Understanding the rheology of yield stress materials
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Wall slip and fluidity in emulsion flow

5.1 Wall slip in simple yield stress materials - An overview

The boundary conditions for the Navier-Stokes equation describing fluid flow have been debated ever since the original paper of Navier appeared in 1823 [1]. However, it has been reported that ‘simple’ yield stress materials, such as emulsions, foams and cabopol gels, tend to slip rather than to flow near smooth surfaces [2, 3], leading to wall slip. Wall slip can then be understood as a phenomenon that is observed during rheological test as a discontinuity in shear rate near the wall [2].

For many complex fluids, wall slip has been reported, causing misinterpretation of rheological data and being a limiting factor in production processes such as fiber spinning or food extrusion [2, 4, 5]. Additionally, recent works show that confinement affects the flow of concentrated dispersions in an entirely different fashion, namely through collective rearrangements of the dispersed phase [6]. With the increasing miniaturization of flow devices, the Navier-Stokes equation describing fluid flows is debated again [7].
Interestingly, both effects, slip and confinement, lead to a gap-dependent viscosity. The problem is that, in ‘blind’ rheological measurements, usually any dependence of the viscosity on the size of the gap of the measurement geometry is interpreted as wall slip [4, 8].

In this Chapter I use macroscopic and microscopic measurements to show that in fact two types of apparent wall slip exist for a silicone oil-in-water emulsion—a model complex fluid. The first type is due to the formation of a liquid layer with a low viscosity close to the wall. The second is due to a spatial gradient of the viscosity [6] and is only observable when the flow is strongly confined. I find that these two types of apparent wall slip are usually strongly coupled, making their interpretation problematic. By controlling the wetting properties of the walls, I succeed in decoupling the two effects and show in addition that the finite-size effects can be translated into an effective slip velocity.

Macroscopic rheological data are obtained using a rheometer (Anton Paar MCR 301) with cone-plate (CP) and plate-plate (PP) geometries. For simple (Newtonian) fluids, the CP geometry provides a homogeneous distribution of the stress throughout the sample, meaning that it has spatially constant stress ($\sigma$) and shear rate ($\dot{\gamma}$), while the PP geometry allows working with different gaps. Microscopic rheological measurements are performed by means of a confocal laser scanning microscope (CLSM, Zeiss Pascal Live) coupled to a rheometer (Anton Paar DSR 301), enabling the acquisition of velocity profiles in the flowing material by direct visualization of the droplets motion thorough the bottom plate of both CP and PP geometries. Finally to compare the results with previous works [6, 9], I also obtain velocity profiles in glass microchannels (length $L = 10$ cm, breadth $b = 4$ mm and width $w = 400 \mu$m). In all cases, from the measured local velocity gradients and stresses the local viscosity is obtained.

5.2 Samples and surfaces preparation

5.2.1 Model system - Transparent emulsion

The model system is a transparent silicone oil-in-water emulsion that allows for flow visualization. This emulsion was prepared by dispersing silicone oil (Rhodorsil
Wall slip and fluidity

®47 V 500) in an aqueous phase consisting of 46.7 %wt water (Milli-Q ®) and 53.3 %wt glycerol (99 % GC, from Sigma Aldrich). Glycerol was added to the continuous phase in order to match its refractive index with that of the silicone oil; in addition, sodium dodecyl sulfate (SDS, Ultrapure from Sigma-Aldrich) was also added to the continuous phase in such a proportion that the final concentration within it was 1 % wt. This concentration of SDS is high enough to stabilize the emulsion, though low enough to aoid depletion forces that can lead to flocculation, and hence thixotropy [10]. Nile red (from Sigma Aldrich) was added to silicone oil and the oil was subsequently dispersed in the aqueous solution using an IKA T18 emulsifier at 24,000 rpm for 5 min. The resulting emulsion has average-drop size $5 \mu m$ and internal volume fraction, $\phi \approx 0.8$.

