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# Tailoring the Flow Properties of Soft Colloidal Dispersions

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**Summary:** The dynamics and the non-linear rheology of concentrated dispersions of soft particles are shown to exhibit generic properties. They display both solid-like and liquid-like properties depending on the applied stress. Below the yield point, dispersions exhibit history-dependent phenomena that have all the hallmarks of ageing in glasses. The close-packed disordered structures of the dispersions lie at the heart of this behaviour. Other properties such as the propensity of pastes to slip on solid surfaces appear to be governed by specific contact interactions between the squeezed particles.

**Keywords:** ageing; emulsion; glasses; microgels; rheology; shear-thinning

## Introduction

Colloids and polymers have distinct structures and properties. Today it is possible to synthesize materials that share common features with polymers and colloids. Classical examples are microgel networks,[1] multi-arm star polymers,[2] nanoparticles particles covered with grafted or adsorbed polymer chains[3] and block copolymer micelles.[4] In these systems, the elementary objects are inherently soft and deformable because of their polymeric nature and, at the same time, they are partially impenetrable like colloidal particles. At high concentration, they form gel-like pastes that behave like weak solids at rest but flow like liquids when subjected to high stresses. Recently, it has been argued that this remarkable rheological property shared by many concentrated colloidal dispersions might simply reflect the presence in such materials of glassy dynamics.[5–7]

Glassy dynamics is associated with the structural relaxation of elements that are trapped by their neighbours into cages and that have to overcome energy barriers before rearranging. Rearrangements occur under the combined action of thermal motion and mutual interactions between sheared elements. Models of glassy dynamics capture several important features of the rheology of concentrated dispersions at least qualitatively. In this context, an important and open question is whether the analogy between concentrated dispersions and glasses provides a complete and universal description of soft colloidal dispersions.

In this article, we address this question for the case of soft particle pastes made of polyelectrolyte microgels and emulsions. We show that the local dynamics exhibits all the characteristic features of $\beta$ relaxation processes in glasses. Below the yield stress, the macroscopic rheology is a combination of ageing and partial rejuvenation associated with the frustration and the cooperative relaxation of steric constraints between interlocked neighbouring particles. When the applied stress is larger than the yield stress, large-scale rearrangements become possible and particles exchange their position very rapidly. The flow curves exhibit a great sensitivity to the experimental parameters. Nevertheless, they collapse onto a universal master curve when the shear rate is rescaled by the local relaxation time $\tau_\beta$. The concept of glassy dynamics borrowed to the physics of disordered systems is particularly appealing

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in this context. However, there exist other generic properties of pastes such as their propensity to slip on surfaces that appear to be governed by specific contact interactions between the squeezed particles. Recent advances in this direction suggest novel strategies to design and synthesize complex dispersions with well-controlled properties.

## Soft Particle Dispersions

In the following, we study microgel pastes and emulsions. The microgel particles used in this study are pH-responsive colloidal particles consisting of cross-linked polymer networks of acrylate chains bearing ionized methacrylic acid groups, which are swollen by water.[8] The cross-link density is characterized by the average number of monomers between two cross-links ($N_X$). Microgel particles are synthesized by direct emulsion polymerisation. The emulsions are dispersions of silicon oil in water, stabilized by a surfactant. In dilute suspensions the particles have a spherical shape with a radius $R$ ($R \cong 100$–$200$ nm for microgels depending on the cross-link density; $R \cong 1.5 \pm 1$ μm for emulsions). At high volume fraction, they pack into concentrated pastes and emulsions with solid-like properties. The bulk rheology of microgel pastes can be tuned by changing the solvent viscosity, the cross-link density of the particles, the total polymer concentration and the ionic strength. Pastes and emulsions are widely used to impart yielding properties to complex formulations. In the case of polyelectrolyte microgels, since particles contain up to 98% of solvent these properties can be achieved with very small quantities of polymer. In essence both systems, whilst very different in composition, can be considered as dispersions of soft elastic spheres. The elasticity of microgel particles is due to the osmotic pressure of the counter-ions associated with the fixed charges borne by the polymer network. The elasticity of emulsion droplets comes from the interfacial energy of the oil-water interface.

