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Physical age of soft-jammed systems

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We study experimentally the liquid-solid transition in a soft-jammed system and focus on its aging in the solid regime. We investigate the impact of temperature, density, and load changes on the material behavior. We show that all elastic modulus versus time curves fall on a single master curve when rescaled by an appropriate factor function of the density, the temperature, the load, and the time elapsed since preshear. This allows us to distinguish the effect of temperature and density on the mechanical properties and their effect on aging. Since the time evolutions of the elastic modulus under various conditions are similar within a factor, we suggest that the rescaled time reflects the *physical age* of the material; i.e., it describes the degree of progress of the structural organization relative to a state of reference of the system in the solid regime and constitutes a means for characterizing the effective state of such systems.

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I. INTRODUCTION

Various systems such as foams, emulsions, or colloidal suspensions exhibit a transition from a liquid state (they flow) to a solid state (they are jammed) when submitted to an insufficient stress (i.e., below the yield stress). This ability to undergo a liquid-solid transition has found a wide range of applications in industry and has aroused the interest of physicists as it appears typical of a fourth state of matter with some analogy with glass behavior. The generality of the jamming transition led to the proposal of a unifying description based on a jamming phase diagram in temperature, density, and stress coordinates with a critical surface limiting the solid and liquid states [1,2]. Moreover, in the solid state, soft-jammed systems (or pastes) form an out-of-equilibrium system with a structure continuously evolving in time; they are said to age. It was shown [3] that, when the stress is lowered below the yield stress, this aging bears some analogy with that observed in glasses or amorphous polymers when the temperature is lowered below the glass transition temperature [4]. Aging is also at the origin of the apparent gelification of various systems at rest, which results in an increase of mechanical strength [5–7] with the time of rest, another feature of practical importance. Although it was shown that jamming and aging are intimately linked properties [8], there is still lacking a clear view of this link and of its interplay with the different variables of the systems; in particular, it is of fundamental interest to see if the apparent equivalence of temperature, density, and stress in driving the liquid-solid transition holds for driving the out-of-equilibrium dynamics in the solid state. In other words, is there any link between the jammed (solid) states attained by different routes to jamming in the phase diagram? Or more precisely, how do the solid-state properties depend on temperature, density, and stress?

In order to address these questions we study experimentally the influence of aging on the viscoelastic properties of various soft-jammed systems after a flow (preshear) at a high velocity (equivalent to a quench for glasses) and focus on the impact of temperature, density, and load changes on the materials behavior. We first show that the liquid-solid transition occurs after a certain time which can be properly identified from the evolution of material characteristics. Then we show that the G' vs t_w curves for different temperatures, solid fractions, and shear stresses fall on a single master curve when rescaled by appropriate factors. This allows us to distinguish the effect of temperature and density on the mechanical properties and their effect on aging. This also suggests that a *physical age*, describing the degree of progress of the structural organization relative to a state of reference, can be defined as a function of the density, the temperature, the load, and the time elapsed since preshear.

II. MATERIAL AND PROCEDURES

Here we focus on reversible aging—i.e., variations of the internal state which can be reversed by a strong agitation of the material (rejuvenation). Such effects induce variations of the material viscosity, which are referred to as thixotropy in mechanics. We used a typical thixotropic material—i.e., a Na-bentonite suspension. Bentonite is a naturally swelling clay with slightly flexible, large-aspect-ratio particles inside which water tends to penetrates [9], but which can somewhat aggregate via edge-to-face links, so that the suspension may be seen as a colloidal gel [7]. In this context the aging at rest may take its origin in a progress of either the swelling or aggregation process or an evolution of the particle configuration. Each sample was prepared by a strong mixing of the solid phase with water, then left at rest for 3 months before any test, which avoids further irreversible (chemical) aging over the duration of the experiments.

The reproducibility and relevance of long-duration, rheological tests with such jammed systems is challenging because various perturbating effects can occur such as wall slip, drying, edge effects, phase separation, etc. [10]. In order to avoid these problems we used a controlled-stress Bohlin C-VOR200 rheometer equipped with a thin-gap Couette geometry (inner radius $r_1 = 17.5$ mm, outer cylinder radius $r_2 = 18.5$ mm; height $h = 45$ mm) with rough surfaces (roughness 0.1 mm). The geometry was topped with a lid which left a very small path towards ambient air and thus strongly limited drying. We checked the absence of drying effects from the reproducibility of successive similar tests.

