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Wall slip and fluidity in emulsion flow

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The microscopic origin of apparent wall slip is studied systematically using a confocal laser scanning microscope coupled to a rheometer. We obtain flow curves on a model emulsion from classical macroscopic measurements that are compared with flow curves obtained from microscopic measurements. By controlling the wetting properties of the shearing walls, we show that the characteristic length used in the so-called fluidity model, proposed by Goyon et al. [Nature (London) 454, 84 (2008)], can be understood in terms of roughness induced by adsorbed droplets on the surface. Additionally, we disentangle two different effects that contribute to the difference between micro- and macro rheology. Both effects manifest themselves as gap-dependent viscosities due to either the formation of a lubricating layer close to the shearing walls or cooperative effects when the flow is strongly confined. Finally, we show that the cooperative effects can also be translated into an effective slip velocity.

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The boundary conditions for the Navier-Stokes equation describing fluid flows have been debated ever since the original paper of Navier appeared in 1823 [1]. For simple (Newtonian) fluids, a no-slip boundary condition is sufficient for most practical situations; however, the increasing miniaturization of flow devices has led to further debate on this issue [2]. Wall slip has been reported for concentrated dispersions such as emulsions, foams, or gels. This has resulted in misinterpretations of rheology data, and it has become a limiting factor in production processes such as fiber spinning or food extrusion [3–6].

In addition, confinement may affect the flow of concentrated dispersions in an entirely different fashion, namely through collective rearrangements of the dispersed phase. This can be accounted for using the recently proposed fluidity model [7], which introduces a length scale (ξ) characteristic of the spatial cooperativity that is at the origin of the spatial variation of the viscosity (η). The fluidity (f) is the inverse of the viscosity (f = 1/η), and its spatial variation, considering a fluid flowing in the x direction, can be modeled as f = f_{bulk} + ξ^2 σ/η, where f_{bulk} is the fluidity of the bulk and z is the coordinate perpendicular to the x-y plane. This implies that in the absence of any cooperativity, the fluidity would reduce to its bulk value, f_{bulk} = γ/σ_{bulk}, where σ_{bulk} is the shear stress at the bulk.

It has been reported that slip and confinement affect the stability of two-phase flows in microfluidic channels [8]; when considering the flow of concentrated dispersions, both effects lead to gap-dependent viscosities, which in rheology is usually interpreted as wall slip [3,6].

In rheology, an apparent viscosity that depends on the dimensions of the measuring device is usually interpreted in terms of wall slip (see, e.g., [9]) without assuming anything about the involved physical mechanism. The slip length in the classical sense as introduced by Mooney [10] is then simply a way of correcting the gap dependence of the viscosity. The most commonly accepted mechanism is that there is a layer of different viscosity material close to the shearing walls [3]. When considering nonlocal viscosity, the effect is the same as that of wall slip, i.e., the macroscopically measured viscosity becomes a function of the gap size. However, the so-called fluidity model [7] supposes a viscosity that continuously varies in space and that is due to local rearrangements. For example, Bocquet et al. [11] claim that the fluidity model equation "yields a nonlocal constitutive law for the flow, exhibiting as a key dynamic quantity the local rate of plastic rearrangements." Therefore, the interpretation in the two situations, namely wall slip and nonlocal viscosity, is very different [7,9].

In this paper, we perform local measurement of the velocity profiles for two different boundary conditions near the wall and in three different geometries. We conclude that, when fluidity becomes important, the results can also be interpreted in terms of wall slip. This is because the cooperativity length scale is microscopic, and it changes the velocity profile only very close to the wall, on a length scale comparable to the size of the emulsion droplets. A detailed local study of the wall slip by changing the boundary condition shows that the relevant length scale for slip is also the emulsion drop size.