## Glassy Dynamics of Soft Particle Dispersions

At rest or at low stresses pastes behave like weak elastic solids, whereas at sufficiently high stresses they flow like viscous liquids. The existence and significance of a well defined yield stress beyond which pastes flow is still a subject of vivid controversy.[9] In that respect it is essential to identify the microscopic mechanisms that control the yielding behaviour of pastes.

The local dynamics of pastes has been probed by diffusive wave spectroscopy (DWS).[10] This technique is a recent development of light scattering that is well adapted to turbid materials.[11] Pastes are seeded with tracers that strongly scatter light without altering the dynamics and the rheological properties. In the following, we use polystyrene beads (168 nm in diameter) at a volume fraction of 0.005. In a typical experiment, a paste is illuminated uniformly by a laser beam. Photons are multiply scattered as they propagate through the paste. They interfere and form a speckle pattern on the detector situated at the entrance (back-scattering) or at the exit of the sample (forward-scattering). A monomode optical fibre with low acceptance angle collects the light emerging from a single speckle. Because of the internal dynamics of the material, the intensity that is detected fluctuates in time. It is analysed in terms of intensity or electric field correlation functions. Here, the interpretation is complicated by the fact that pastes are not ergodic: the temporal variations of the light detected in a particular speckle do not reflect directly the actual dynamics of the system. Different methods have been developed to obtain ensemble-averaged intensity correlation functions from time-averaged correlation functions collected at different locations in the speckle pattern.[12]

Ensemble-averaged correlation functions give access to the mean square

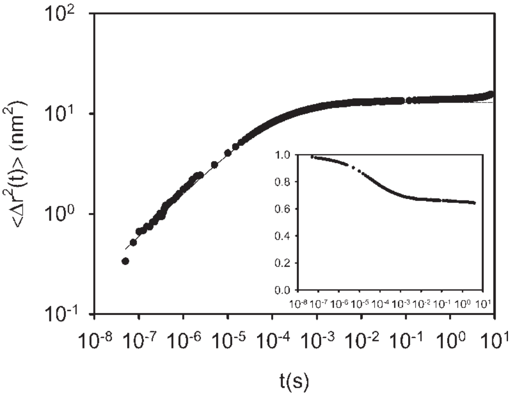

***Figure 1.***
MSD of tracer particles in a microgel paste ($C = 0.03$ g · g$^{-1}$). The continuous line represents the best fit to a stretched-exponential. The inset shows the ensemble-averaged correlation function of the electric field from which the MSD is extracted.

displacement (MSD) of the tracers.[13] A typical result obtained for microgel pastes is shown in Figure 1. The MSD is measured over a broad interval of time scales ranging from Brownian time scales to macroscopic time scales and over very short distances. The MSD exhibits a plateau that expresses the arrest of the dynamics and the jamming. This plateau is due to a cage effect, particles cannot move freely through the paste because they are trapped in the cages formed by their neighbours. At short time, particles move in their cage. At long time, particles are trapped and there is no evidence for long-time relaxation even at the longest time scales accessible. The macroscopic manifestation of this particular dynamics is the fact that the material behaves like a solid that yields only when a sufficiently large stress is applied. The yield stress is associated with the break-up of the cages. It has been shown that emulsions behave in a similar way.[14]