A straightforward measurement of the mechanical properties of solid-liquid systems consists in determining their storage (G') and loss (G'') moduli (see below) in the solid regime. Here we follow such characteristics of different materials for different solid-volume fractions (ϕ), temperatures (T), and loads (i.e., the stationary applied stress σ) as a function of the time of rest (t_w). The value of the elastic modulus and its time variations are expected to reflect both some basic strength of the network of interactions between the soft elements (say, in complete disorder) and the evolution of this structure in time as a result of rearrangements leading to material aging.

In order to identify properly the liquid-solid transition we used a powerful technique which consists in applying a constant stress in order to induce a macroscopic flow and superimposing small oscillations in order to probe the actual material strength. A comparison of the time evolutions of the apparent flow resistance and the response to oscillations allows us to identify the liquid and solid states (see below). After its preparation each sample was set up in the geometry and presheared at a large apparent shear rate ($\dot{\gamma}_p = 200\ \mathrm{s}^{-1}$) and under a given temperature (T) during a sufficient time for temperature stabilization. Then the material was submitted to a shear stress including a constant component and an oscillating component: $\sigma + \sigma_0 \sin 2\pi F t$, in which $F = 1$ Hz and $\sigma < \sigma_c$ (σ_c, the material yield stress, will be defined below). σ_0 is chosen so as to ensure that we test the materials in their linear regime: the resulting deformation is well represented as $\gamma(t) + \gamma_0 \sin(2\pi F t + \varphi)$ and γ_0 is smaller than 0.1%. The storage and loss moduli are then computed from $G'(t) = \tau_0 \cos \varphi / \gamma_0$ and $G''(t) = \tau_0 \sin \varphi / \gamma_0$. With this procedure relevant values for G' and G'' can be determined only when the characteristic time of the oscillations ($1/F = 1$ s) is smaller than the characteristic time for significant changes of material properties. The latter was generally much larger than 1 s except during about 5 s (10 s for $\phi = 3\%$) after the liquid-solid transition. Note that such oscillations do not affect the mechanical properties of the material as shown from the very good correspondence between $G'(t_w)$ and the elastic modulus estimated from creep tests after the same time (t_w) at rest without oscillations [7]. From such tests we get both information on the apparent structure [via the apparent viscosity (i.e., $\eta = \sigma / \dot{\gamma}$, in which $\dot{\gamma} = d\gamma / dt$)] and information on the actual structure [via $G'(t)$ and $G''(t)$]. If the material is in a liquid state, we expect the evolutions of G'' and η with time to be similar; if the material is in its solid state, these evolutions are not necessarily similar but the response to oscillations should be mainly elastic.

III. RESULTS AND DISCUSSION

A. Liquid-solid transition

For a typical test as described above in a first stage the material undergoes a large deformation: it flows, and the flow is continuously decelerating. During this stage, G'' is larger than G' and increases in time, and G'' is proportional to η times $2\pi F$ (see Fig. 1); this indicates that the material is in a liquid state (although not simply Newtonian), as pointed out in Sec. II. Afterwards, G'' reaches a peak and starts to decrease (see Fig. 1), while η tends to infinity around the peak, indicating that the material stops flowing. In parallel the materials develops some elasticity: G' abruptly increases and crosses over the G'' curve at the peak. This indicates that the material is now in a solid state. This transition from the liquid to the solid regime also corresponds to the beginning of a plateau of deformation (see inset of Fig. 1).

