

## Glassy Dynamics and Flow Properties of Soft Colloidal Pastes

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The local dynamics and the nonlinear rheology of soft colloidal pastes are shown to exhibit a remarkable universal behavior in terms of a unique microscopic time scale. This variable is associated with structural relaxation under the combined action of local frictional forces and elastic driving forces. These results establish a link between the local dynamics of pastes and their nonlinear flow behavior and provide a unified description of paste rheology.

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Many concentrated materials consist of soft particles which are closely packed into an amorphous state. At high concentration, steric constraints are so important that the motion of individual particles is drastically reduced unless a finite external force is applied. A striking consequence is that soft concentrated materials behave like weak elastic solids at low stresses  $\sigma$  whereas they flow like viscous liquids above the so-called yield stress  $\sigma_y$ . Yielding properties dominate the behavior of materials as different as emulsions [1], pastes [2], biological tissues [3], and geological fluids [4]. They also play an essential role in many modern engineering processes such as ceramic extrusion, ink technology, and high-solid coating. Experimentally, the existence of a yield stress is often associated with peculiar flow properties which are well described by equations such as the Herschel-Bulkley equation [5]:  $\sigma = \sigma_y + a\dot{\gamma}^n$ ,  $\sigma_y$  and  $a$  are phenomenological parameters and  $\dot{\gamma}$  is the shear rate,  $\sigma_y$  and  $a$  are very sensitive to the experimental conditions making it difficult to achieve a precise control over the rheology. In that respect, it is crucial to relate the macroscopic behavior of concentrated dispersions to the experimentally accessible parameters through microscopic models.

Recently, it has been argued that the common rheological properties shared by concentrated dispersions might simply reflect the presence in such materials of glassy dynamics [6,7]. Glassy behavior in pastes is associated to structural relaxation of elements which are locally trapped by their neighbors and have to overcome energy barriers before rearranging. This cannot be done by thermal motion alone but by some internal noise, or effective temperature, due to mutual interactions between sheared elements. At sufficiently low stresses, elements are trapped in a metastable and disordered state. At high stress, elements can cross local energy barriers leading to macroscopic flow. These models capture important rheological features currently observed in experiments. In particular, the nonlinear behavior they predict closely matches the Herschel-Bulkley equation. However, a significant challenge that remains is to elucidate the underlying parameters that effectively control the flow

properties and the very nature of the physical mechanisms at work.

In this Letter, we establish a link between the structure and the dynamics of pastes at the microscopic level and their rheological properties. The pastes are made of soft colloidal particles. We probe the local dynamics by diffusive-wave spectroscopy (DWS). At short time, the particles undergo subdiffusive motion in the cages formed by their neighbors. At long times, they are trapped. The crossover between the two regimes occurs at a characteristic time  $\tau_\beta$ . We measure  $\tau_\beta$  for different pastes varying the concentration and the physicochemical parameters to a large extent. We show that  $\tau_\beta$  scales as  $\eta_s/G_0$  where  $\eta_s$  is the solvent viscosity and  $G_0$  is the storage modulus of the paste. We propose a simple model that accounts for this scaling by considering that local relaxation motion results from the competition between elastic restoring forces and viscous friction between the particles. Physically,  $\tau_\beta$  represents the shortest relaxation time and sets the duration of a rearrangement. A spectacular consequence is that the nonlinear flow properties  $\sigma(\dot{\gamma})$  measured for different pastes can be rescaled onto a universal master curve when the stress is scaled by the yield stress  $\sigma_y$  and the shear rate is scaled by  $\tau_\beta$ . These results offer a universal description of paste rheology in terms of microscopic parameters that can be easily tuned to get the desired behavior.

The pastes studied here consist of polyelectrolyte microgels made of cross-linked acrylate chains bearing methacrylic acid units. When the acidic units are ionized, the microgels swell. The degree of swelling depends on the microscopic structure of microgels through several physicochemical parameters such as the cross-link density, the number of ionized units, and the ionic strength [8]. It is convenient to quantify the cross-link density by the average number of monomeric units between two cross-links,  $N_x$ . Two batches of microgels with  $N_x = 28$  and  $N_x = 140$  are studied below. The solvent is pure water or a water/glycerol mixture. In dilute suspensions, microgel particles are spherical micronetworks with hydrodynamic radius  $R$  ( $R = 220$  nm for  $N_x = 140$  and

$R = 125$  nm for  $N_x = 28$ ). Near the overlap concentration  $C_m$ , suspensions begin to exhibit solidlike properties ( $C_m = 0.0085$  g/g for  $N_x = 140$  and  $C_m = 0.038$  g/g for  $N_x = 28$ ). It is possible to concentrate microgels much further and to get pastes because individual particles are deformable and able to de-swell. In pastes, microgels adapt their volume and shape to steric constraints by developing flat facets at contact. They are surrounded by thin films of water which lubricate the contacts between the facets. Since the cross-link density is large, there are no entanglements between the microgels.