5.2.2 Surfaces preparation

The bottom plates in both CP and PP geometries and the walls of the microchannels consist of chemically treated glass, making it possible to change the wettability to both the continuous (water) and dispersed (oil droplets) phases. Hydrophilic surfaces were obtained by cleaning the glass with piranha solution (70% v/v sulphuric acid and 30% v/v hydrogen peroxide, both from Sigma Aldrich), while oleophilic ones were prepared by treating the glass with a hydrogenated silane (OCTEO Dynasylan ®from Degussa) [11, 12]. The upper plate of the PP geometry consists of an oleophilic glass slide, whilst the CP geometry has a roughened cone.

5.2.2.1 Treatment with piranha solution

Glass cover slides and microchannels were sonicated for 15 min in a 2% v/v Decon 90 (from Decon Laboratories Limited) solution. Subsequently the glass surfaces were rinsed with ultra-pure water (Milli-Q ®) and immersed piranha solution for 15 min at 150 °C (the piranha solution was prepared by gently adding 30 mL of hydrogen peroxide to 70 mL of sulphuric acid). The glass surfaces were removed from the piranha solution, rinsed with ultra-pure water and placed in the oven at 200 °C for at least 1 h.
Figure 5.1: Pictures of water, silicone oil and the emulsion’s continuous phase droplets on a glass surface treated with the piranha solution and with the hydrogenated silane (Octeo)

Table 5.1: Contact angles of chemically treated glass surfaces with different liquids, obtained from pictures shown in Figure 5.1

<table>
<thead>
<tr>
<th>Substance</th>
<th>Hydrophilic (°)</th>
<th>Oleophilic (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>35 ± 1.4</td>
<td>90 ± 2.5</td>
</tr>
<tr>
<td>Silicone oil</td>
<td>24 ± 2.5</td>
<td>10 ± 0.6</td>
</tr>
<tr>
<td>Aqueous phase</td>
<td>10 ± 3.0</td>
<td>60 ± 3.0</td>
</tr>
</tbody>
</table>

5.2.2.2 Silanization procedure

For silanizing the glass surfaces, after being treated with the piranha solution and dried in the oven, these were brought to room temperature in a desicator. Subsequently, they were immersed in a silane solution for 30 min, followed by rinsing with iso-propanol (from Sigma Aldrich) and drying in the oven at 75 °C for 1 hour. The silane solution consisted of 48.4 g iso-propanol (from sigma Aldrich), 1.0 g ultra-pure water, 0.1 g hydrochloric acid (from Sigma Aldrich) and 0.5 g silane (OCTEO, Dynasylan ® from Degussa)

The modification of the wetting properties is confirmed by measuring the contact angles of the treated surfaces with ultra-pure water, silicone oil and the emulsion’s continuous phase, as shown in Figure 5.1 and Table 5.1.

Silanization mechanism

Silanization of the glass surfaces consists in the deposition of organic monolayers with controlled architecture, which modify the wettability of the substrate [13]. The general formula of a silane molecule is: $R_nSiX(4 - n)$, where $R$ is a nonhydrolyzable organic moiety that—for the silane used in our experiments—is an alkyl group. Silanes with alkyl groups are widely used to provide hydrophobic surfaces
and to improve, for example, properties related to improved pigment dispersion [14]. The X represents the groups responsible of providing the linkage of the silane with inorganic substrates, in our case, with glass surfaces. These groups are alkoxy moities, such as methoxy or ethoxy, which react with the hydroxyl groups, liberating methanol or ethanol.

The silanization of a substrate involves in a general way, the following steps [14–16]:

(a) Hydrolisis of the three labile-alkoxy-groups attached to the silicon.

(b) Condensation to oligomers (from IUPAC [17] an oligomer is “a molecule of intermediate relative molecular mass, the structure of which essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lowe relative molecular mass.”