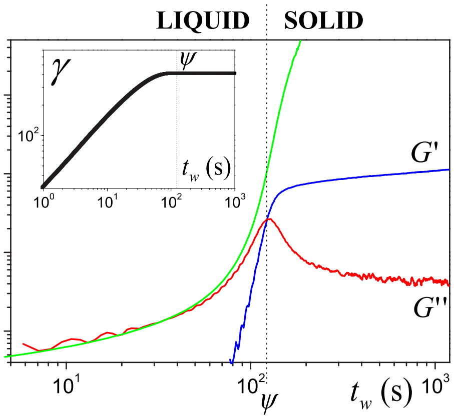

FIG. 1. (Color online) Storage and loss moduli of a bentonite suspension ($\phi = 5\%$) as a function of the time t_w after preshear for $\sigma / \sigma_c = 87\%$. The third solid (green) line is the apparent viscosity divided by a factor 3.5. ψ is the critical time for the liquid-solid transition, and the dotted line defines the boundary between the liquid and solid regimes. The inset shows the deformation as a function of time.

Finally, these observations allow us to identify precisely and unambiguously the liquid and solid regimes of the material, which are thus associated with the regions, respectively, before and after the G'' peak and G'-G'' crossover. A percolation phenomenon well explains this effect: the initial G'' increase results from the progressive formation of solid aggregates in the fluid; when they reach a critical concentration, the aggregates form a continuous, solid network; this structure is reinforced in time (resulting in a sharp increase of G') as the material goes on aging while G'', which is now related to the viscous behavior of this structure, decreases.

The transition occurs after a time ψ, increasing with σ, and which tends to infinity when $\sigma \to \sigma_c$ (see Fig. 10, below); i.e., the material remains indefinitely in a liquid state for $\sigma > \sigma_c$. This technique thus provides a precise means for observing the liquid-solid transition and for defining the yield stress σ_c of such pastes. Experiments at different temperatures T and concentrations ϕ show that σ_c depends on T and ϕ, but remarkably, the transition time ψ solely depends on the ratio σ / σ_c.

The age of the material in its solid state is thus $t_w - \psi(\sigma / \sigma_c)$. The curves $G'(t_w - \psi(\sigma / \sigma_c))$ then describe the effect of aging on the structure strength. These curves are simply similar by a factor $J_0(\sigma)$ (see Fig. 2), which means that the applied stress (σ) strengthens the material [by a factor $J_0(\sigma)$] and delays the liquid-solid transition [of a time $\psi(\sigma / \sigma_c)$], but does not affect the dynamics of the aging process in the solid regime since, whatever the stress value, the

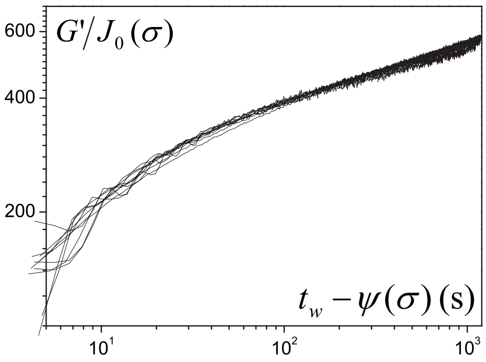

FIG. 2. $G'(t_w-\psi)/J_0$ curves (in the solid state) for the bentonite suspension ($\phi=5\%$) for $t_w>\psi$ [see values of $\psi(\sigma)$ and J_0 in Figs. 10 and 11].

relative evolution of the elastic modulus is solely a function of the absolute time spent in the solid state only; it would thus simply change the state of reference of this aging (see below). Note that we will not study here the influence of the oscillation frequency and its possible interplay with aging in the solid regime.

B. Effect of the temperature

Let us now examine the effects of temperature on the aging curves [i.e., the elastic modulus as a function of the age in the solid state, $G'(t_w-\psi(\sigma/\sigma_c))$] for a constant σ/σ_c. Typical results are presented in Fig. 3. The main apparent change is the increase of the elastic modulus with temperature, which is likely due to the dependence of particle interactions with T. In this context we can expect some superposition of the curves along a single curve by scaling G' by a factor $H_0^*(T)$. As an example we used a scaling factor such as to get a crossover of the curves at $t_w=30$ s and we see in Fig. 4 that the curves do not superimpose. This is so because not only the level but the shape of the G' vs t_w changes with T. In particular the extent of the range of variation of G' over a given range of t_w decreases when T decreases. This is somewhat expected since aging results from exploration of the energy landscape: as this exploration is driven by thermally activated processes, aging should then be faster when the temperature is larger. We can thus suggest that as the temperature is decreased, the dynamics is slowed down, say, by a simple scaling factor of time, $\theta(T)$, while there is in parallel a variation of the elastic modulus of the initial structure, which leads to the introduction of a scaling factor of G', $H_0(T)$. Remarkably such a scaling effectively makes it possible to get a single master curve (see Fig. 5). To sum up, $H_0(T)$ represents the strengthening of the material by a change in temperature, while $\theta(T)$ is a characteristic time of structuration at a given temperature. Even if at this stage we cannot provide straightforward physical explanations (see Sec. III D for a sketch) of the variations of the scaling factors with T, as far as we know, this result provides the first (phenomenological) quantification of the effect of temperature on aging dynamics in pastes.