Our model system is a transparent silicone oil-in-water emulsion that allows for flow visualization. It has an average drop size 5 μm, internal volume fraction φ ≈ 0.80, and 21% polydispersity [12,13]. Macroscopic rheology data are obtained using a rheometer (Anton Paar MCR 301) with cone-plate (CP) and plate-plate (PP) geometries. The cone has a 12.5 mm radius and 1°, while the plates in the plate-plate geometry have a 12.5 mm radius. For Newtonian fluids, the CP geometry admits nearly uniform shearing flows, i.e., spatial shear stress stress (σ) and shear rate (γ) that are nearly uniform, as described by [9]; in addition, the PP geometry enables us to work with different gaps (w). Microscopic rheological measurements are performed using a confocal microscope (Zeiss Pascal Live) coupled to a rheometer (Anton Paar DSR 301) that enables the acquisition of velocity profiles in the flowing material by direct visualization of the droplet motion. This is done by looking through the bottom plate of both CP and PP geometries, in which the cone of the CP geometry has a 6 mm radius and a 2° angle, while the upper plate of the PP geometry has a 4 mm radius. Finally, for comparing our results with those obtained by Goyon et al. [7,14], we also acquire velocity profiles in glass microchannels. In all cases, from the measured local velocity gradient (γ_{local}) and stress (σ_{local}) we obtain the local viscosity.
The bottom plates of the CP and PP geometries and the walls of the microchannels consist of chemically treated glass. Hydrophilic surfaces are obtained by cleaning the glass with piranha solution (70% v/v sulfuric acid and 30% v/v hydrogen peroxide, both from Sigma Aldrich), according to the following procedure: (i) sonicate the glass for 15 min in a 10% Decon 90 aqueous solution, (ii) rinse the glass with water, (iii) immerse it in piranha solution for 15 min at 100 °C, (iv) rinse the glass with water, and (v) dry the glass in the oven at 200 °C for 1 h. Additionally, hydrophobic surfaces are prepared by treating the glass with a hydrogenated silane (Dynasylan® from Degussa), according to the following silanization procedure: (i) bring the glass treated with piranha solution and dried in the oven to room temperature in a desiccator, (ii) rinse the glass with isopropanol (from Sigma Aldrich), and (iii) dry the glass in the oven at 75 °C for 1 h [15,16]. The upper plate of the PP geometry consists of a hydrophobic glass slide, while the CP geometry has a roughened cone. The modification of the wetting properties is confirmed by measuring the equilibrium contact angle (θ) of the treated glass surfaces with silicone oil and the continuous phase of our emulsion surrounded by air. We also measure the equilibrium contact angle (θ) of the treated glass surfaces with silicone oil and the continuous phase of our emulsion surrounded by air. We also perform local velocity measurements in microchannels (w = 400 μm), for which there is a spatial variation of the stress [7,14]. For these, the results are similar [Fig. 2(a)]: we observe “plug flows” for hydrophobic walls, while for hydrophilic ones we obtain velocity profiles that are perfectly described by the Herschel-Bulkley model, taking into account the stress variation over the channel [19] [see Eq. (1)] and with the same parameters used for fitting the reference flow curve in Fig. 1, i.e., \( \sigma_w = 33.32 \text{ Pa}, K = 13.43 \text{ Pa s}^{0.53}, \text{ and } n = 0.53 \). We now investigate the microscopic origin of this slip/no-slip behavior. Figure 2(d) shows that half-spherical oil droplets stick to the hydrophobic glass surfaces, resulting in a “self-generated roughness.” This completely suppresses wall slip, well for emulsions in the absence of wall slip [12]. Conversely, for hydrophobic plates at smaller gaps (w \( \lesssim 50 \mu m \)), but also for the hydrophilic ones, we observe different and in addition gap-dependent viscosities, as shown in Fig. 1. As will be shown later in Fig. 2, when performing rheological measurements using hydrophilic lower plates, almost all of the sample moves as a solid block with the same speed of the upper plate (or cone).

Interestingly, for the hydrophobic plates, the flow curves can also be fitted to the Herschel-Bulkley model, with the same K and n parameters given by the fit of the reference flow curve; these fits are not shown, but the values of the fitting parameters are shown in Table I. It is worth noting that the values of \( \sigma_w \) given by the Herschel-Bulkley fit of the flow curves at \( w = 50 \) and 30 μm would correspond to emulsions having a lower internal volume fraction [18], i.e., a flow curve at \( w = 50 \mu m \) would correspond to emulsions having an internal volume fraction \( \phi \approx 0.77 \) with \( \sigma_w \approx 28.90 \text{ Pa} \), while a flow curve at \( w = 30 \mu m \) would correspond to emulsions having an internal volume fraction \( \phi \approx 0.74 \) with \( \sigma_w \approx 16.80 \text{ Pa} \). Therefore, a person performing rheological measurements using our model system in a gap \( w \lesssim 50 \mu m \) would, wrongly, think that either the yield stress of the sample having \( \phi \approx 0.80 \) is much lower than 33.32 Pa, or that the sample has an internal volume fraction \( \phi < 0.80 \).