Glass surface - Substrate
(c) Hydrogen bonding of the oligomers with hydroxy groups of the substrate.

(d) Bond formation during curing or drying, i.e. the formation of a covalent linkage with the substrate with concomitant loss of water.

5.3 Macroscopic rheological measurements

Macroscopic rheological data is obtained by means of traditional shear rate sweeps [3]. Figure 5.2 shows that oleophilic plates completely suppress wall slip, as the flow curves obtained using these surfaces in both CP and PP geometries coincide with a reference curve obtained using roughened surfaces; the latter is a standard method to prevent wall slip [8, 18]. These curves can be very well described by the classical Herschel-Bulkley equation [19]: \( \sigma = \sigma_y + K\dot{\gamma}^n \), where \( \sigma_y \) is the yield stress, and \( K \) and \( n \) are model adjustable parameters; this model is known to work well for ‘simple’ yield stress materials in the absence of wall slip [3, 20].

Conversely, for oleophilic surfaces at smaller gaps (\( w \leq 50\mu m \) using the PP geometry), but also for the hydrophilic ones, different and in addition gap-size dependent
values of the viscosity are observed, i.e. the same \( \dot{\gamma} \) is obtained for different \( \sigma' \)'s, as shown in Figure 5.2.

### 5.4 Microscopic rheological measurements

Microscopic data is obtained using the CLSM coupled to the rheometer, showing that the surface wettability is key for the boundary conditions. I perform experiments using the CP and PP geometries, observing a constant \( \dot{\gamma} \) for oleophilic plates at large gaps, as observed for simple (Newtonian) fluids. However, when using a hydrophilic plate, all of the material turns as a solid block with the moving upper cone or plate, as shown in Figure 5.3 (a,b). Local velocity measurements are also performed in microchannels (Figure 5.3 (c)), as many of the recent measurements on emulsions were made in microchannels, for which there is a spatial variation of the stress [6, 9]. For these, the results are similar, i.e. for large channel size (\( w = 400 \mu m \) in the smallest direction), “plug flows” are observed for hydrophilic walls, while oleophilic ones result in velocity profiles that can again be perfectly described by the Herschel-Bulkley model, with the same parameters as in Figure 5.2, while taking into account the stress variation over the channel [21].

**Figure 5.2:** Macroscopic flow curves using hydrophilic and oleophilic glass plates in CP and PP geometries. Red symbols correspond to oleophilic surfaces and blue symbols to hydrophilic surfaces. The black line is a fit of the flow curve obtained using roughened surfaces (black symbols) to the Herschel-Bulkley model [19], with \( \sigma_y = 33.32 \text{ Pa}, \ K = 13.43 \text{ Pa} \cdot \text{s}^{0.53}, \) and \( n = 0.53. \)
Figure 5.3: Microscopic measurements using a confocal laser scanning microscope coupled to a rheometer and to a rectangular microchannel. (a), (b) and (c) velocity profiles in: (a), cone-plate geometry (12 mm radius and 1° angle, measured at a radial position equivalent to a gap $w = 90 \, \mu m$) and imposed shear rates $0.25, 0.5$ and $1 \, s^{-1}$ (bottom to top); (b), plate-plate geometry (3.5 mm radius, gap $w = 100 \, \mu m$) and imposed overall shear rates $0.25, 0.5$ and $1 \, s^{-1}$, measured at a radial position where the measured local shear rates are $0.33, 0.17$ and $0.08 \, s^{-1}$ (bottom to top); (c), rectangular microchannel (length $L = 10$ cm, breadth $b = 4$ mm and width $w = 400 \, \mu m$) at $0.2, 0.5$ and $1.2 \times 10^{-2} \, ml/min$ (from bottom to top curves). (d) and (e), microscopic origin of the wettability dependence of wall slip: (d), microscopic image showing that droplets of the flowing emulsion stick to oleophilic glass surfaces, resulting in ‘self-generated roughness’; (e), the same droplets do not stick on hydrophilic glass surfaces, leading to wall slip. In (a), (b) and (c) blue symbols and lines correspond to oleophilic surfaces, red symbols and lines to hydrophilic surfaces. A rheometer is used to induce a deformation in the model emulsion by rotating either a cone or a plate, while flow in the rectangular microchannel is induced using a syringe pump. In (d) and (e) images in the X-Y plane are taken at $z = 0 \, \mu m$, the black bar is $20 \, \mu m$ and arrows are $10 \, \mu m$. 
In a microchannel of length $L$ and width $w$, under an applied pressure drop $\Delta P$, $\sigma$ at a position $z$ is given by the following relation [21]:

$$\sigma(z) = \left( \frac{\Delta P}{L} \right) \left[ z - \left( \frac{w}{2} \right) \right]$$

(5.1)

Then, considering that the flow of the fluid obeys the Herschel-Bulkley model [19, 21], the velocity $v(z)$ is given by:

$$v(z) = \frac{w/2}{\frac{1}{n} + 1} \cdot \frac{1}{\sigma_w K^{1/n}} \left[ (\sigma_w - \sigma_y)^{\frac{1}{n}+1} - \left( \sigma_w \frac{z}{w/2} - \sigma_y \right)^{\frac{1}{n}+1} \right]$$

(5.2)

### 5.4.1 Microscopic origins of slip/no-slip behavior

From the microscopic images shown in Figure 5.3 (d,e), the microscopic origins of the slip/no-slip behavior when using treated glass surfaces is revealed. Figure 5.3 (d) shows that half-spherical oil droplets stick to the oleophilic glass surfaces, which results in a ‘self-generated roughness’. This completely suppresses wall slip, similarly to what happens for roughened surfaces (see Figure 5.2). Conversely, the microscopy image for the hydrophilic system shown in Figure 5.3 (e) reveals that a thin layer of water is present at the surface. Due to the experimental resolution, it is not possible to accurately determine the thickness of this layer; however, since the viscosity of water is many order of magnitude smaller than that of the emulsion, this induces an effective slip of the sample.

Consequently, changing the wettability allows us to suppress or reduce wall slip. However, this does not explain why a gap-dependent viscosity is also observed for strongly confined oleophilic systems. I therefore focus on the gap-dependent viscosity in the oleophilic systems without wall slip. In the CP and in the PP geometries, for gaps $w \gtrsim 50\mu m$, neatly linear velocity profiles that extrapolate to zero at the stationary wall are obtained, as shown in Figure 5.3 (a,b). Conversely, for smaller gaps the situation changes dramatically.
Figure 5.4: Velocity profiles using a PP geometry in: (a), gap $w = 50\mu m$, and (b), gap $w = 30\mu m$. Blue symbols and dashed lines correspond to hydrophilic surfaces, red symbols and lines to oleophilic surfaces. The dashed-black line is referential to the velocity profile that would be obtained in the absence of cooperative effects. The dashed-gray lines are the fittings of the curves after transforming cooperative effects into an effective slip velocity. The same overall shear rates were imposed in both gaps, from bottom to top: 0.25, 0.5 and 1 $s^{-1}$. Profiles were measured at a radial position where the imposed-local-shear rates are 0.33, 0.17 and 0.08 $s^{-1}$. In the absence of wall slip, velocity profiles can be fitted using the fluidity model with $\xi \approx 4.13\mu m$. If wall slip is present, velocity gradients are zero.

5.4.2 Gap-dependent viscosity without wall slip

When the emulsion is sheared in gaps $w \lesssim 50\mu m$, although the velocity profiles do appear to extrapolate to zero, they are non-linear, as shown in Figure 5.4. This indicates that the viscosity varies spatially, since $\sigma$ is constant and the local shear rate $\dot{\gamma}_{\text{local}}$, varies.

