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Wall slip mechanisms in direct and inverse emulsions

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Abstract

We carry out a series of experiments with the aim of completing our knowledge of wall slip characteristics, through a deductive approach based on macroscopic behavior observations. More precisely, we use model materials (direct and inverse emulsions) and determine the variations of wall slip properties depending on the material parameters (droplet size, concentration) and boundary conditions of the flow (free surface or flow between two solid surfaces, normal force, flow beyond yielding, and coated or rough surface). The wall slip characteristics are determined from long creep tests at different levels and from internal measurements of the velocity profile in the capillary or the Couette flow as determined by magnetic resonance imaging. First, we show that the slip yield stress is due either to edge effects in relation with evaporation then pinning around the line of contact or to a kind of adhesion of the suspended elements to the wall. This adhesion effect varies with the characteristics of the solid surface (interaction with elements, roughness), and wall slip (below the yield stress) disappears when the adhesion or adherence leads to a wall slip yield stress expected to be larger than the material yield stress. Then, we show that, below the yield stress, the slip velocity vs shear stress (from which the slip yield stress has been removed) relationship is linear. The corresponding value for the apparent slip layer made of interstitial liquid appears to be independent of the concentration and to vary only slightly with the droplet size. Moreover, it is independent of the normal force (below the critical value inducing elongation) and other experimental conditions, e.g., it is the same for free surface flows. Although the origin of this phenomenon remains to be found, the following scheme appears to be consistent with all observations: the droplets are attracted at a very short distance from the wall, forming regions of small area in which the liquid layer thickness is very small, the shear stress being dominated by the shear in these regions. Finally, this apparent layer thickness increases at the approach of the yield stress and beyond, or if a slightly rough surface is used, leading to a faster (quadratic?) variation of the slip velocity as a function of the stress. © 2018 The Society of Rheology. <https://doi.org/10.1122/1.5046893>

I. INTRODUCTION

Concentrated suspensions, which are yield stress fluids, flow only when submitted to a stress greater than a critical stress, called yield stress (τ_c) [1,2]. However, on smooth surfaces, they can move even under smaller stress, a phenomenon called wall slip. When it occurs, the bulk material moves as a rigid block for stress below τ_c , which defines a slip velocity V_S , but it has also been observed that some wall slip can still occur at larger stress [3,4]. Wall slip has a critical impact on rheological characterization since in that case the apparent flow does not reflect the bulk properties of the fluid. It may also play a critical role in various applications involving food [5], cosmetic [6], civil engineering [7,8], and biological [9] materials.

To gain quantitative insights into wall slip properties, it is usual to compare rheological measurements, obtained with smooth surfaces, with measurements under similar flow history but now with rough surfaces assumed to suppress

46 wall slip. This, in particular, provides a straightforward mea- 47
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liquid layer separating soft suspended objects from the wall is maintained by the balance between the lubrication flow in the slip layer, which creates a lifting force that pushes the suspended particles away from the solid surface, while the elastic force induced by particle deformation and related to the osmotic pressure in the concentrated system tends to reduce the slip layer thickness. This approach basically leads to a quadratic dependence of the slip velocity with regard to the shear stress. A later work [17] completed this theory by considering various short-range interactions between the first layer of the soft particles and the solid surface. In the case of the dry foams, Denkov *et al.* [18] proposed the shear stress to depend on a sum of two terms involving the wall slip velocity at different powers. This expression has later been revised by Le Merrer *et al.* [19].

In the case of hard sphere suspensions, Ballesta *et al.* [20,21] performed a detailed analysis of rheological data and showed that the relationship between the shear stress and the slip velocity is an affine function with a constant term corresponding to the residual stress τ'_c , beyond which wall slip is apparently observed to occur. The existence of this wall slip yield stress had in fact been remarked in previous works with other material types, in particular, emulsions [22] and microgels [11]. However, it was reckoned that the physical origin of τ'_c is unclear [11,20,22]. It seems indeed somewhat contradictory to have both wall slip *a priori* associated with the shear of some liquid layer covering the wall and a constant stress term *a priori* associated with some kind of friction of the elements in contact with the wall. Recently, Zhang *et al.* [23] showed that if τ'_c is considered as an edge effect and removed from the stress to get the flow curve strictly associated with wall slip, then a linear wall slip law applies to a wide range of systems, similar to previous results for hard sphere suspensions [20,21].

The fact that such a general behavior is obtained for different material types (soft or hard particles, plateletlike, or rounded particles) and structures (large or small porosity) suggests that some generic origin of wall slip should be sought, but this seems rather challenging. At first sight, it is natural to consider that such a result corresponds to the hydrodynamic lubrication regime proposed by Meeker *et al.* [16], associated with a constant thickness (δ) of lubricating liquid layer. However, for such different materials, we hardly see what could be the origin of this regime and how it could lead to similar values for δ . In fact, the existence of a uniform and constant liquid layer separating the bulk and the wall is difficult to support if we consider that the bulk is a heterogeneous material made of elements forming a jammed, disordered structure; such a structure is necessarily rough, with a roughness of the order of the element size, and thus, in general much larger than δ (at least for the above listed material types). As a consequence, we rather expect that this rough structure would tend to approach the wall at the closest possible distance. The question now is why we still get some apparent wall slip under such conditions. For emulsions, Princen [22] considered that there always remains a thin liquid layer between suspended droplets and a solid wall, which would result from various repulsive and attractive forces, but did not provide more explanation. Recently, Le

Merrer *et al.* [19] provided a detailed approach of this problem, considering that this layer results from a balance between the osmotic pressure (due to capillary forces) in the foam and repulsive van der Waals and electrostatic forces. They, thus, estimated the value of δ between 5 and 50 nm.