We have studied the local dynamics of pastes by DWS [9]. Pastes are seeded with small polystyrene tracers which strongly scatter light. The diameter of the tracers is 168 nm and their volume fraction is  $5 \times 10^{-3}$ . We have carefully checked that they do not alter the rheological properties of the pastes. The pastes are kept at rest during at least 48 h before any measurement to ensure that the local stresses created during the cell loading have relaxed [2]. The transport mean free paths for the samples studied in these experiments ( $l^* = 0.39$  mm and  $l^* = 0.60$  mm) are much smaller than the cell thickness ( $L = 10$  mm), ensuring strong multiple scattering. Samples are illuminated uniformly by a 1-cm-diameter laser beam. A mono-mode optic fiber with low acceptance angle collects the light emerging from a speckle on the opposite side of the sample and sends it to an EMI photomultiplier. A Brookhaven BI9000 correlator calculates time-averaged intensity correlation functions (ICF). A time-averaged ICF depends on the speckle that is analyzed: pastes are nonergodic. To get ensemble-averaged ICF, we have extended to DWS a method initially developed for conventional light scattering [10]. This method enables calculation of the ensemble-average ICF from one single measurement of the time-averaged ICF. The ensemble-averaged ICF gives access to the ensemble-averaged field correlation function by using the Siegert relation [11]. A typical ensemble-averaged field correlation function,  $g_1(t)$ , is represented in the inset of Fig. 1. At long time scales,  $g_1(t)$  exhibits a plateau which expresses the arrest of the dynamics: particles are trapped in cages formed by their neighbors and they cannot move freely through the paste. The plateau extends over several decades and there is no evidence for long-time relaxation. At short time scales,  $g_1(t)$  exhibits an initial decay which is associated with local motions of particles within the cages. This is analogous to the so-called  $\beta$  relaxation observed in colloidal glasses. Previous studies have focused their measurements to the vicinity of the glass transition [12–14]. Here, we explore a range of concentration that extends far into the glass phase.

The general DWS formalism provides analytical expressions of the field correlation function in terms of the mean-square displacements of the scatterers (MSD). In the following, we calculate the MSD of the tracers by numerically inverting  $g_1(t)$  using the expression for the

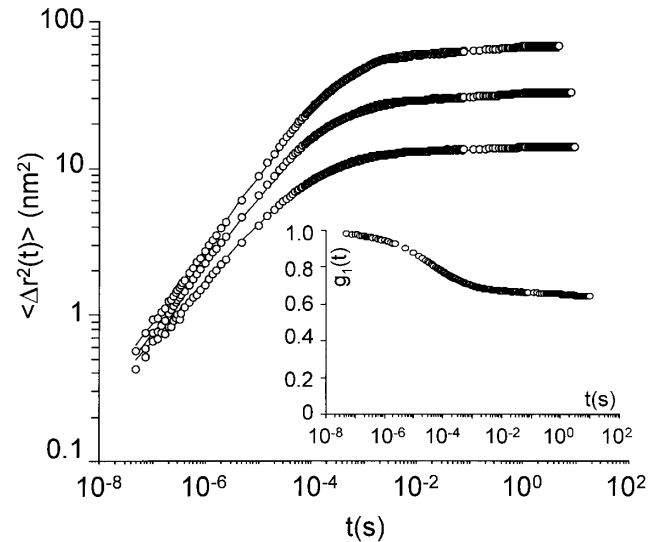


FIG. 1. MSD of the tracers;  $\circ$ : experiment; —: best fit to the data by a stretched exponential. From top to bottom:  $C = 0.018$  g/g,  $C = 0.02$  g/g,  $C = 0.03$  g/g ( $N_x = 140$ ;  $\eta_s = 1$  mPa  $\cdot$  s). The inset shows an ensemble-averaged field correlation function ( $C = 0.03$  g/g).

transmission geometry [15]. In Fig. 1, we represent the MSD for different pastes. The data are well described for all times by stretched exponentials:  $\langle \Delta r^2(t) \rangle = \delta^2 \{1 - \exp[-(t/\tau_\beta)^\beta]\}$ . Physically, stretched exponentials are frequently associated with the existence of a wide spectrum of relaxation times [16]. The fitting procedure works well for all the pastes investigated, enabling us to determine  $\beta$ ,  $\delta$ , and  $\tau_\beta$  over a wide range of experimental parameters.