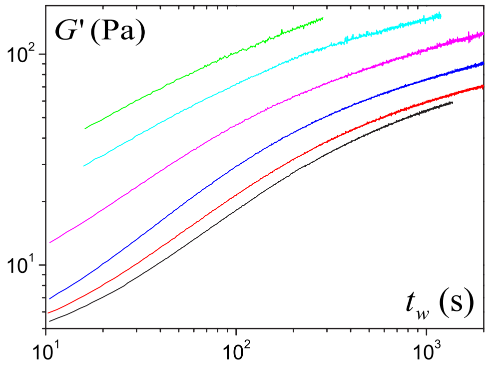

FIG. 3. (Color online) Elastic modulus as a function of time for a bentonite suspension ($\phi=3\%$, $\sigma=0$) at different temperatures: (from bottom to top) 5 °C (black), 25 °C (red), 40 °C (dark blue), 55 °C (magenta), 70 °C (light blue), and 80 °C (green). Qualitatively similar results were obtained for the bentonite suspension for other ϕ and σ.

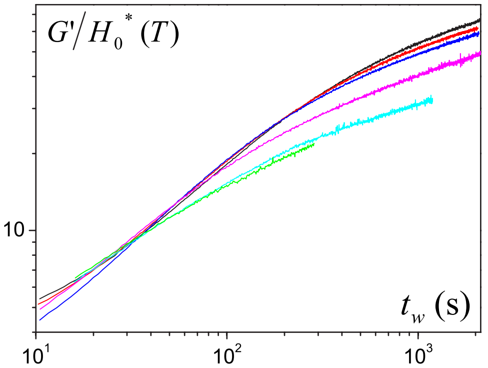

FIG. 4. (Color online) Elastic modulus as a function of time (data of Fig. 3 with the same colors) scaled by a factor $H_0^*(T)$ so as to have a crossover of the curves for $t_w=30$ s.

C. Effect of the solid fraction

Since for the liquid-solid transition of jammed systems an equivalence of the effects of temperature and density was suggested [1], it is interesting to see whether such an equivalence holds for the aging dynamics. More precisely, with

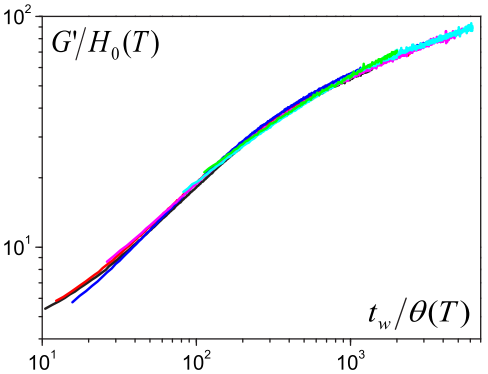

FIG. 5. (Color online) Elastic modulus as a function of time (data of Fig. 3 with the same colors) scaling G' by $H_0(T)$ and t_w by $\theta(T)$ (see the values of these parameters in Figs. 10 and 11).