Here, we carry out a further exploration of wall slip characteristics, which might provide further elements toward the understanding of the origin of wall slip. Since a direct view of the phenomena at the scale of the liquid layer along the wall, i.e., the ideal solution, is extremely challenging, our approach will be essentially macroscopic and deductive, relying on precise characterization under various conditions. More precisely, we will carry out different types of experiments with model systems to observe the variations of wall slip properties depending on material parameters (droplet size, concentration) and boundary conditions of the flow [free surface or flow between two solid surfaces, normal force, flow beyond yielding, coated surface, “intermediate” rough surface (not much larger than the particle size)]. In this frame, we will rely either on systematic creep tests at different levels or on internal measurements of the velocity profile in the capillary or the Couette flow as determined by MRI. Finally, the physical mechanisms at the origin of wall slip, seen as the interaction between the rough bulk and the wall, will be reanalyzed in the light of these results.

II. MATERIALS AND METHODS

A. Emulsions

First, we used oil-in-water (direct) emulsions with two different compositions: composition A has silicone oil (viscosity 0.35 Pa s) as dispersed phase and a continuous phase (viscosity 5 mPa s) made of 48.5 wt. % distilled water, 48.5 wt. % glycerol, and 3 wt. % myristyltrimethylammonium bromide (TTAB, Sigma-Aldrich); composition B contains dodecane oil (viscosity 1.36 mPa s) as dispersed phase and a continuous phase made of distilled water with 3 wt. % sodium dodecyl sulfate (SDS, Sigma-Aldrich). In addition, we used water-in-oil (inverse) emulsions at different water concentrations; 150 kg of CaCl_2 per cubic meter of water was added; the corresponding ions are dispersed in the droplets in a nonhomogeneous way, which induces some electrostatic field and finally, some repulsion between the droplets covered by the nonionic surfactant, which further contributes to stabilize the emulsion; the continuous phase is a dodecane oil with 7.5 wt. % of Span 80 (a commercial mixture of long chain sorbitan esters, including sorbitan monooleate). The preparation methods were similar to those used in previous works [24,25]. Two emulsifiers were used to prepare the emulsions. The first one is a Couette emulsifier (only for composition A), with a 100 μm gap between stator and rotator and a relative rotation velocity up to 600 rpm, inducing a shear rate of 16 200 s^{-1} . A Silverson mixer (model L4RT), equipped with a rotating steel blade inside a punched steel cylinder, was also used as the emulsifier. During the preparation, the fluids are sheared and the oil phase is broken into small droplets while the water or water/glycerol phase fills the surrounding environment, and the interface is stabilized by surfactants (TTAB and SDS). For composition

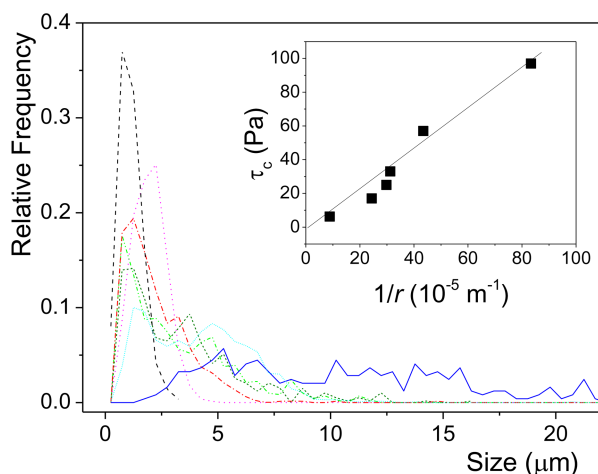


FIG. 1. (a) Droplet relative frequency as a function of size for emulsions made either with a Couette emulsifier at different rotation velocities: A1a, 600 rpm (light green dash dot dot), A1b, 600 rpm (dark green short dash), A2 300 rpm (light blue short dot), A3 150 rpm (dark blue) or with a Silverson emulsifier: A4 6000 rpm (black dash), A5 2400 rpm (red dash dot), B 6000 rpm (magenta dot). The oil concentration of the emulsions is 82 vol. %. The mean droplet sizes and polydispersities for these emulsions are A1a, 3.2 μm , 0.8; A1b, 3.4 μm , 0.7; A2, 4 μm , 0.6; A3, 11 μm , 0.8; A4, 1.1 μm , 1.6; A5, 2.3 μm , 0.7; B, 2 μm , 0.4. The inset shows the yield stress of each material as a function of the inverse of the mean droplet size for the same composition (A1–A5).

