

SLIP AND FLOW IN PASTES

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Summary Slip in soft particle pastes is dominant at low shear rates. By directly imaging the flow of pastes using video-microscopy, we show that slip is characterized by universal properties, which depend on solvent viscosity, bulk elasticity and particle size. A generic slip model based on elasto-hydrodynamic lubrication between the squeezed particles and the wall explains these properties quantitatively.

INTRODUCTION

Concentrated dispersions and pastes of soft particles are ubiquitous in everyday life (mayonnaise), in biology (biological fluids and tissues) and in geology (lava and mud). These materials share in common many properties. At high concentration, steric constraints are so important that the motion of individual particles is drastically reduced unless a finite external force is applied. This is at the origin of many fascinating bulk properties such as yield stress, shear thinning, aging and memory. In practice however, the motion of pastes is often dominated by wall slip, with dramatic effects when they move within confined smooth surfaces. This can have a dramatic effect on the rheology and the processing of yield stress materials.

Wall effects in dispersion flows have often been described in terms of an apparent slip [1]. Slip is generally inferred from macroscopic rheology, and very few studies have tried to correlate the rheology with direct flow visualizations [2]. Slip is believed to arise from particle depletion at the shearing surface. Many mechanisms have been evoked to cause particle depletion; they can be static (*e.g.*, steric, physico-chemical interactions between the particle and the surface) or dynamic (*e.g.*, shear rate gradients, hydrodynamic interactions) in origin. Several important questions remain open. What are the microscopic mechanisms at work when concentrated dispersions flow along surfaces? How are wall phenomena coupled to the bulk rheology? Is there any underlying universality? During the talk, we will answer these questions for the case of soft particle pastes.

SLIP PROPERTIES IN SOFT PARTICLE PASTES

Microgel pastes and emulsions

We have studied pastes of microgel particles and emulsions. A microgel particle consists of a cross-linked polymer network of acrylate chains bearing ionized methacrylic acid groups, which is swollen by a solvent [3]. 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. 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 ($R \cong 100$ -250 nm for microgels and $R \cong 1.5 \pm 1 \mu\text{m}$ for emulsions). At high volume fraction, they pack into concentrated pastes and emulsions with solid-like properties. In essence both systems, whilst very different in composition, can be considered as dispersions of soft, elastic spheres. The elasticity of the 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 the emulsion droplets comes from the interfacial energy of the oil-water interface.

Direct measurements of slip velocity

We have measured simultaneously the non-linear rheology and the local velocity profiles for smooth and rough shearing surfaces. The rheometer is a stress-controlled apparatus with cone and plate geometries. The flow profiles are obtained using video microscopy. 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 during time. The spatial resolution is $\sim 20 \mu\text{m}$ and the range of measurable velocities is $1 \mu\text{m s}^{-1} \leq v \leq 3 \text{ mm s}^{-1}$.

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. 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. The relative importance of slip depends on the shear stress σ . We can distinguish three regimes of slip. At shear stress much larger than the yield stress σ_y ($\sigma/\sigma_y \geq 1.5$), slip is negligible compared to the bulk flow. Just above the yield

stress ($1 < \sigma/\sigma_y < 1.5$), slip becomes significant and the total deformation of the pastes result from a combination of bulk flow and slip. At and below the yield stress ($\sigma/\sigma_y \leq 1$), the bulk flow is negligible and the apparent motion is entirely to the slipping of the paste.

Scaling properties of slip

Direct measurements of the slip velocity for a typical paste are presented in Fig. 1 as a function of the excess stress $\sigma - \sigma'_y$, where σ'_y is the apparent yield stress in the presence of slip. In regime III ($\sigma/\sigma_y \leq 1$), the slip velocity decreases as the applied stress is decreased. The data are well represented by the quadratic form $V/V^* \sim (\sigma/\sigma_y)^2$. In regime II ($1 < \sigma/\sigma_y < 1.5$) the slip velocity remains equal to a plateau value V^* . V^* is a characteristic velocity that depends only on the solvent viscosity, η_s , on the shear modulus of the paste, G_0 , and on the particle radius R . Interestingly, Fig. 2 shows that V^* is of the form: $V^* \sim G_0 R / \eta_s$ for all except the most concentrated pastes.

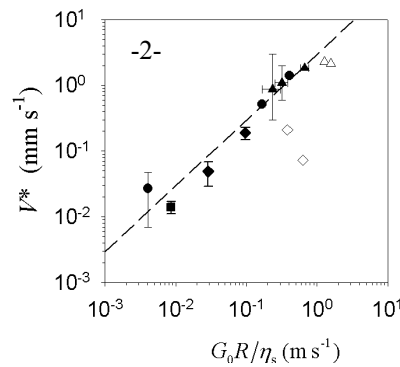
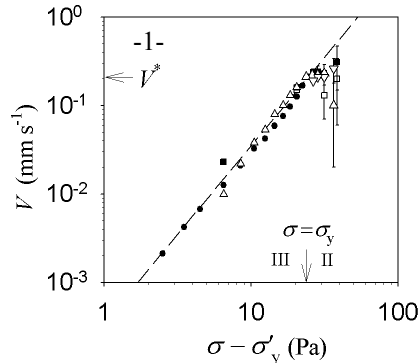


Fig.1: scaling of the slip velocity versus the excess stress for a microgel paste.

Fig.2: scaling of the characteristic velocity V^* . Each symbol refers to a paste or emulsion

ELASTO-HYDRODYNAMIC MODEL OF SLIP

For concentrated suspensions of soft particles, we propose that elasto-hydrodynamic lubrication is responsible for the slip [4,5]. Elasto-hydrodynamic slip can be described qualitatively 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 behavior 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 with 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 Figs 1 and 2.

CONCLUSIONS

Soft particles pastes exhibit a generic slip behavior near smooth surfaces. A model, which is based on elasto-hydrodynamic lubrication between the squeezed particles and the wall, explains quantitatively the slip properties when stresses are small enough that there is no bulk flow. We think that this elasto-hydrodynamic slip mechanism should apply to many concentrated dispersions of soft particles. Moreover, since jammed particles must 'slip' past one another in order to move, similar mechanisms are likely to occur in the bulk of the material.

References

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