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]: \( \sigma = \sigma_y + a \gamma^n \), \( \sigma_y \) and \( a \) are phenomenological parameters and \( \gamma \) 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 \( \tau_B \). We measure \( \tau_B \) for different pastes varying the concentration and the physicochemical parameters to a large extent. We show that \( \tau_B \) 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, \( \tau_B \) represents the shortest relaxation time and sets the duration of a rearrangement. A spectacular consequence is that the nonlinear flow properties \( \sigma(\gamma) \) 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 \( \tau_B \). 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 microgel 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, \( N_c \). Two batches of microgels with \( N_c = 28 \) and \( N_c = 140 \) are studied below. The solvent is pure water or a water/glycerol mixture. In dilute suspensions, microgel particles are spherical microwebs with hydrodynamic radius \( R \) (\( R = 220 \) nm for \( N_c = 140 \)) and...