To characterize the droplet size distribution, we used images of diluted emulsion samples captured with a confocal microscope and evaluated the particle size histogram with the software ImageJ. From the size distribution, we calculate mean droplet radius, r , and polydispersity (i.e., $\sqrt{[\text{mean}(\text{size}^2) - \text{mean}^2(\text{size})]/\text{mean}(\text{size})}$) (see Fig. 1). Although the distributions are not similar, there is a clear variation of the mean radius. In the inset of Fig. 1, the yield stress value of each emulsion is shown as a function of the inverse of the mean droplet size. It appears to follow a linear relationship, which is in agreement with the theoretical prediction of Princen and Kiss [26].

B. Surfaces

Different surface types were used for rheometry and inclined plane tests. Smooth silicon wafers are single side polished single-crystalline silicon wafers (Si-Mat). These surfaces are extremely smooth, with a root mean squared roughness (from the mean surface level) smaller than 0.3 nm, which is in the order of a single atomic silicon monolayer. This roughness was measured by atomic force microscopy [27]. This surface is later named “smooth surface.” As silicon oxidizes itself naturally when exposed in air, parts of the surface may have become SiO_2 .

A Teflonlike surface produced on top of a silicon wafer is also prepared by depositing a fluorocarbon thin film layer on the polished side of silicon wafers. Such a fluorocarbon thin film coating was produced by exposing the silicon surface for 20 s to a plasma of C_4F_8 under a flow rate of 200 cm^3/min , a pressure of 20 Pa, and a radio-frequency source power of 1800 W with bias power of 10 W. The resulting Teflonlike thickness is in the order of 100 nm. The plasma process resulted in a conformal deposition with no observable roughness under scanning electron microscope (SEM) and under interferometric optical profiler, which led us to the conclusion that it is much below 10 nm.

Black Silicon is a submicrometer scale structured silicon surface obtained by surface-modification of a silicon wafer. The surface has a needle-shaped microtexture and the needles have a very high aspect ratio (typically 10) [28,29]; the depths of the holes are about 5 μm . Due to its structure, it

A (at an 82% oil volume concentration), the rotation velocity of the rotator (for the Couette emulsifier) or the rotating blade (the Silverson emulsifier) were varied (see Fig. 2) to obtain emulsions (named A1 to A5) with different mean droplet sizes. Note that the final emulsion characteristics are also dependent on other parameters such as the time of shear and the exact sample volume so that we could not precisely control the droplet size distribution (around the mean value): two emulsions A1 prepared through the same protocol may lead to slightly different droplet size distributions (see Fig. 1). For direct emulsions of composition B and inverse emulsions at different concentrations of the suspended phase (from 72% to 92% for composition B and 72% to 86% for the inverse emulsions), we only used the Silverson emulsifier at 6000 rpm. The characteristics of these different materials are also recapped in the Appendix.

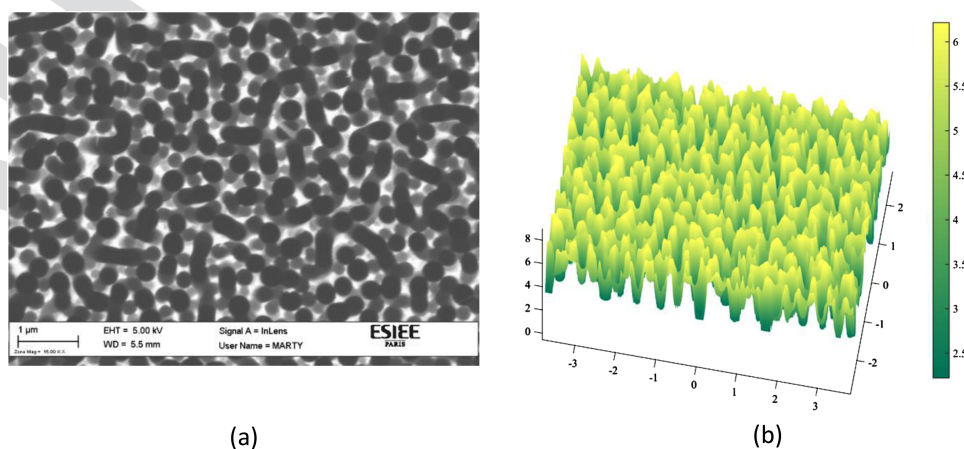


FIG. 2. (a) Top-view SEM image of Black Silicon and (b) 3D reconstruction; the unit of the scale bar is μm .