Qualitatively, the variations of the MSD represented in Figure 1 are similar to those measured in colloidal glasses above the glass transition.[15] Quantitatively the data are well represented by stretched exponentials of the form: $\langle \Delta r^2(t)\rangle = \delta^2\{1-\exp[-(t/\tau_\beta)^\beta]\}$. The exponent $\beta$ (=0.8–0.4) characterizes the cage dynamics. The displacement at the plateau, $\delta$, represents the maximum excursion of the probes before they feel the presence of the cages. $\tau_\beta$ is the time scale associated with local relaxation. $\delta$ and $\tau_\beta$ can be expressed in terms of a limited number of experimental variables.[10] We consider that particles move in their cage under the combined action of stochastic forces, elastic restoring forces exerted by the cage, and frictional forces that particles exert one on the other. A particle of radius $R$ then moves over a distance $\delta$ within a time $\tau_\beta$, which is the time scale associated with local relaxation. This particle deforms elastically the cage that subsequently pushes it back. The restoring force is of the order of $G_0\delta R$ and the elastic energy is $G_0\delta^2 R$, $G_0$ being the local cage elasticity. At the maximum excursion, we have $G_0\delta^2 R \sim \mathrm{kT}$ and $G_0 \sim \mathrm{kT}/\delta^2 R$. Thus, we can determine $G_0$ from the variations of the MSD. Experimentally, the results match the variations of the macroscopic storage modulus measured by shear rheology within the experimental accuracy. Similarly, we can derive an expression for $\tau_\beta$. For microgel pastes, we have shown that $\tau_\beta$ is a universal function of the solvent viscosity $\eta_S$, of the storage modulus $G_0$ and of geometric factors regardless of all other parameters: $\tau_\beta \sim \eta_S/G_0$.[10]

## Slow Dynamics and Ageing

Below the yield stress, it is technically difficult to perform rheological measurements. The properties of soft concentrated dispersions vary in time and depend strongly on sample preparation and measurement history. In the case of microgels pastes, these history-dependent phenomena exhibit all the characteristic features of ageing and can be rationalized in terms of concepts borrowed from physics of disordered systems.[16,17]

Rheological measurements below the yield stress are not reproducible unless the initial preparation and the stress history are perfectly controlled. To prepare pastes in a reproducible mechanical state, a pre-shear stress much larger than the yield stress, resulting in a high shear rate, is applied to the sample prior to each measurement. Upon flow cessation, the material recovers and solidifies. The recovery cannot be characterized by an intrinsic relaxation time like in conventional visco-elastic materials. Instead, it is logarithmic in time and persists up to the longest times experimentally accessible. This indicates that mechanical equilibrium is never reached and that subsequent measurements probe an out-of-equilibrium material. Nevertheless, it is possible to obtain valuable information just by controlling the time elapsed after preparation.

This is shown in Figure 2(a) where we plot the strain response of a paste to a stress applied at time $t_w$. $t = 0$ marks the end of the pre-shear sequence, $t_W$ represents the time the paste has spent under zero stress, i.e., its age. At short times, the strain jumps instantaneously to a value that is proportional to the applied stress. This is the typical response of an elastic material. At long time, the paste creeps. Creep begins later and is slower when the paste is older. To account for this unusual behaviour, we plot the variations of the responses at different ages as a function of a variable of the form:

$$\mathrm{f}(t, t_\mathrm{w}) = \frac{t_0^{\mu}}{1-\mu}\left[t^{1-\mu} - t_\mathrm{w}^{1-\mu}\right]$$

where $\mu$ is a positive constant smaller than 1 and $t_0$ is a microscopic time scale that will be taken as equal to 1 in the following. This scaling variable was originally proposed to characterize the ageing of polymeric glasses.[18] Other expressions can be found in the literature. Figure 2(b) shows that the creep curves measured at different ages collapse perfectly onto a universal curve.

These results express the fact that the age $t_w$ of the paste is the only characteristic

