Rheological Study of Granular Suspensions and Polymer Glasses

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Complex fluids cover a large range of materials. This thesis focuses on two types of such systems: granular suspensions that show shear thickening and polymer glasses, viscoelastic solid materials. Suspensions of granular particles have sparked great interest in recent years, not only due to interest from fundamental research but also because of their potential in industrial applications in areas like food production, pesticides, cosmetics, construction and oil well engineering. Depending on the suspending-liquid properties, particle sizes and volume fractions, granular suspensions show very rich rheological behaviours such as shear thickening, elevated normal stresses and an intriguing elongational rheology. Precisely these three rheological behaviours are systematically studied in three chapters (Chapters 3-5) of this thesis. The final chapter (Chapter 6) deals with the issue of the polymer glass transition. Traditionally, for thermoplastics, the so-called glass transition temperature (Tg) determines the transition between solid-like and liquid-like material. Accordingly, when the temperature is decreased below Tg, the initially liquid polymer melt becomes hard and brittle, and behaves like a glass. Our experiments show that besides increasing the temperature, a glass to liquid transition can also be achieved by imposing shear; thus, a critical glass-transition strain amplitude is defined. Knowledge of the polymer glass rheology is important for understanding and optimizing their performance in industrial as well as in everyday applications.

In Chapter 1, we give a brief introduction to the subject of soft matter or complex fluids, and contrast these with simple viscous liquids and elastic solids. For non-Newtonian fluids, emphasis is put on shear-thickening granular suspensions. We describe their rheological properties from different points of view, for each of which we briefly review recent research progress. We provide the basic context on polymer glasses and discuss the free volume theory that has been developed to explain the glass transition behaviour. The motivation of the current research is given, and the scope of this thesis is presented.

In Chapter 2, we present the experimental techniques for performing rheology measurements, fluorescence measurements and droplet pinch-off experiments. Specifically for the rheology part, we define the relevant rheological terms, describe the rheometers and rheometer geometries used, and outline the experimental protocols used to conduct both rotational and oscillatory measurements. Subsequently, the materials and methods used for preparing granular suspensions and polymer glasses are described. Two different fluorescent probes used for fluorescence measurements are also introduced here.

In Chapter 3, we focus on a current "hot" topic in the area of granular suspensions: the mechanism behind the shear thickening phenomenon. We present direct evidence showing that friction is at the origin of shear thickening. We start by showing non-monotonic shear thickening behaviour in concentrated suspensions, characterized by an S-shaped flow curve (shear stress vs shear rate) with a negative slope between the low-viscosity Newtonian regime and the high-viscosity shear thickened regime. This behaviour is observed when the shear stress is varied, with a hysteresis that depends on the rate at which up-and-down stress sweeps are performed. In shear rate-controlled rheology measurements, discontinuous shear thickening occurs. For dilute suspensions, however, the flow curves obtained from both stress-controlled and shear rate-controlled rheology measurements are indistinguishable. For S-shaped flow curves, when a constant stress is imposed that is intermediate between the high- and low-stress branches, our fluorescence visualization experiments suggest that the flow remains homogeneous during the transition from the Newtonian to the shear-thickened state. The S-shaped shear thickening is then due to the discontinuous formation of a frictional force network between particles upon increasing the stress. We also show that the flow in shear-thickened state is stable, indicating that jamming is not a prerequisite for observing the shear thickening behaviour.

In Chapter 4, we extensively study the normal stress of granular suspensions and how it relates to the shear-thickening behaviour. In order to quantify the non-trivial normal stress response, we focus on a typical particle volume fraction at 56\% and ensure that the shear-thickened state is reached in rheological measurements. We first perform oscillatory measurements by using a parallel-plate geometry, and observe a transition from positive to negative normal stresses, upon increasing the particle diameter or decreasing the gap size between the two plates. It is shown that the solvent mobility through the inter-particle space, in terms of the relaxation time, plays a decisive role in determining the sign and magnitude of the normal stresses. We conclude that the particle pressure contributes positively to the normal stress and induces frictional shear thickening behaviour; the contribution from the liquid phase is negative. At a certain particle diameter and gap size, the latter dominates, resulting in negative normal stresses. We show that the relative contributions from the two phases can be estimated using the two-fluid model. The results from rotational measurements, performed by using the same parallel-plate geometry, support the above findings. The rheological measurements are also done by employing a cone-plate geometry; the normal stress difference N_1 is disentangled from N_2 by combining the results from the parallel-plate and cone-plate geometries. We also establish how these parameters determine $N_1 - N_2$.

In Chapter 5, the elongational rheology of shear-thickening granular suspensions is studied by looking at droplet formation. Our studies focus on the influence of the presence of particles on the droplet breakup behaviour and the ensuing finite-time singularity. By systematically varying the particle diameters and volume fractions, we show that the droplet breakup happens in three different manners, and that we can thus distinguish three different regimes. For dilute suspensions, droplet formation follows the predictions for inertial breakup and exhibits the same dynamics as the suspending liquid, i.e., water. The breakup is strongly asymmetric in this case. Only for concentrated suspensions does the presence of particles change the dynamics and two other regimes, i.e., a symmetrical inertial regime and a Bagnoldian regime, are uncovered. In the Bagnoldian regime, the breakup dynamics is exponential and the final geometry of the thinning filament is cylindrical. Furthermore, its elogational rheology is found to be correlated with shear rheology. Finally, we establish a phase diagram that allows us to understand and predict the droplet breakup behaviour in granular suspensions.

In Chapter 6, we present a study on the effect of shear on a polymer glass. We show that deforming a polymer glass can result in a glass transition even at temperatures below Tg, and the molecular free volume is key to understanding this phenomenology. We employ environment-sensitive fluorescence probes dispersed in a polymer matrix to locally detect the free-volume changes. Calibrating the florescence intensity to the temperature-induced glass transition, we can directly measure free-volume changes in the shear-induced glass transition experiments. We show that shear is equally effective as temperature in promoting the glass transition with similar free-volume increases. A shear-induced mechanical instability that leads to a localized deformation in the material is observed. The Eyring model considering the potential-energy landscape does not predict such an instability; however, a modified Eyring model based on lowering the activation energy barriers by deformation works well. Finally, a non-affine deformation model is introduced to explain the free-volume changes during the glass transition as well as the mechanical instability. The fact that both models explain the same physical observation indicates that the modified Eyring model in fact considers the free-energy landscape, in which the energy barriers are lowered due to the contribution of non-affine displacements.