241 appears Black to the naked eye and has interesting wetting
 242 properties, as it can be made either superhydrophilic or
 243 superhydrophobic by subsequent thin film coatings. For
 244 instance, Teflon coating of Black Silicon makes it super-
 245 hydrophobic, while silicon dioxide coating makes it
 246 superhydrophilic [30]. While different techniques can be
 247 implemented to produce Black Silicon, our samples were
 248 produced by plasma etching at cryogenic temperatures [29].
 249 Silicon wafers were exposed to a plasma compound of SF₆
 250 and O₂ at −120 °C under a flow rate of 200 sccm of SF₆ and
 251 10 sccm of O₂, a pressure of 1.5 Pa, and a radio-frequency
 252 source power of 1000 W with bias voltage of −10 V. The
 253 etching time was varied from 5 to 15 min so as to reach dif-
 254 ferent needle depths and related aspect ratios. Optionally, the
 255 resulting structured Black Silicon surface was subsequently
 256 conformally coated with a Teflonlike layer produced follow-
 257 ing the process described in the previous paragraph. From a
 258 top-view scanning electron microscope [Fig. 2(a)], it is possi-
 259 ble to reconstruct the 3D topology of Black Silicon
 260 [Fig. 2(b)] by a conversion of grey level to height [31].
 261 Figure 2 corresponds to a total etching time of 10 min. When
 262 we increase the time to 30 min, we see no noticeable change
 263 in the mean height of the needles. Teflon-coated Black
 264 Silicon is known to be a superhydrophobic surface for pure
 265 water, exhibiting large contact angles (also known as the
 266 Lotus effect) [32,33]. However, we observed that the intersti-
 267 tial liquid of our emulsions has a very small contact angle on
 268 Black Silicon (<5°), possibly because the liquid (water with
 269 surfactants or water + glycerol with surfactant) wets all the
 270 space between the needles, thus, the surface appears to be
 271 hydrophilic with respect to the interstitial liquid (water and
 272 glycerol mixture) of the direct emulsions.

273 Finally, these Black silicon surfaces provide an intermedi-
 274 ate roughness, i.e., of the order of the droplet size. Besides,
 275 we used what we will call in the following “rough surfaces,”
 276 either provided by the manufacturer (Malvern Kinexus, stain-
 277 less steel, roughness = 600 μm) or made by sticking a
 278 medium grit emery cloth (OTG®, roughness ≈ 200 μm) on
 279 the shearing surfaces. These roughnesses are much larger
 280 than the element size, and *a priori* no slip is expected to
 281 occur in that case.

282 For all the three surfaces (silicon/silica, silicon with
 283 Teflonlike coating, and Black Silicon), we have measured the
 284 equilibrium contact angle of a droplet of the dispersed phase
 285 lying on the solid surface and surrounded by the continuous
 286 phase. The data are reported in the Appendix.

287 For MRI measurements, we used the capillary and
 288 Couette geometries. Different glass capillary diameters were
 289 used: 2, 1.2, 1, 0.8, and 0.6 mm. As for the Couette cell, the
 Q3 290 inner cylinder (diameter 16 mm) is made of PMMA, and the
 291 cup (diameter 17.95 mm) is made of glass. The gap is finally
 292 0.975 mm. Although it is likely that the roughness of these
 293 surfaces is situated much below 1 μm, we have no more
 294 precise information.

295 C. Rheometry

296 For the rheometrical tests, we used a stress controlled
 297 Malvern Kinexus pro+ rheometer equipped with parallel disk

geometries of radius R . Except when mentioned, the disk 298
 diameter was 50 mm. The working gap (h) was 1 mm. The 299
 top plate was a serrated surface. Different surfaces are used 300
 as bottom plate: first, a serrated surface with the same rough- 301
 ness as the top surface and then, silicon wafers or Black 302
 Silicon surface to look at the slip behavior. The experimental 303
 procedure is as follows. We set up the sample on the bottom 304
 surface and approach the upper plate until the fixed gap is 305
 reached. Then, we remove the excess of material at the 306
 periphery. Then, we cover the sample in a water-saturated 307
 environment and start the tests. Note that the rheometer is 308
 able to impose simultaneously a vertical force and a torque to 309
 the rotating axis. 310

The rheometer applies a torque M to the upper plate and 311
 measures its rotation velocity Ω . The rotation of the rough 312
 upper plate implies that the velocity of the material along the 313
 upper plate and at a distance r from the axis is equal to Ωr so 314
 that the apparent shear rate in the material at a distance r is 315
 $\dot{\gamma}_0 = \Omega r/h$. Thus, the shear rate and, as a consequence, the 316
 shear stress vary with the distance from the axis. In this 317
 context, the usual approach involves computing a “mean” 318
 stress by dividing the torque by $2\pi R^3/3$. The resulting 319
 shear stress is also that which would be obtained if the 320
 stress was homogeneous in the gap since in that case: 321
 $M = \int_0^R 2\pi r^2 \tau_0 dr = 2\pi R^3 \tau_0/3$. The corresponding “mean” 322
 shear rate is taken as that observed at the distance $0.75R$ from 323
 the axis: $\dot{\gamma} = 3\Omega R/4h$. In fact, mean values do not mean 324
 anything in the absence of knowledge of the effective rheo- 325
 logical behavior of the material and the resulting stress field 326
 in the gap. So it is more appropriate to call these variables 327
 the apparent shear stress and the apparent shear rate and 328
 write them as, respectively, τ and $\dot{\gamma}$. It is, nevertheless, worth 329
 noting that for a Newtonian behavior, the exact stress at a 330
 radial distance $0.75R$ is $3\tau_R/4 = 3M/2\pi R^2$. This means that 331
 the apparent shear rate and shear stress correspond to the 332
 exact values for the local shear stress and shear rate at this 333
 distance, and thus reflects the exact rheological behavior of 334
 the material. Furthermore, for a yield stress fluid, it may be 335
 shown that this approach provides an excellent approximation 336
 of the relationship between the shear stress and the shear rate 337
 (see the Supplementary Material of [24]). 338