Microscopic measurements show that the surface wettability is key for the boundary conditions. We perform experiments using the CP and PP geometries, observing a uniform \( \gamma \) for hydrophobic plates at large gaps, as observed for Newtonian fluids. However, when using hydrophilic plates, the material turns as a solid block with the moving upper cone or plate [Figs. 2(b) and 2(c)].

We also perform local velocity measurements in microchannels (w = 400 μm), for which there is a spatial variation of the stress [7,14]. For these, the results are similar [Fig. 2(a)]: we observe “plug flows” for hydrophilic walls, while for hydrophilic ones we obtain velocity profiles that are perfectly described by the Herschel-Bulkley model, taking into account the stress variation over the channel [19] [see Eq. (1)] and with the same parameters used for fitting the reference flow curve in Fig. 1, i.e., \( \sigma_w = 33.32 \text{ Pa}, K = 13.43 \text{ Pa s}^{0.53}, \text{ and } n = 0.53 \).
similarly to what happens for roughened surfaces (Fig. 1). Conversely, for hydrophilic systems, Fig. 2(e) shows that a thin layer of water is present at the surface, which induces an effective slip of the emulsion.

However, in hydrophobic systems without wall slip, gap-dependent viscosities are also observed. In the CP and PP geometries, for \( w \gtrsim 50 \mu m \), neatly linear velocity profiles that extrapolate to zero at the stationary wall are obtained [Figs. 2(b) and 2(c)]. For \( w \lesssim 50 \mu m \) in the PP geometry, although the velocity profiles extrapolate to zero—at the bottom plate the oil droplets stick to the glass surface—they are nonlinear [Figs. 3(a) and 3(b)]. This indicates that the viscosity varies spatially, since \( \sigma_{\text{local}} \) is constant and \( \dot{\gamma}_{\text{local}} \) varies.
From the velocity profiles, we obtain the local flow curves shown in Fig. 4 [20], which are the result of plotting $\sigma_{\text{local}}$ as a function of $\gamma_{\text{local}}$. Figure 4 shows that the local flow curves only correspond to the reference flow curve above a critical gap size. Below this size, we again find gap-dependent and different viscosities, as for a given $\sigma_{\text{local}}$ different values of $\gamma_{\text{local}}$ are obtained.

Velocity profiles in Fig. 3 were fitted considering the fluidity model [14, 21], taking as a starting point the fluidity model equation:

$$\frac{\xi^2 f^2}{d^2 z} + f_{\text{bulk}} - f = 0,$$

(3)

where $f_{\text{bulk}}$ is the fluidity of the bulk emulsion at the applied $\sigma$ and corresponding $\dot{\gamma}$.

Equation (3) is solved with the boundary conditions: (i) at the static lower plate, i.e., at $z = 0$, the fluidity is denoted as $f_{\text{LP}}$; (ii) at the moving upper plate, i.e., at $z = w$, the fluidity is denoted as $f_{\text{UP}}$; and (iii) as the upper plate is always hydrophobic, wall slip is not present at this surface, and the fluidity is assumed to be that of the bulk, thus $f_{\text{UP}} = f_{\text{bulk}}$.

Solving Eq. (3) yields

$$f = f_{\text{UP}} + (f_{\text{UP}} - f_{\text{LP}}) \frac{\sinh[(z - w)/\xi]}{\sinh(w/\xi)}.$$

(4)

By integrating Eq. (4), the velocity field $v(z)$ is determined as $dV/az = \sigma f(z)$. Then

$$v(z) = V_0 + (z - w)\dot{\gamma}_{\text{UP}}$$

$$+ \frac{\xi(\dot{\gamma}_{\text{UP}} - \dot{\gamma}_{\text{LP}})}{\sinh(w/\xi)} \left\{ \cosh \left( \frac{(z - w)}{\xi} \right) - 1 \right\},$$

(5)

where $V_0$ is the velocity of the upper plate, $\dot{\gamma}_{\text{UP}}$ is the shear rate at the upper plate (corresponding to the locally imposed shear rate), and $\dot{\gamma}_{\text{LP}}$ is the shear rate at the lower plate.

From the fits of flow curves shown in Fig. 3 to Eq. (5), the characteristic length scale $\xi \approx 4.5 \pm 0.7 \mu m$ and $\dot{\gamma}_{\text{LP}}$ are obtained; it should be noted that $\xi$ is the same for all fits shown in Fig. 3 and on the order of the droplet diameter.