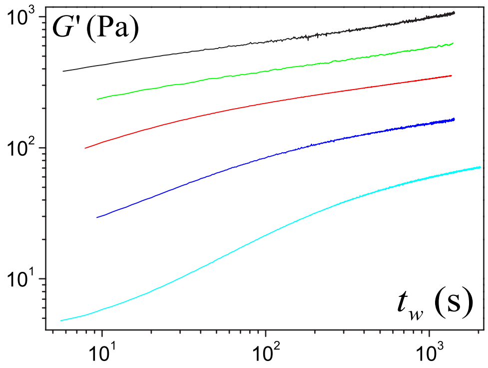

FIG. 6. (Color online) Elastic modulus as a function of time for the bentonite suspension at different solid fractions: (from bottom to top) 3% (light blue), 4% (dark blue), 5% (red), 6% (green), and 7% (black).

regards to the above results for temperature, we could expect some slowing down or acceleration of the structure rearrangement relatively to a structure of reference, for different solid fractions ϕ. Effectively the G' vs t_w curves for different ϕ (for the bentonite suspension) look similar (see Fig. 6) with a dependence in time which depends on the concentration. As a consequence, as for the temperature there is no superimposition of the curves along a single curve when just scaling G' by a factor $I_0^*(\phi)$ (see Fig. 7) in order to get a crossover of the curves at $t_w = 30$ s. A master curve is nevertheless obtained (see Fig. 8) when both G' is scaled by a factor $I_0(\phi)$ and t_w by a characteristic time $\alpha(\phi)$. The factor α decreases with ϕ (see Fig. 8), which means that aging is accelerated by an increase of ϕ; it may be explained by the fact that for a larger ϕ the electrostatic forces are larger so that the particles are more rapidly pulled towards local, provisional, equilibrium positions. Here the factor I_0 accounts for the dependence of particle interactions with the distance (which decreases with the solid fraction). It is worth emphasizing that with the aim of characterizing the variations of particle interactions with the solid fraction we here have a parameter (I_0) which is more relevant than that of most previous works which simply used the elastic modulus or the apparent yield stress after a given flow history (see Sec. IV).

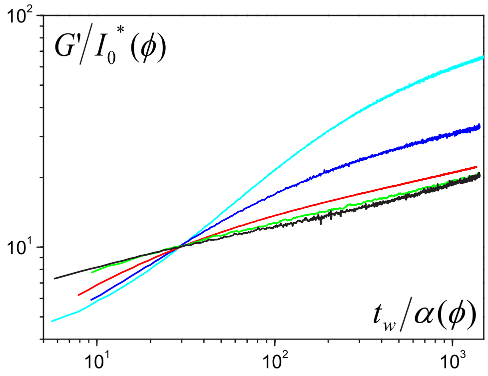

FIG. 7. (Color online) Elastic modulus as a function of time (data of Fig. 6 with the same colors) scaled by a factor $I_0^*(\phi)$ so as to have a crossover of the curves for $t_w = 30$ s.

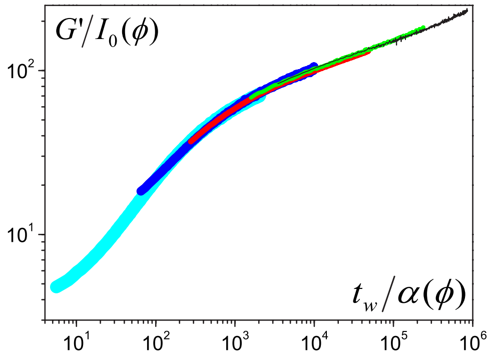

FIG. 8. (Color online) Elastic modulus as a function of time (data of Fig. 6 with the same colors) scaling G' by $I_0(\phi)$ and t_w by $\alpha(\phi)$ (see the values of these parameters in Figs. 10 and 11).

D. General master curve

It is worth noting that the impact of one of the variables (T, ϕ, σ) is independent of the other variables; i.e., θ does not depend on ϕ and σ, α does not depend on T and σ, and ψ does not depend on T and ϕ. In other words, for example, the effect of a density increase on the aging dynamics is the same whatever the temperature and the stress. As a consequence a single master curve (see Fig. 9) can be obtained for all the data by plotting G' scaled by $H_0(T)I_0(\phi)J_0(\sigma)$ as a function of $t_w - \psi(\sigma/\sigma_c)$ scaled by $\theta(T)\alpha(\phi)$. We emphasize that this result is not fortuitous as we cannot expect to find such a full consistency of a set of curves over two-decade ranges and obtained under different conditions except if these curves effectively reflect a physical consistency.