To obtain the flow curves, we apply a sequence of creep 339
 tests, in which we impose a constant stress τ while recording 340
 the shear strain as a function of time. When the steady state 341
 flow is reached, i.e., the strain increases linearly as a function 342
 of time in log–log scale (see Fig. 4), we calculate the shear 343
 rate $\dot{\gamma}$ as the slope of the strain–time curve in the linear scale. 344
 After 5 s of rest, we repeat the same sequence for another 345
 level of τ , until obtaining the flow curve. During this 346
 sequence, we also check the reproducibility of the data at 347
 some stress values, in order to be sure that there is no signifi- 348
 cant irreversible evolution of some material characteristics or 349
 sample shape. 350

D. Inclined plane tests 351

The inclined plane is prepared by mounting the wafer on a 352
 rotary stage, by which we can control the angle of inclination 353
 i with a precision down to 0.5°. We place a sample volume, 354

355 controlled with a graduated syringe, just below the top of the
 356 wafer. Different volumes were used between 0.2 and 2 ml.
 357 For each volume, we carried out tests for different i from the
 358 lowest to the largest possible values (depending on the mate-
 359 rial behavior). When placed on the solid surface, the sample
 360 may slightly spread and move along the steepest slope.

361 To record the form and the displacement of the drop, a
 362 camera was placed above the wafer. We started recording
 363 immediately after loading the sample. The sampling fre-
 364 quency ranged between 0.125 and 1 frames per second. To
 365 quantify the displacement and the contact area of the sample
 366 with the solid surface, we covered a part of the wafer with a
 367 graph paper. We used ImageJ to calculate and plot the instan-
 368 taneous position (with respect to the initial position) as a func-
 369 tion of time. To do so, we set the scale of the image using the
 370 graph paper in the recorded images to convert pixels into SI
 371 units, then we fitted the image of the sample with a polygon to
 372 calculate the contact surface S . After binarizing the images, we
 373 used Multitracker plugin in ImageJ to obtain the position of the
 374 centroid of the image as a function of time.

375 E. MRI velocimetry

376 MRI Velocimetry in capillaries has been performed in
 377 LEMTA at Université de Lorraine. A flow rate-controlled
 378 syringe injects the inverse emulsion (72 vol. %) to the capil-
 379 lary positioned inside the magnet at different flow rates.
 380 Longitudinal velocity measurements start once a stationary
 381 flow is established. The velocity profile acquisition was
 382 carried out with Bruker Avance III 600 Wide Bore spectrom-
 383 eter (magnetic field $B = 14.1$ T, 600 MHz proton resonance
 384 frequency) with 150 G/cm gradient system. The microimag-
 385 ing probe (MicWB40) used is manufactured by Bruker and it
 386 is equipped with a 10-mm-diameter resonator. The velocity
 387 profiles are acquired using a flow encoding spin-echo proto-
 388 col: classical spin-echo MRI experiment with in addition
 389 bipolar gradient pulses in order to encode the phase shift
 390 arising from the flow [34]. The geometrical parameters are as
 391 follows: the field of view (FOV) is $0.3 \text{ cm} \times 0.3 \text{ cm}$ (for the
 392 capillaries of 2 and 1 mm diameter) and $0.4 \text{ cm} \times 0.4 \text{ cm}$ (for

the capillaries of 1.2, 0.8, and 0.6 mm diameter); the thick- 393
 ness slide ranges from 0.2 to 1.5 cm and the matrix is $256 \times$ 394
 256 pixels. The acquisition time is about 1 min. The velocity 395
 profiles (pixel size) obtained have a spatial resolution of 396
 about $10 \mu\text{m}$ (for the capillaries of 2 and 1 mm diameter) and 397
 $16 \mu\text{m}$ (for the capillaries of 1.2, 0.8, and 0.6 mm diameter). 398
 For each 2D flow map, we represent the velocity in each 399
 pixel as a function of its distance to the center, then average 400
 to finally obtain a single velocity profile for each flow rate. 401