Additionally, with the values of $\dot{\gamma}_{\text{LP}}$ and $\dot{\gamma}_{\text{UP}}$ the fluidities at the upper and lower plates are determined as $f = \dot{\gamma}/\sigma$. To do this, shear stress was determined by performing macroscopic rheological measurements, which consist in imposing the locally imposed shear rate and measuring the corresponding shear stress; these measurements were performed using the same surfaces used to perform the microscopic measurements.

The values of the fluidities at the upper and lower plates are shown in Table II. This table shows that the fluidity is higher at the lower plate than at the upper plate, which indicates that the shear rate is higher at the stationary bottom plate thanks to the noncooperative effects induced by the fluidity field, as described in [7].

The fact that this characteristic length scale, $\xi \approx 4.5 \pm 0.7 \mu m$, for the spatial variation of the viscosity is so small explains why when the gap becomes large compared to $\xi$, the effect of the fluidity becomes negligible.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>$\sigma_f$ (Pa)</th>
<th>$K$ (Pa s$^n$)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>33.32</td>
<td>13.43</td>
<td>0.53</td>
</tr>
<tr>
<td>PP 100 $\mu$m</td>
<td>33.32</td>
<td>13.43</td>
<td>0.53</td>
</tr>
<tr>
<td>PP 50 $\mu$m</td>
<td>28.90</td>
<td>13.43</td>
<td>0.53</td>
</tr>
<tr>
<td>PP 30 $\mu$m</td>
<td>16.78</td>
<td>13.43</td>
<td>0.53</td>
</tr>
</tbody>
</table>

FIG. 3. (Color online) 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 correspond to hydrophobic surfaces, and red lines correspond to the fittings of the velocity profiles using the fluidity model, with $\xi \approx 4.5 \pm 0.7 \mu m$. The 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 locally imposed shear rates, from bottom to top, are 0.11, 0.24 and 0.48 s$^{-1}$; at this radial position, the velocity of the upper plate was 5.5, 12, and 24 $\mu m$/s, respectively, for $w = 50 \mu m$, and 3.3, 7.2, and 14.4 $\mu m$/s, respectively, for $w = 30 \mu m$.
The pertinent question with regard to rheology is then at what degree of confinement these effects appear. Previous works show that cooperative effects appear at gaps even 250 times larger than the particle size; however, these works have always concerned experimental situations with a certain amount of wall slip [7,14,21], as shown in Table III; the authors of the works shown in Table III explicitly state that wall slip was present in all cases, but in some cases the values of the slip velocities were not reported. The results shown in Table III suggest that the two effects that we consider here are usually strongly coupled. For example, gap-dependent viscosity can also be due to a combination of cooperative effects and wall slip.

Wall slip is determined by the roughness of the shearing surfaces; therefore, we can argue that $\xi$ is highly influenced by the roughness of the shearing surfaces. To demonstrate this, we silanized glass surfaces with a fluorinated silane (Dynasylane®F8261 from Degussa), following the silanization procedure previously described. After treatment with the fluorinated silane, glass slides were immersed in ethanol (from Sigma Aldrich) and left to dry at 20 °C. The solid/liquid/air contact angle of the treated surfaces with the continuous phase and with the oil is $\theta \approx 66 \pm 5^\circ$ and $\theta \approx 55 \pm 1^\circ$, respectively; this shows that, in this case, the surface is less hydrophobic.

By comparing the contact angles of glass surfaces treated with hydrogenated silane, fluorinated silane, and cleaned with piranha solution, we can conclude that when the glass surfaces are more hydrophobic, more oil droplets stick to the glass surface, leading to a suppression of wall slip. The inset in Fig. 5 is an X-Y microscopic image of a glass surface treated with a fluorinated silane, which shows that fewer oil droplets stick to the glass surface, leading to a more inhomogeneous surface. Additionally, we have observed that larger oil droplets slide on the glass surface rather than sticking to it.

We obtained velocity profiles using the shearing surfaces treated with the fluorinated silane in a CP geometry, with a cone having a 6 mm radius and 2° at $\omega = 80 \mu m$ and in the presence of partial wall slip, as shown in Fig. 5.

Partial wall slip is defined as a velocity profile that has a gradient but does not extrapolate to zero; at the same imposed shear rates (0.5 and 1 s$^{-1}$), when “total” wall slip is present, the material moves like a solid block at the speed of the upper cone, as shown in Fig. 2(c). The emulsion used to obtain the velocity profiles shown in Fig. 5 is the same as that used to obtain the velocity profiles shown in Figs. 4 and 3.