As a consequence G' may be written as $G' = G_0 f(x)$, in which $G_0 = H_0 I_0 J_0$, $x = (t_w - \psi)/\theta\alpha$, and f is a function independent of T, ϕ, and σ (the values of α, θ, and ϕ are shown in Fig. 10). Remarkably this shows that the value of the elastic modulus is a function of two independent factors: one solely depending on T, ϕ, and σ; the other depending on a single variable involving, among others, t_w. Thus G_0 is the elastic modulus of some state of reference of the material,

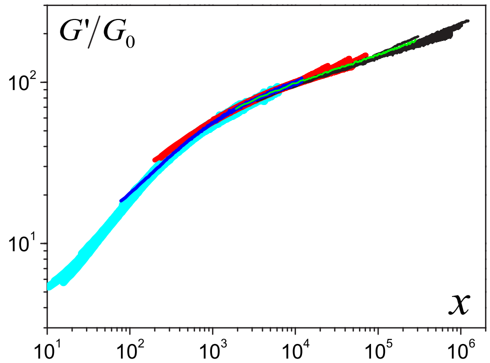

FIG. 9. (Color online) Master curve of the elastic modulus scaled by the factor G_0 as a function of the physical age x for the bentonite suspension at different solid fractions (in the range 3–7 %), temperatures (in the range 5–80 °C) and applied shear stresses (below σ_c). For the sake of clarity solid lines of different colors and thicknesses were drawn for the different solid fractions (light blue, 3%; dark blue, 4%; red, 5%; green, 6%; black, 7%).

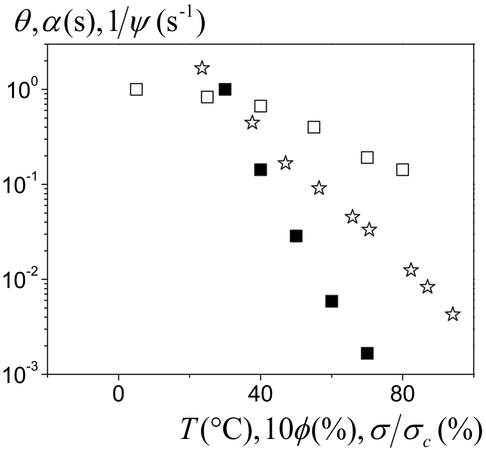

FIG. 10. Time factors—i.e., $\theta(T)$ (open squares), $\alpha(\phi)$ (solid squares), and $\psi(\sigma/\sigma_c)$ (stars) for the bentonite suspension.

while $f(x)$ is a characteristic of its actual aging state relative to this state of reference. In this context we can refer to x as the *physical age* of the material: namely, the degree of advancement of physical aging relative to the state of reference. The physical age—i.e., the time elapsed in the solid regime and written in a temperature- and volume-fraction-dependent time unit—is the time which is relevant for effectively describing the structuration. This equivalence of the effect of time of rest, concentration, temperature, and stress on the physical age of the material explains, for example, the evolution of the microscopic aging observed from dynamic light scattering as t_w or ϕ increases [11].

The values of the parameters H_0, I_0, and J_0 are presented in Fig. 11. Their variations are consistent with some basic physical analysis. H_0 increases with ϕ and I_0 increases with T as expected from the fact that the structure strength increases with the number of particle interactions per unit volume (related to ϕ) and their strength which, according to the usual double-layer theory [12], increases with the Debye length (which is proportional to $\sqrt{T}$). The proportionality of I_0 with ϕ^2 is consistent with a fractal approach of the elastic modulus of colloidal gels [6,13].

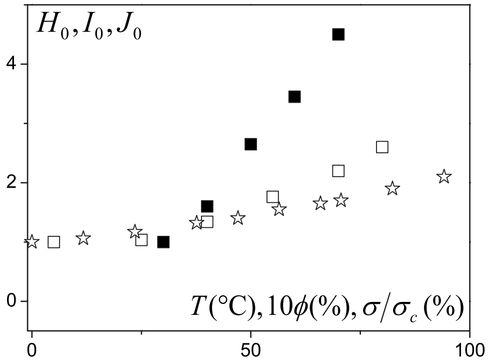

FIG. 11. Strength factors—i.e., $H_0(T)$ (open squares), $I_0(\phi)$ (solid squares), and $J_0(\sigma)$ (stars) for the bentonite suspension.

