlying microscopic model [6].

A phase reentrance mechanism.—Let us review briefly a microscopic mechanism [15] for freezing induced by heating (inverse freezing). Suppose one has an ensemble of molecules (e.g., polymers) that have a low temperature ("folded") state in which they are mutually weakly interacting, and a higher temperature ("unfolded") state which is favored entropically and in which they interact strongly with each other. As temperature is increased, each polymer unfolds and reaches out to the other polymers; the resulting entangling thus may lead to a glass transition. A further increase of temperature will eventually lead back to a liquid phase.

In order to obtain a minimal model of a liquid that upon heating is driven by entropy into a glass, one can consider [15] spins taking values 0, ± 1, and a Hamiltonian consisting of a term $\propto \sum_i s_i^2$ favoring the folded configurations $s_i = 0$, and an interaction term $\sum_{ij} J_{ij} s_i s_j$ that is active when the spins are in the unfolded states $s_i = \pm 1$:

$$H = -2\sum_{ij} J_{ij} s_i s_j + D\sum_i s_i^2. \tag{1}$$

The entropic favoring of the $s_i = \pm 1$ configurations is enhanced by making these states r-fold degenerate. Schupper and Shnerb chose the interactions J_{ij} from a fully connected Gaussian distribution, thus obtaining a *spin-glass*-like phase [16]. If instead one wishes to model a *structural* (fragile) glass behavior, one may choose interactions as in either the random orthogonal model [17], or to consider a p-spin interaction model with spin 1 variables like in Ref. [18]. We have studied the equilibrium phase diagram of the former model in detail and found, for large enough r, a reentrant behavior in both the dynamic and static glass transition line. The structural glass transition in this model can be either thermodynamically first or second order (i.e., with or without latent heat), depending on the value of D [19].

Shear-thickening models.—As mentioned above, stirring is somewhat analogous (and in the example above exactly equivalent) to coupling to a high temperature bath. One can thus imagine that in a problem with phase reentrance, stirring might induce a transition from the liquid to the glassy phase. This is clear in the folded polymer problem described above: taking into account the known fact that shearing [20] or random stirring [21] can make polymers unfold to the interacting state, this may result in an increase in the viscosity of the polymer melt. Shear thickening is in such cases a form of phase reentrance [22].

What we have discussed so far suggests that one can model shear thickening by considering a nonconservative forcing acting on a reentrant model, for example, a force field $f_i^{\rm stir}$ acting on the ith spin of (1):

$$f_i^{\rm stir} = \varepsilon \sum_j J_{ij}^{\rm as}(1 - s_j^2) + \delta \sum_j K_{ij}^{\rm as} s_j, \tag{2}$$

where $J_{ij}^{\rm as} = -J_{ji}^{\rm as}$ and $K_{ij}^{\rm as} = -K_{ji}^{\rm as}$ are independent Gaussian random variables with zero mean and variance $1/N$. The two components of the force field act independently on the folded and the unfolded configurations with stirring strengths ε and δ, respectively [23].

Phase diagram—metastability and coexistence.—Figure 1 shows the evolution of the energy of a small system after stirring terms (2) were applied to the noninteracting "liquid" state. The fraction of ± 1 spin becomes appreciable and in the energy versus time plots we observe intermittent arrest and flow behavior with jumps between long-lived interacting states. If the temperature is low and stirring is not too strong, the system quickly falls in a state that is for all practical purposes stable. Increasing the stirring strength the trapping times become shorter, and for sufficiently high stirring rates the system becomes a normal (nonaging) liquid. We shall not discuss in detail the shear-thinning (or rejuvenation) aspect, as it has been already extensively discussed in the literature [13,14]. Intermittent situations where the system jams and unjams as in Fig. 1 have been observed [24].