MRI velocimetry measurements in the Couette cell have 402
 been carried out in Bruker Biospin GmbH. The NMR 403
 method for the velocity measurement is a ‘‘Pulsed Gradient 404
 Spin Echo Velocity Imaging’’ sequence [35], generating 2D 405
 spatially resolved velocity maps from which 1D velocity pro- 406
 files across the gap of the Couette cell are extracted. The 407
 Couette cell characteristics are the following: the inner cylin- 408
 der, made of PMMA, has a diameter of 16 mm and a length 409
 of 99 mm, and the outer cell, made of glass, has a diameter 410
 of 17.95 mm and a length of 103 mm. The inner cylinder is 411
 mounted to a motor, capable of controlling the rotation 412
 velocity from 0 to 10 Hz (0.5 m/s on the surface of the inner 413
 cylinder). The outer cup is kept static. The Couette cell is 414
 immersed into a static field of 300 MHz (7 T). The tempera- 415
 ture is fixed at 25°C . In the plane perpendicular to the axis 416
 of the cylinder, the acquisition window is a parallelogram of 417
 radial length 6.4 mm, tangential width 10 mm, and thickness 418
 (along cylinder axis direction) 12 mm. We then obtained a 419
 2D velocity map in a plane perpendicular to the cylinder 420
 axis, from which we extract the velocity profile along a 421
 radius by averaging data over a (tangential) thickness of 1.25 422
 mm. To determine the slip velocity along the inner cylinder 423
 surface, we fit the profiles near the wall with a linear function 424
 and the velocity associated with its intersection with the wall 425
 is then subtracted from the imposed tangential velocity of the 426
 cylinder. The slip velocity at the outer cup wall is directly 427
 obtained from the intersection of a linear function fitted to 428
 the profile near the wall. The validity of this (basic) approach 429
 was confirmed by checking that it gives a negligible wall slip 430
 velocity from measurements with a Newtonian fluid (water + 431
 glycerol). 432

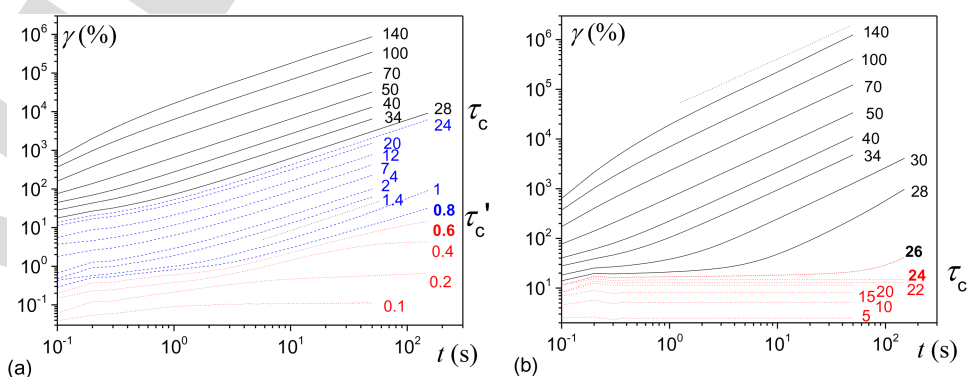


FIG. 3. Typical aspect of creep tests for a yield stress fluid (emulsion A1) and different solid surfaces: shear deformation as a function of time. (a) Smooth bottom surface; red dotted curves correspond to the solid regime, blue dashed curves to the slip regime, and black curves are the shear regime; in this example, the slip yield stress τ'_c is situated between 0.6 and 0.8 Pa; (b) rough surfaces; red dotted curves indicate the solid regime, black curves indicate the shear regime; here the yield stress τ_c is situated between 26 and 28 Pa, even if there is some residual deformation at long times at 26 Pa, it does not seem to reach a steady state flow (with a slope 1 in the logarithmic scale). The stress levels in Pascals are indicated in the figures. The short straight dotted lines in both figures with a slope 1 serve as a guide for the eye; a linear evolution of the deformation with time corresponds to a steady simple shear.

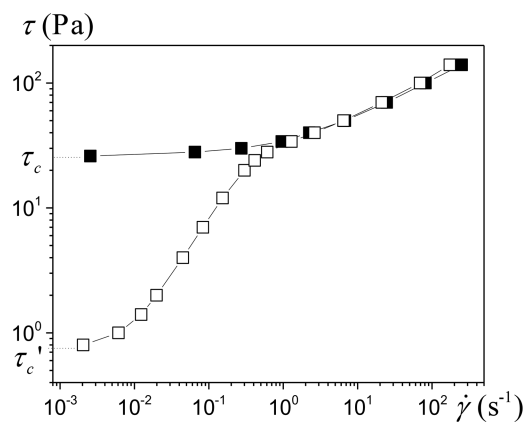


FIG. 4. Flow curves deduced from the steady state flow data of Fig. 3: bottom smooth surface (open squares) and rough surfaces (filled squares).

that no steady state flow or wall slip can be obtained for a stress below τ'_c . This makes it possible to distinguish clearly the slip regime below the yield stress and then deduce the slip velocity. Note that around the yield stress the two curves (with smooth or rough surfaces) flatten and tend to superimpose. In that case, there may still exist some wall slip for smooth surfaces, but since now the apparent velocity results from both a bulk flow and a wall slip the above straightforward reasoning, allowing to deduce the wall slip velocity is not sufficient. An approach would involve withdrawing, for each stress value, the shear rate observed with rough surface from the apparent shear rate with smooth surfaces, to get the apparent shear rate resulting from wall slip. However, this procedure can hardly provide reliable data due to the high sensitivity of shear rate to stress for the bulk flow and the sensitivity of the stress to the exact shape of the sample at its periphery [2]. A measure of the possible wall slip when a bulk flow exists should be carried out with a technique allowing a direct internal measurement.