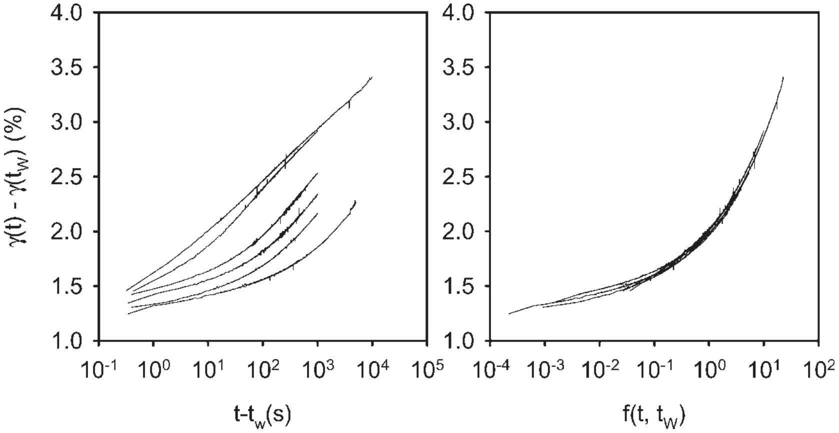

***Figure 2.***

Left (a): Creep curves measured at different waiting times for a microgel paste ($C = 0.02$ g · g$^{-1}$). The yield stress of the paste is $\sigma_y = 22$ Pa. The applied stress is $\sigma_m = 5$ Pa. The waiting times are: $t_w = 15$ s, $t_w = 30$ s, $t_w = 300$ s, $t_w = 1\,000$ s, $t_w = 2\,000$ s, $t_w = 10\,000$ s (from top to bottom). Right (b): Collapse of the creep curves measured at different waiting times onto a master curve; f($t$, $t_w$) has the form given in the text with $\mu = 0.80$.

time. This is one of the key features of ageing phenomena. Ageing has been found in many glasses and disordered systems like polymer glasses,[18] structural glasses[19] and spin glasses.[20] Rheological ageing in pastes is closely associated with the metastability and frustration arising from the peculiar glass-like structure found in the previous section. However, there is a major difference between ageing in structural glasses and in pastes. In glasses, a metastable state is reached when the system is brought below the glass transition temperature and rejuvenation happens when the temperature is increased. In pastes, rejuvenation is due to macroscopic flow whereas metastability appears upon flow cessation. Recently, similar ageing phenomena have been described in various concentrated dispersions.[21–23]

## Flow and Non-Linear Rheology

Above the yield stress, pastes flow like liquids. In this regime, macroscopic rheology is well adapted to probe the flow behaviour as a function of the experimental parameters. Flow curves are built by applying a constant stress $\sigma$ and measuring the resulting shear rate $\dot{\gamma}$ at steady state. Typical results for microgel pastes are shown in Figure 3(a) where we vary the polymer concentration, the solvent viscosity, the ionic strength and the cross-link density of the polymer network. All flow curves have the same characteristic shape: a constant stress plateau at low-shear rates followed by power-law variation at large shear-rates. We define the yield stress $\sigma_y$ as the lowest stress for which steady state is achieved within the duration of a measurement. $\sigma_y$ is proportional to the storage modulus of the pastes through the yield strain $\gamma_y \cong 0.05$: $\sigma_y = G_0\gamma_y$. Figure 3(a) highlights the great sensitivity of the non-linear rheology of pastes to small changes in the experimental parameters. A great challenge at this point is to elucidate the underlying parameters and the physical mechanisms that effectively control the flow properties.

Our approach is based on the glass-like structure of pastes.[10] At rest, microgels are trapped in cages but, when a stress is applied, they can break the cage, escape and relax back to another position. We argue that the duration of a rearrangement is set by the shortest relaxation time $\tau_\beta$ ($\sim\eta_S/G_0$) measured in the previous section. To test this idea, we now rescale the shear-rate $\dot{\gamma}$ by the characteristic time $\eta_S/G_0$ and the stress $\sigma$ by the yield stress $\sigma_y$. In Figure 3(b), we plot the flow curves in the set of coordinates $\left(\dot{\gamma}\eta_s/G_0, \sigma/\sigma_y\right)$. All the flow curves collapse onto a universal curve. Remarkably this master curve also describes the rheology of emulsions.

In conclusion, concentrated dispersions of soft particles exhibit generic flow properties. To achieve perfect control over the flow properties of pastes it suffices to tune the solvent viscosity and the storage modulus independently of all other parameters. The solvent viscosity can be adjusted by changing the temperature or by adding rheological additives like thickeners. The storage modulus of pastes depends on the volume fraction of particles on their molecular architecture and their chemical composition.[24]

## Non-Homogeneous Flow in Soft Particle Pastes: Wall Slip

The mechanical behaviour of concentrated dispersions depends not only on the bulk flow properties but also upon the nature of the confining surfaces. In the following, we show that the motion of microgel pastes and emulsions is often dominated by wall slip, with dramatic effect on the macroscopic rheology.