The analysis of the temporal evolution of the energy and the spin-spin correlation function allows to identify different dynamical regimes and construct the dynamical phase diagram by varying the several parameters characterizing the system. Figure 2 shows a section of such a dynamical phase diagram in terms of D and stirring strength ε. The weakly stirred liquid phase I has a low density of interactive sites $\rho \simeq 0$. The "jammed" phase II is characterized

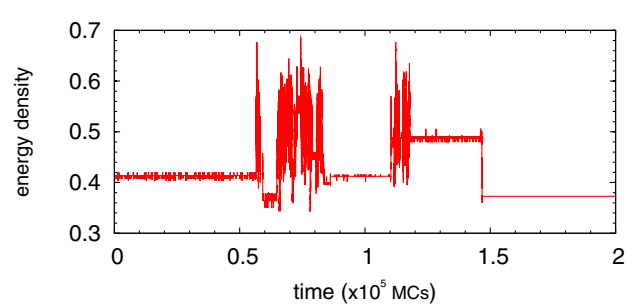

FIG. 1 (color online). Energy density vs time after a system (size $N = 128$) in the liquid phase at $T = 0.03$ and $D = 3.0$ was taken to the jammed phase by a stirring force with $\varepsilon = 1.6$ and $\delta = 0.2$.

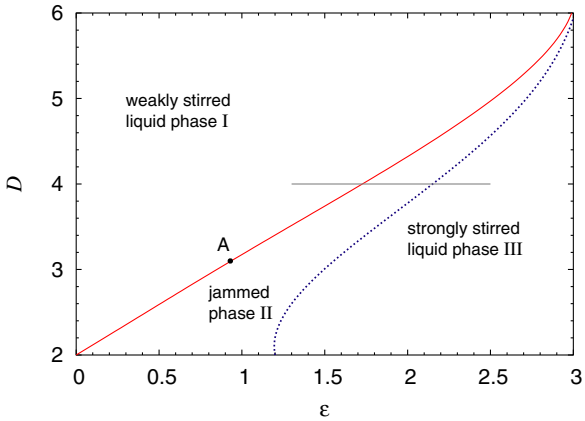

FIG. 2 (color online). A section of the dynamical phase diagram for temperature $T = 0.05$, $\delta = 0.0$, and $r = 6$. The transition between the phases I and II is first order below the point A and second order above it.

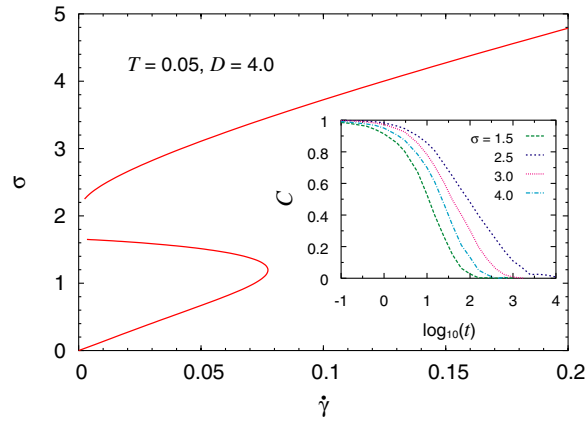

FIG. 3 (color online). Flow curve along the constant $D = 4$ line for $T = 0.05$. $\sigma \equiv \varepsilon$ and $\dot{\gamma} \equiv \sigma/\tau_\alpha$ are the analogue of stress and shear rate for a mean-field system. Note how the intersection of the line $D = 4$ with the jammed phase in Fig. 2 is reflected here. The inset shows the corresponding spin-spin correlation function, C, vs time t, for increasing stress (system size $N = 500$).

by a fraction of spins in the interactive ± 1 state and aging (i.e., the progressive trapping in ever deeper interacting states), and the liquid III regime for high stirring rates is just the result of shear thinning of the jammed state. For $D < 2$ and low temperature the system is glassy in the absence of stirring. On increasing D and the stirring force there is "first-order" jamming transition (below the point A in Fig. 2) with hysteresis in ε: along this curve the liquid and jammed phases coexist. Above the point A the transition from phase I to phase II is a "second-order" jamming transition without hysteresis, but with a regime in which the system forms under stress an aging glass. For much larger values of D there is no jamming for any stirring, but there is continuous shear thickening when the $T - \varepsilon$ trajectory followed passes near a transition line in phase space.