Although the qualitative trends of creep tests for all materials are similar, a distinction appears between direct and inverse emulsions concerning the characteristics of their flow curve. For direct emulsions, τ'_c may slightly fluctuate if we repeat the test. For inverse emulsions, τ'_c appears to be significantly larger than the values observed with direct emulsions and varies in a wider range. This point will be discussed further in Sec. III B.

B. Origin of the wall slip yield stress

1. Direct emulsions

In inclined plane tests, we observe that while the drop of (direct) emulsion slowly moves downward, two lines of deposit of material remain along the sides of the drop [23]. We also note that a very thin liquid layer may appear on the solid surface at the rear of the sample, but quickly evaporates, and then we do not detect any more liquid on the solid surface in this region. It can be concluded that the material slips along most of its surface of contact with the plane, but some bulk material may be sheared along the edge of the sample.

Let us now examine the consequences of this effect on rheometrical tests. To start with, we check that it also occurs in a rotational geometry. Instead of a full circular layer as for standard rheometrical tests, we confine a smaller volume (i.e., a drop) of material between the two disks of the rheometer, with the drop center placed at some distance from the axis. Under these conditions, when the upper (rough) disk rotates, it drifts the material in rotation around the axis and the squeezed drop slips over the smooth bottom surface. Then, we observe that there remains a circular track of bulk material around the internal and external edges of the sample [see Fig. 5(a)]. These tracks are typically a few hundreds micrometers to 1 mm thick and wide. From this observation, we deduce that there is such a small volume of material sheared at the periphery during a standard rheometrical test, i.e., with the sample filling all the gap between the tools, but it is not directly visible since the material always covers the whole surface of contact.

III. EXPERIMENTAL RESULTS

A. First results

Let us first look at the material behavior during creep tests with a smooth surface [Fig. 3(a)]. For stress below a critical yield stress τ'_c , also called the slip yield stress, the material undergoes a small deformation, typically below a few percents, which finally reaches a plateau, indicating that there is no more motion; the material's response in that case is that of a solid. For stress larger than τ'_c , the deformation is larger and finally, increases linearly with time, indicating that a steady state flow is reached (apparent liquid regime). A critical point in this approach is that we determine the slip yield stress, not by fitting some function in the slip regime, but by determining its exact value from the observation of the transition between two regimes (i.e., flow or stoppage).

Creep tests with rough surfaces, i.e., for which we *a priori* do not have wall slip, yield similar results but the transition between the apparent solid and liquid regimes occurs at a higher level [see Fig. 3(b)], which now corresponds to the yield stress τ_c , the stress for which the bulk starts to flow in its liquid regime. Beyond this yield stress, the material behaves as a simple yield stress fluid, with no significant time effects: the flow curve is the same whatever the procedure (after different times of rest or by starting from high shear rates). From these results, we deduce that between τ'_c and τ_c , the bulk is in its solid regime so that it only undergoes limited deformations which cannot be at the origin of the steady state flow observed with smooth surfaces. As a consequence, in this regime, the bulk material moves as a rigid block along the solid surface of the tool. Moreover, there necessarily exists, between the bulk and the solid surface of the tool, some layer of a material of different nature (e.g., the interstitial liquid, possibly with some suspended elements) which is sheared between the bulk and the wall. Thus, we may compute the slip velocity, i.e., the relative velocity between the bulk and the smooth wall, from the apparent shear rate, $V_s = \dot{\gamma}h$.

The slopes of the deformation vs time curves in the steady state flow regime may be used to plot the apparent flow curves, with or without rough surfaces (see Fig. 4). Note that here both τ_c and τ'_c are precisely defined, i.e., we are sure

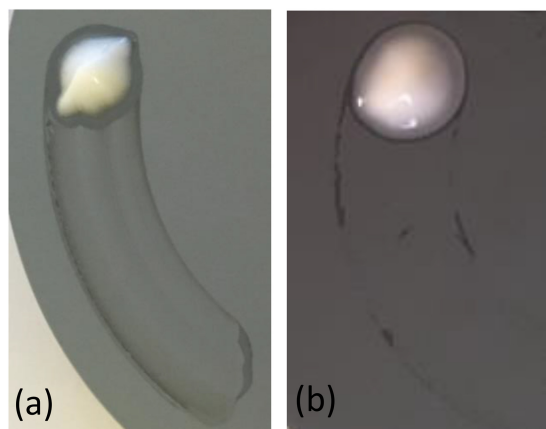


FIG. 5. Aspect of a drop of material drifted by the top plate of the rheometer, after separation of the plates and a circular motion: (a) direct emulsion (width 1.6 cm) and (b) inverse emulsion (width 1.35 cm).

torque becomes $M_0 + 2\pi R^2 e \tau_c$, and the apparent stress has now an additional component: $\tau \approx \tau_0 + 3e\tau_c/R$. Note that this approach is a rough description of reality as we ignore the exact shape of the sheared region, its possible variation with velocity, and the slight increase of the stress from τ_c as the local shear rate increases.