We have measured simultaneously the macroscopic properties and the local velocity profiles of microgel pastes and emulsions for smooth and rough shearing surfaces. The rheometer is a stress-controlled apparatus with cone and plate geometries. The flow profiles are measured

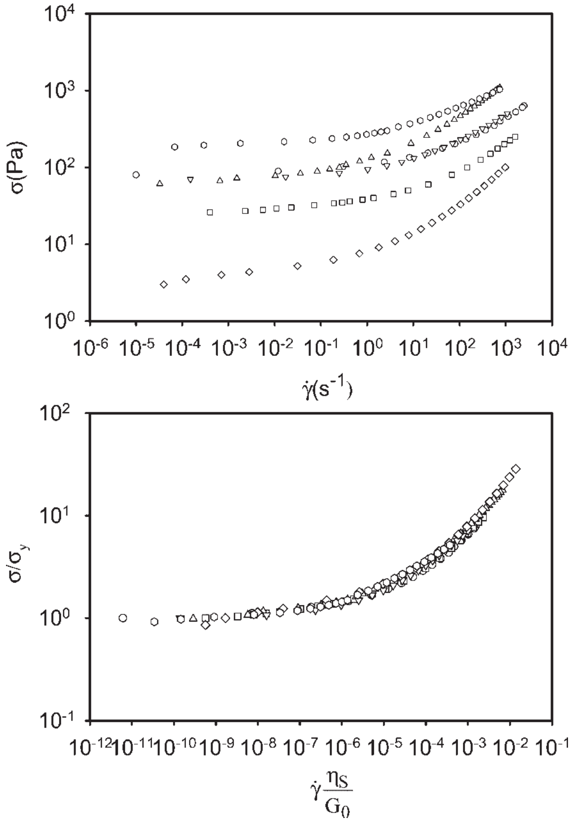

***Figure 3.***
Top (a): Flow curves of microgel pastes. ○, $N_X = 28$, $C = 0.06$ g · g$^{-1}$, $\eta_S = 1$ mPa · s; □, $N_X = 28$, $C = 0.06$ g · g$^{-1}$, $\eta_S = 1$ mPa · s, [NaCl] = 0.1 M; △, $N_X = 140$, $C = 0.03$ g · g$^{-1}$, $\eta_S = 10$ mPa · s; ▽, $N_X = 140$, $C = 0.03$ g · g$^{-1}$, $\eta_S = 1$ mPa · s; ◇, $N_X = 140$, $C = 0.015$ g · g$^{-1}$, $\eta_S = 1$ mPa · s; ⬡: $N_X = 140$, $C = 0.06$ g · g$^{-1}$, $\eta_S = 1$ mPa · s. Bottom (b): Collapse of flow curves shown in (a) onto a master curve.

using video microscopy.[25] The pastes, which are translucent, are seeded at very low concentration with small glass spheres with a diameter of about 10 μm, which reflect light when illuminated. They are observed from the side using a CCD camera equipped with a high magnification zoom lens. Local velocities are obtained by tracking the successive positions of the tracers and by measuring their displacement as function of time. The spatial resolution is ~20 μm and the range of measurable velocities is $1\ \mu m \cdot s^{-1} \leq v \leq 3\ mm \cdot s^{-1}$.

Figure 4(a) presents velocity profiles of microgel pastes. When sheared with rough surfaces, pastes and emulsions flow homogeneously in the whole range of stresses and shear rates accessible by our experimental set-up. When one or both of the shearing surfaces are smooth, wall slip occurs and a slip velocity $V$ is detected. The slip layer is not resolvable in our set-up. The bulk flow is homogeneous but the actual shear rate to which the paste is subjected is much smaller than the apparent shear rate deduced from rheology.

Figure 4(b) presents direct measurements of the slip velocity $V$ as a function of the excess stress $\sigma - \sigma'_y$, where $\sigma'_y$ is the apparent yield stress that is measured in the presence of slip.