In these mean-field models the dissipated power scales as $\varepsilon^2/\tau_\alpha$, where τ_α is the α-relaxation time of the system [13]. Comparing to a standard shear flow this suggests that the amplitude of the driving force, ε, plays the role of a stress, σ, while ε/τ_α is analogous to a shear rate, $\dot{\gamma}$. We may thus obtain the standard σ versus $\dot{\gamma}$ flow curves by increasing the stirring rate at constant D: they turn out to be strikingly similar to those of Ref. [6]. In the main frame of Fig. 3 we show an example of such flow curves corresponding to the "full jamming" scenario of Ref. [25]. In this case, one observes an interval of stress, in Fig. 3 between 1.65 and 2.2, within which the flow rate vanishes, even if the system is ergodic at rest. The relaxation time, τ_α, was estimated as the time integral of the normalized spin-spin correlation function. Examples of correlation curves are shown in the inset of Fig. 3: shear-thickening behavior (a slower decay of C) is observed when σ increases from 1.5 to 2.5, while shear thinning (a faster decay of C) appears for higher stress (for σ increasing from 2.5 to 4 in the inset of Fig. 3).

In Ref. [26], an experiment is described in which a concentrated suspension of non-Brownian particles is driven by stirring from the liquid to a metastable jammed phase. It would be interesting to see experimentally whether the opposite situation, when the liquid is the metastable phase, may occur.

Chain fragility and aging of the jammed phase.—One of the properties of materials that are jammed by stirring that we may wish to test in this model is the fragility with respect to incremental stresses in a different direction [27]. If in a system in phase II we change the realization of stirring forces from $J_{ij}^{\rm as}$ to $J_{ij}^{\rm as}\cos\theta + J_{ij}^{\prime\rm as}\sin\theta$, and similarly for $K_{ij}^{\rm as}$, even for small θ we find that the system responds by rearranging its configuration, the faster the larger the value of $\theta(\theta \in [0, \pi/2])$, see Fig. 4.

Conclusions.—In this Letter we discussed a connection between the mechanisms of entropy-driven phase reentrance and shear thickening. This relation may exist in some cases just in principle, as the temperatures or chemical potentials needed to actually affect substantially the particles may be in practical situations extremely high. The present models are clearly schematic, but not much has been put into them and yet we see the elementary constituents self-organize to produce stirring-induced jamming with aging and intermittency, non-Newtonian rheological behavior like shear thinning and thickening, metastability, and chain fragility.

Let us finally mention that one can also construct a reentrant continuous model with p-spin interactions H_p following the same idea outlined above [28]. From this model one can immediately obtain mode coupling with reentrance—and also shear thickening by adding stirring forces of the form (2) to the Langevin dynamics $\dot{x}_i = -\partial_{x_i} H_p + \eta_i$. Another interesting approach is to introduce

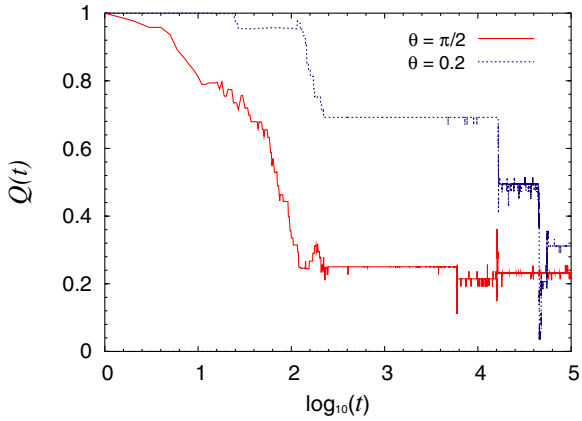

FIG. 4 (color online). Chain fragility: mutual correlation, $Q(t)$, of two identical jammed systems, in one of which the stirring direction has been changed at time $t = 0$. $\theta = \pi/2$ corresponds to the case in which the two systems have independent random stirring forces, while in the case $\theta = 0.2$ the random stirring forces are correlated.

stirring terms in the mode-coupling models of colloids with short-range attractive potentials [29]. This would allow to investigate the intriguing perspective that stirring can drive the liquid-liquid, the liquid-glass, and also the glass-glass transition in such systems. Work along these lines is in progress [28].

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