These results confirm that the cooperativity length scale is microscopic, on a length scale comparable to the size of the emulsion droplets. The local study of the wall slip by changing the boundary condition shows that the relevant length scale for slip is also the emulsion drop size.

Our results then confirm that $\xi$ is influenced by the boundary conditions [21]. In the absence of wall slip and for our highly jammed and confined system, $\xi$ is of the order of the diameter of one drop (Fig. 5), in agreement with recent simulations [23]. Conversely, if wall slip and cooperative effects are present (Fig. 5), $\xi$ is found to be larger for the same material ($\xi \approx 12 \mu m$), due to the inhomogeneous stress field induced by the presence of partial slip [24]. In addition, Fig. 5 shows that in this case, we observe nonlocal effects in a geometry that has

![FIG. 4. (Color online) Microscopic flow curves obtained from the velocity profiles using a hydrophobic microchannel as well as hydrophobic plates in CP and PP geometries. The black line is the fit of collapsing curves to the Herschel-Bulkley model used as a reference.](image)
TABLE III. Comparison of different characteristic lengths ($\xi$) used for applying the fluidity model.

<table>
<thead>
<tr>
<th>System</th>
<th>Gap ($\mu$m)</th>
<th>Surface</th>
<th>$V_s$ ($\text{mm/s}$)</th>
<th>$\xi$ ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion with drop diameter $= 6.5 \mu$m</td>
<td>Polydispersity = 20%</td>
<td>Rough</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>$\phi = 0.85$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polydispersity = 36%</td>
<td></td>
<td></td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>$\phi = 0.85$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polydispersity = 20%</td>
<td>Rough</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>$\phi = 0.80$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polydispersity = 36%</td>
<td>Rough and smooth</td>
<td>0.02–1.2</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>$\phi = 0.75$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polydispersity = 36%</td>
<td>Rough and smooth</td>
<td></td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>$\phi = 0.70$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polydispersity = 36%</td>
<td>Rough and smooth</td>
<td></td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$\phi = 0.66$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polydispersity = 20%</td>
<td>Rough and smooth</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>$\phi = 0.75$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polydispersity = 20%</td>
<td>Rough and smooth</td>
<td></td>
<td>22.5</td>
</tr>
<tr>
<td>Emulsion with drop diameter $\approx 3 \mu$m</td>
<td>Weakly adhering</td>
<td>Not reported</td>
<td></td>
<td>750</td>
</tr>
</tbody>
</table>

a nearly uniform stress and thus should not have those effects. This suggest that, at least in the absence of wall slip, $\xi$ can be understood in terms of a homogeneous roughness induced by the adsorbed oil droplets on the wall. However, as Fig. 5 also shows, there is still a small amount of wall slip present in the sense that the velocity profiles do not exactly extrapolate to zero. This clearly makes it difficult to disentangle wall slip and fluidity effects. Since the velocity profiles are necessarily averaged over a certain surface area, this may even imply that different near-wall regions with locally varying surface roughnesses have a slightly different interaction with the flow.

In conclusion, we show that by changing the surface chemistry, i.e., the wettability, we change the roughness of the shearing surfaces. If the surface chemistry is such that drops of oil adhere onto the surface, the attached drops generate a roughness that is exactly on the scale of the drops. This is known to be the most effective way of preventing slip; in experiments on granular materials, a layer of the same grains is usually glued onto the surface, similarly to what happens here with the wall. Therefore, by changing the surface chemistry, wall slip can be controlled due to the formation of a “self-generated roughness” induced by the preferential wettability of the disperse phase with the solid surface. The cooperative effects due to confinement appear only below a critical width, which for our emulsion is a diameter of about ten droplets. In the absence of wall slip and for highly confined systems, the viscosity varies over a characteristic length scale $\xi$, which for our emulsion is of the order of the diameter of one drop. This implies that the observed effects might be due to the fluid elements or droplets that “bump” into the roughness of the wall, and the effect of the wall extends over the distance $\xi$, implying that $\xi$ can be understood in terms of roughness induced by the adsorbed oil droplets on the wall. We also succeed, in some but not all cases, in disentangling the effect of wall slip and confinement on obtaining gap-dependent viscosities by changing the wettability of the shearing surfaces. Finally, “cooperative effects” 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.