At high stresses ($\sigma/\sigma_y > 1$) the slip velocity remains equal to a plateau value $V^*$. $V^*$ only depends on the solvent viscosity $\eta_S$, on the shear modulus of the paste $G_0$ and

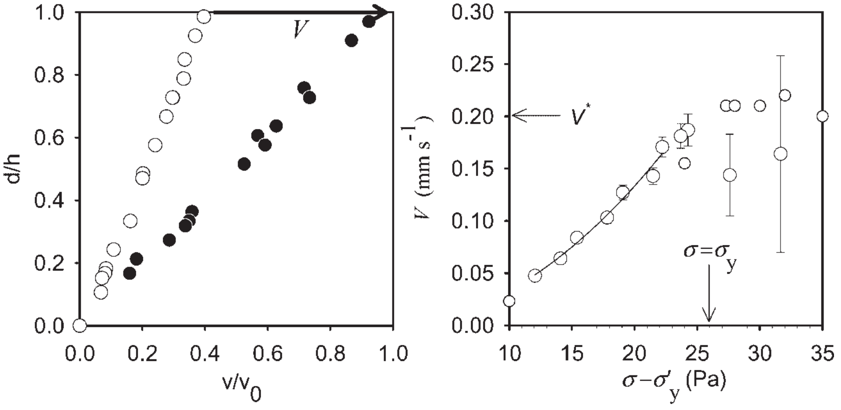

***Figure 4.***
Left (a): Typical microgel paste flow profiles ($N_X = 140$, $C = 0.02$ g · g$^{-1}$) measured with rough (●) and smooth (○) cone and plate geometries. *d* is the distance from the bottom plate that is rough and motionless; *h* is the gap thickness (0.9 mm). The local velocity $v$ is scaled by the cone velocity $v_0$. Slip occurs only at the top. Right (b): Variations of the slip velocity versus the excess stress. The solid line is a quadratic fit to the data.

on the particle radius *R*. $V^*$ is of the form: $V^* \sim G_0R/\eta_S$ for all except the most concentrated pastes. At low stresses ($\sigma/\sigma_y \leq 1$), the slip velocity decreases as the applied stress is decreased. The data are well represented by the quadratic form $V/V^* \sim (\sigma/\sigma)^2$. Remarkably, all these results also stand for emulsions.

These experimental results show that the slip behaviour and the macroscopic rheology of pastes are coupled. To account for this observation, we have proposed a model based on elasto-hydrodynamic lubrication.[25,26] Elasto-hydrodynamic slip can be described as follows. At rest, the osmotic pressure of the compressed suspension or emulsion forces the particle into contact with the bounding surfaces. If these contacts were to persist during flow, no-slip behaviour would be expected. However, a thin layer of fluid between a soft particle and a smooth surface in relative motion can be maintained due to the non-linear coupling of the flow in the lubrication layer and the elastic deformation of the particle. Indeed, under motion, the particle deforms asymmetrically and the resulting pressure field creates a force pushing the particle away from the wall. This force must balance the osmotic force due to the compressed suspension or emulsion acting on the particle to maintain the lubricated layer, and this balance determines the thickness of the lubricated gap, and ultimately the drag between the particle and smooth surface. These arguments can be formalized using a scaling analysis of the elasto-hydrodynamic lubrication equations. The predictions are in excellent agreement with the experimental results, in particular with the variations depicted in Figure 4a and b.

In conclusion, soft particle pastes and emulsions exhibit a generic slip behaviour near smooth surfaces. Slip is localized in a very thin layer near the shearing surfaces. The bulk of the pastes is sheared homogeneously with no evidence of the shear banding phenomena that have been observed experimentally and numerically in other soft glassy materials.[27–29] The reason why heterogeneous flows are found in some concentrated dispersions and not in others is an interesting and open issue.

## Conclusion

Jamming and yielding make soft particle pastes extremely useful in applications and fascinating scientifically. The analogy between these materials and glasses account for the local dynamics and several remarkable features such as ageing and rejuvenation. Other generic properties such as the non-linear rheology or wall slip are governed by specific contact interactions. Our results suggest novel strategies to design and synthesize complex dispersions with well-controlled properties.

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