The exponent  $\beta$  is smaller than 1. It decreases with increasing concentration ( $\beta = 0.75$  for  $C \cong 1.1C_m$  and  $\beta = 0.45$  at  $C \cong 3C_m$ ). This shows that the short time dynamics associated with the motion of the particles inside their cages is subdiffusive, even at very short times, and that it is related to the degree of compactness of the pastes. The displacement at the plateau,  $\delta$ , represents the maximum excursion of the probe particles before their neighbors trap them.  $\delta$  is only a small fraction of the particle size. As  $C$  increases,  $\delta$  becomes smaller, reflecting the smaller cage size. The parameter  $\tau_\beta$  is the time scale associated with local relaxation. Interestingly,  $\tau_\beta$  mainly depends on the storage modulus  $G_0$  and on the solvent viscosity  $\eta_s$ .  $G_0$  and  $\eta_s$  are known independently from conventional rheological measurements. There is a slight dependence on the cross-link density but all other experimental parameters play no role. In Fig. 2, we plot the variations of  $\tau_\beta$  as a function of  $\eta_s/G_0$  when the polymer concentration, the solvent viscosity, and the cross-link density are varied. In the inset, we give the variations of the plateau modulus  $G_0$  with the cross-link density and the concentration. Figure 2 shows that  $\tau_\beta$  is proportional to  $\eta_s/G_0$  through a coefficient, which depends on the cross-link density.



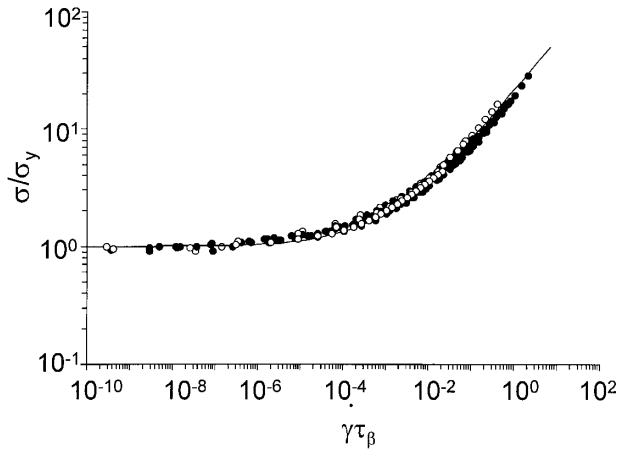


FIG. 4. Universal flow curve. Full symbols:  $N_x = 140$  and different concentrations from  $C = 0.015$  g/g to  $C = 0.07$  g/g. Open symbols:  $N_x = 28$  and different concentrations from  $C = 0.05$  g/g to  $C = 0.07$  g/g. The continuous line has the equation:  $\sigma/\sigma_y = 1 + (\dot{\gamma}\tau_\beta/\gamma_0)^{0.45}$  with  $\gamma_0 = 0.001$ .

state and a shear rate  $\dot{\gamma}$ , at steady state can be measured. It is interesting to note that the crossover between these two regimes is fairly sharp. We define the yield stress  $\sigma_y$  of a paste as the lowest stress for which a stationary state is achieved within the duration of a measurement ( $\sim 1$  h). We have checked that this value is in good agreement with that found from other determinations such as the oscillatory strain sweep method.  $\sigma_y$  is proportional to the elastic modulus  $G_0$ :  $\sigma_y = G_0\gamma_y$  where  $\gamma_y = 0.05$  is defined as the yield strain.

Figure 3 shows flow curves  $\sigma(\dot{\gamma})$  measured for different pastes. It highlights the great sensitivity of the nonlinear rheology to small changes of the experimental parameters. Nevertheless, it is possible to scale all the flow curves onto a universal curve using the local relaxation time  $\tau_\beta$ . Our approach is based on the glasslike structure of pastes. At rest, microgels are trapped in cages but, when a stress is applied, they can escape and relax back to another position. We argue that the duration of a rearrangement is set by the competition between elastic restoring forces and interparticle friction. Therefore, the characteristic duration of a rearrangement has to scale with  $\eta_s$  and  $G_0$  in the same way as the relaxation time  $\tau_\beta$ . In Fig. 4, we plot the flow curves of different pastes in the set of coordinates  $(\dot{\gamma}\tau_\beta, \sigma/\sigma_y)$ . The shear rate is scaled by the local relaxation time  $\tau_\beta$  deduced from Fig. 2 and the stress is scaled by the experimental yield stress. Remarkably, all the flow curves collapse onto a universal curve. The master curve is well represented by an equation of the Herschel-Bulkley form. The new result here is that the coefficients are expressed in terms of microscopic parameters. At low-shear rates, rearranging particles relax back to local equilibrium before the flow induces a

new rearrangement. The stress remains of the order of the yield stress. At high shear rates, the flow induces a continuous sequence of rearrangements. Microgels exchange their position very quickly. The stress increases due to viscous dissipation associated with interparticle friction.

In conclusion, the local dynamics and the nonlinear rheology of microgel pastes exhibit a universal scaling behavior in terms of a single time scale. Our results show that the competition between structural relaxation and shearing plays a central role in the nonlinear rheology. In that respect, we think that it is a general behavior, which should help to achieve a unified description of the rheology of many other systems.

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