From the velocity profiles, the local flow curves shown in Figure 5.5 are obtained [22]. These curves are the result of plotting $\sigma$ as a function of $\dot{\gamma}_{\text{local}}$. Figure 5.5 shows that the local flow curves only correspond to the reference flow curve above a critical gap size. Below this size, gap-size dependent and different viscosities are found, as for a given $\sigma$ different values of $\dot{\gamma}_{\text{local}}$ are obtained.

5.5 Fluidity and gap-size dependent viscosities

The spatial variation of the viscosity as soon as the model emulsion is sheared in a gap $w \lesssim 50\mu m$ can be accounted for using the recently proposed fluidity model [6].
Wall slip and fluidity

Figure 5.5: Local flow curves obtained from the velocity profiles using oleophilic surfaces in a CP and PP geometry, as well as in a microchannel. The black line is the fit of collapsing curves to the Herschel-Bulkley model used as reference.

This model introduces a length scale $\xi$, characteristic of the spatial cooperativity that is at the origin of the spatial variation of the viscosity. The fluidity $f$ is the inverse of the viscosity and its spatial variation in the $z$-direction can be modeled as [6]:

$$f = \frac{\dot{\gamma}}{\sigma} = f_{bulk} + \xi^2 \frac{\partial^2 f}{\partial z^2} \quad (5.3)$$

where $f_{bulk}$ is the fluidity of the bulk.

Velocity profiles in Figure 5.4 were fitted to the following equation [23]:

$$v(z) = v_o + (z - h)\dot{\gamma}_{UP} + \frac{\xi (\dot{\gamma}_{UP} - \dot{\gamma}_{LP})}{\sinh (h/\xi)} \cosh \left[ \frac{z - h}{\xi} \right] - 1 \quad (5.4)$$

where, $v_o$ is the velocity of the upper plate, $h$ is the gap, $\dot{\gamma}_{UP}$ is the shear rate at the upper plate, $\dot{\gamma}_{LP}$ is the shear rate at the lower plate, and $\xi$ is the characteristic length scale.

Considering that $\dot{\gamma} = \frac{dv(z)}{dz}$, (5.3) and (5.4), then the following identification can be made:

$$\xi^2 \frac{\partial^2 f}{\partial z^2} = (f_{UP} - f_{LP}) \frac{\sinh [(z - h)/\xi]}{\sinh(h/\xi)} \quad (5.5)$$
Therefore, for our model system, (5.3) can be written in the following way:

\[ f = f_{\text{bulk}} + (f_{UP} - f_{LP}) \frac{\sinh \left( \frac{(z - h)}{\xi} \right)}{\sinh(h/\xi)} \]  
(5.6)

From the fits one gets the characteristic length scale \( \xi \approx 4.13\mu m \), on the order of the droplets diameter. The fact that this characteristic length scale for the spatial variation of the viscosity is so small explains why when the gap becomes large compared to \( \xi \), the effect of the gradient becomes negligible.

Perhaps more surprisingly, the velocity profiles shown in Figure 5.4 can also be fitted to the standard equation for wall slip with a linear velocity profile that does not extrapolate to zero [4] (5.7), where \( v_s \) is the slip velocity.

\[ v(z) = v_s + \dot{\gamma}_{\text{bulk}} \cdot z \]  
(5.7)

In the experiments presented in this Chapter, the shear rate of the bulk is given by (5.8) with \( f_{\text{bulk}} = f_{UP} \).

\[ \dot{\gamma}_{\text{bulk}} = \sigma \cdot f_{\text{bulk}} \]  
(5.8)

Subsequently, the cooperative effects can be translated into an effective slip velocity, \( v_s \):

\[ v_s = \sigma \int_{z=0}^{z=h} (f_{UP} - f_{LP}) \frac{\sinh \left( \frac{(z - h)}{\xi} \right)}{\sinh(h/\xi)} \, dz \]  
(5.9)

By comparing (5.7) with (5.9) it follows that if this identification is made, \( v_s \) is identical for the two fits—with the standard slip calculation and by considering the cooperative effects.