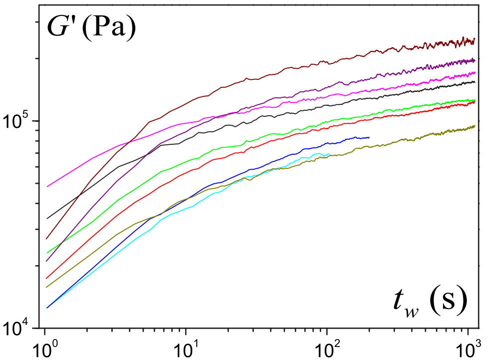

FIG. 12. (Color online) Elastic modulus as a function of time for the Ti-O_2 suspensions ($\sigma=0$) for different temperatures (at $\phi=26.5\%$) and different solid fractions (at $T=25$ °C): (from bottom to top) 23% (dark yellow), 5 °C (light blue), 10 °C (dark blue), 25 °C (red), 40 °C (green), 55 °C (black), 65 °C (magenta), 33.6% (purple), and 29.8% (wine).

In order to test the generality of the validity of this result we carried out similar tests with two other materials: a Ti-O_2 suspension and a mustard. The Ti-O_2 suspensions were prepared with Ti-O_2 particles (Tronox CR-826 from Kerr-McGee Chemical LLC) of 0.2 μm average diameter. The particles were suspended at various concentrations ranging from 23% to 33.6% in a 0.01*M* KCl aqueous solution. The suspension was stirred during 1 h and its *p*H was adjusted to 7. The mustard (*Maille*, France) is a mixture of water, vinegar, mustard seeds particles, mustard oil, and various acids. We may see it as a suspension in an oil-in-water emulsion with a large concentration of elements (droplets and particles). The temperature could be varied for both materials (see the results in Figs. 12 and 14) and for the Ti-O_2 suspension it was also possible to vary the concentration (see Fig. 12). We see that it is again possible to scale all the data along a master curve when using appropriate factors (see Figs. 13 and 14).

IV. DISCUSSION AND CONCLUSION

The present observations have several implications. Previous works discussed the evolution of the strength of a ma-

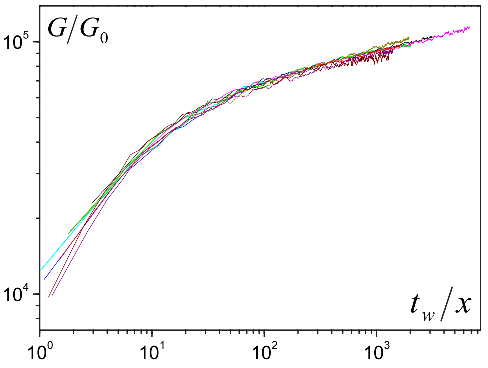

FIG. 13. (Color online) G' scaled by G_0 and t_w by x for the data of Fig. 12 (with the same colors), in which $\theta=1, 0.95, 0.68, 0.56, 0.36, 0.17$ and $H_0=1, 1.1, 1.23, 1.3, 1.48, 1.5$, respectively, for increasing temperatures and $\alpha=0.57, 0.68, 0.8, 0.86$ and $I_0=0.91, 1.27, 2.14, 2.77$ for increasing solid fractions.

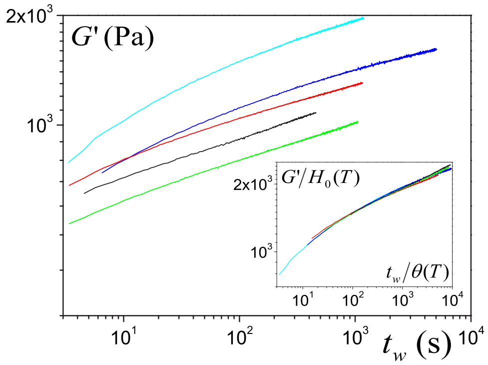

FIG. 14. (Color online) Elastic modulus as a function of time for the mustard ($\sigma=0$) for different temperatures: (from to bottom) 5 °C (light blue), 25 °C (dark blue), 40 °C (red), 70 °C (black), and 55 °C (green). The insets show the same data scaling G' by $H_0(T)$ and t_w by $\theta(T)$, where $\theta=1,1.9,4.5,8,20$ and $H_0=1,0.69,0.6,0.43,0.45$, respectively, for this series of increasing temperatures.

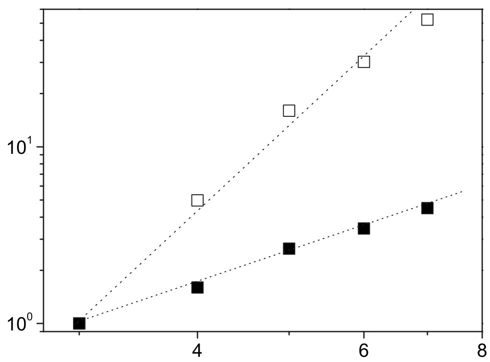

FIG. 15. Values of I_0 (solid squares) and I_0^* (open squares) for the bentonite suspension as a function of the solid fraction.

terial (elastic modulus or yield stress), measured after a given time of rest, as a function of ϕ or T, but our results show that such data cannot be consistently compared for a significantly aging material. Here we provide a relevant way (via time scaling) for estimating an absolute strength (G_0) of a jammed material in its solid regime as a function of temperature and density independently of its physical age (which does not solely depend on t_w). In this context G_0 corresponds to the elastic modulus of the material when its elements are put in complete disorder in a given volume—i.e., before any of their mutual interactions had time to affect their configuration. More precisely this is the elastic modulus of the material in its most "destructured" state. Most previous works in the literature concerning flocculated suspensions or colloidal gels studied the variations of the elastic modulus with the solid fraction by using the value measured at a given time following a given procedure [14–17]. Here we demonstrate that as soon as the solid fraction, the temperature, or the load is varied, a relevant study of the effect of one specific parameter requires a comparison of the data at the same physical age. For example, the evolution of I_0^* at a given time, following the usual method, can strongly differ from the evolution of the relevant parameter for describing the variation of the effect of solid fraction on the elastic modulus: namely, I_0 (see Fig. 15).

Our results with other soft-jammed systems of very different internal structures (mustard, Ti-O$_2$ suspension) suggest that the conclusions of this paper for a bentonite suspension are applicable to other soft-jammed systems. As a consequence our approach provides a parameter—i.e., the physical age—which might constitute a general means of characterization of the effective state of a soft-jammed system in physics and mechanics. For example, as the physical age of a material not only involves t_w but also ϕ and T and σ, this would open the way to a precise control of the mechanical evolution of the material at least in the solid state, which is useful for the preparation of industrial materials with specific properties (foodstuffs, drilling fluids, cosmetics, concrete, etc.). For example, isostates in the solid regime of our material are associated with constant-physical-age surfaces in a $(T,\phi,t_w\text{-}\psi(\sigma/\sigma_c))$ diagram. Usually the mechanical effects of aging (i.e., thixotropy) are modeled with the help of a purely phenomenological structure parameter [10]. Our results suggest that more physically based rheological models can be develop with x as structure parameter.

Our experiments finally provide a quantitative description of the state of the material in a four-dimensional phase diagram (T,ϕ,σ,t_w) when the initial time is taken at the end of preshear (quench). The liquid-solid transition corresponds to a physical age equal to zero [i.e., $t_w=\psi(\sigma/\sigma_c)$] and, since $\sigma_c=\sigma_c(T,\phi)$, this effectively defines a surface in a (T,ϕ,σ) diagram as predicted by Liu and Nagel [1] and modified by Trappe *et al.* [2]. However, now the critical surface for the liquid-solid transition is a function not only of T, ϕ, and σ, but also on t_w. Finally this allows us to find the temperature $T_{eq}(\phi)$ to which the density is equivalent in driving the out-of-equilibrium dynamics of soft-jammed systems: we have indeed shown that increasing the density may have the same effect on the physical age as increasing the temperature.

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