The net effect of wall slip or confinement is then a decrease in the effective viscosity. The reduction of the viscosity of our model system with the gap size can be compared with the well-known Fähræus-Lindqvist effect [24] in blood flow, i.e. if blood is made to flow in tubes with diameters equal 300 \( \mu m \) or smaller, its apparent viscosity will decrease similarly to what happens here for the emulsion. Additionally, if granular materials are sheared in gaps ten times the particle size or smaller, spatial cooperativity manifests itself identically as a gap-dependent viscosity [25].
The pertinent question for the rheology is then *at what degree of confinement do these cooperative effects appear?* Previous works considering yield stress materials show that cooperative effects can appear at gaps even 250 times larger than the particle size; however, these have always concerned experimental situations with a certain amount of wall slip [6, 9, 23] (See Table 5.2 for a comparison of these works, including values of \( \xi \)). This suggests that the two effects that are considered in this Chapter are usually strongly coupled; namely, a gap-size-dependent viscosity can also be due to a combination of cooperative effects and wall slip, so that the parameters determining the fluidity depend on the real wall slip.

To demonstrate this, I performed measurements of velocity profiles in a CP geometry with a gap bigger than 50 µm \((w = 80\mu m)\) and in presence of partial wall slip. In order to obtain partial slip of the samples, the glass bottom plate of the CP geometry was treated with a fluorinated silane (Dynasylane ®F 8261 from Degussa), following the same silanization procedure mentioned before. This treatment leads to the acquisition of partially-oleophilic surfaces, which causes the partial wall slip.
Table 5.2: Comparison of different works, with partial wall slip and applying the fluidity model

<table>
<thead>
<tr>
<th>System</th>
<th>Gap (µm)</th>
<th>Surface property</th>
<th>Slip velocity</th>
<th>Characteristic Length, ξ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion, drop diameter ≈ 3 µm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>φ = 0.85</td>
<td>250</td>
<td>Rough</td>
<td>Not reported</td>
<td>32</td>
</tr>
<tr>
<td>φ = 0.85</td>
<td></td>
<td></td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>φ = 0.8</td>
<td></td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>φ = 0.8</td>
<td></td>
<td></td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>φ = 0.75</td>
<td></td>
<td></td>
<td></td>
<td>12.5</td>
</tr>
<tr>
<td>φ = 0.70</td>
<td></td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>φ = 0.66</td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Emulsion [23], drop diameter ≈ 3 µm</td>
<td>φ = 0.75</td>
<td>250 - 56</td>
<td>0.02 - 1.2 mm/s</td>
<td>22.5</td>
</tr>
<tr>
<td>Emulsion [23], drop diameter ≈ 3 µm</td>
<td>750</td>
<td>Weakly adhering smooth surface</td>
<td>Not reported</td>
<td>55</td>
</tr>
</tbody>
</table>
The measurements with partial slip show convincingly that if wall slip is present in addition to cooperative effects, $\xi$ is much larger than the size of a droplet ($\xi \approx 12\mu m$), due to the inhomogeneous stress field generated in the system, induced by the presence of partial slip (Figure 5.6) [26].

5.6 Conclusion

In this Chapter an emulsion is used to show that by changing the wettability of the shearing surfaces, the effect of wall slip and cooperative effects on obtaining gap-size-dependent viscosities can be disentangled. Wall slip can be controlled by the formation of a ‘self-generated roughness’ induced by the preferential wettability of the emulsion’s dispersed phase with the solid surface. The cooperative effects due to confinement appear only below a critical width, which for our emulsion is about ten droplet diameters and can be translated into an effective slip velocity. These results provide a better understanding of the origin of apparent wall slip, which is of major importance for both fundamental material studies and industrial processes in which complex flows play a role.

References