From this analysis, it is obviously expected that such an edge effect plays a minor role when the sample surface to the perimeter ratio is sufficiently large, e/R , when is sufficiently small. A series of tests with different sample radii effectively show that, for a given material (with a constant yield stress), τ'_c increases when the sample radius decreases [see Fig. 6(a)]. If we consider, for example, the data for a disk radius of 6 cm, τ'_c is typically of the order of 1 Pa, which means that e should be of the order of 250 μm . This is in the same order of magnitude of the width of the tracks left behind the displacement of a drop, which is around 0.5 mm [see Fig. 5(a)]. It is not possible to elaborate further on that point as this would require knowing the exact shape of the arrested layer at the periphery.

The origin of this effect might be that some suspended elements tend to be attached to the solid surface at the contact line, as a result of a slight evaporation effect at the contact line, more or less as in the coffee-ring effect [36]. Here, we further examine the validity of this statement by observing the impact of the time of rest before applying a stress, since it is expected that an effect associated with evaporation should be larger for longer times of drying.

We performed tests under controlled shear rate with smooth surfaces as follows: after setting up the sample in the geometry, we did not surround it with a vapor saturated environment so that it could more rapidly dry; we thus left it at rest for a given time, imposed a low shear rate (0.01 s^{-1}), and recorded the shear stress evolution (see Fig. 7) for some time; then, we cleaned the geometry and set up a new sample for a similar test with a different time of rest. The stress vs time curves look like those obtained for creep tests with yield

It was suggested [23] that this edge effect is at the origin of the residual yield stress with smooth surfaces. Indeed, if wall slip is associated with the flow of a liquid in some given geometry, it is expected to occur and thus allow some flow under any stress value. In contrast, if some region (here along the periphery) of the material is sheared, a stress larger than the yield stress is required in this region, which on average will induce an apparent yielding behavior, even if the rest of the material slips along the solid surface.

More precisely, let us assume that the slip conditions along most of the surface of contact with the bottom plate require to apply a torque M_0 , related to the apparent shear stress $\tau_0 = 3M_0/2\pi R^2$. Then we assume that some edge effect induces a stress (τ_c) acting over a constant width (e) along the sample periphery. This situation would, for example, be encountered if a layer of (radial) width e was stuck to the smooth plate and induced a shear of the surrounding material at the approach of this zone. This effect will induce an additional torque, $2\pi R^2 e \tau_c$ so that the total

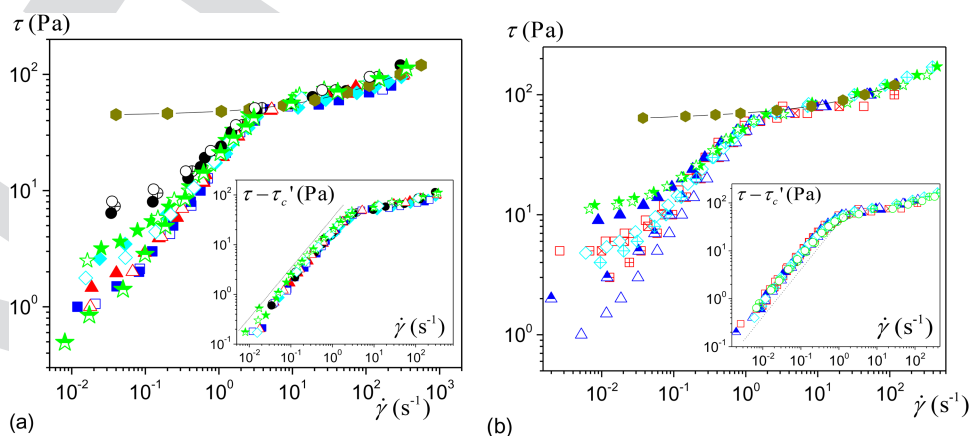


FIG. 6. Apparent flow curves on smooth surface of (a) a direct emulsion (82%) (data from [24]) and (b) an inverse emulsion (82%) for the same gap and different plate diameters: 9 cm (squares), 6 cm (triangles), 4 cm (diamonds), 3 cm (stars), 3 cm with oil film at the sample periphery (half-filled stars), and 2 cm (circles). Hexagons show data with two rough plate surfaces. Several tests were carried out by changing the sample while keeping the same surface are shown for each diameter in order to appreciate the reproducibility of these experiments. Open triangles correspond to test after lens paper cleaning, while the other data correspond to acetone + compressed air cleaning. Note that in order to remove the impact of sample shape at the periphery, which increases when the sample radius decreases, τ has been rescaled by a factor around 1 to get the same stress values at the yielding transition (see [24]). The insets show the stress minus the wall slip yield stress vs shear rate for the same data. The dotted lines of slope 1 are guides for the eye.

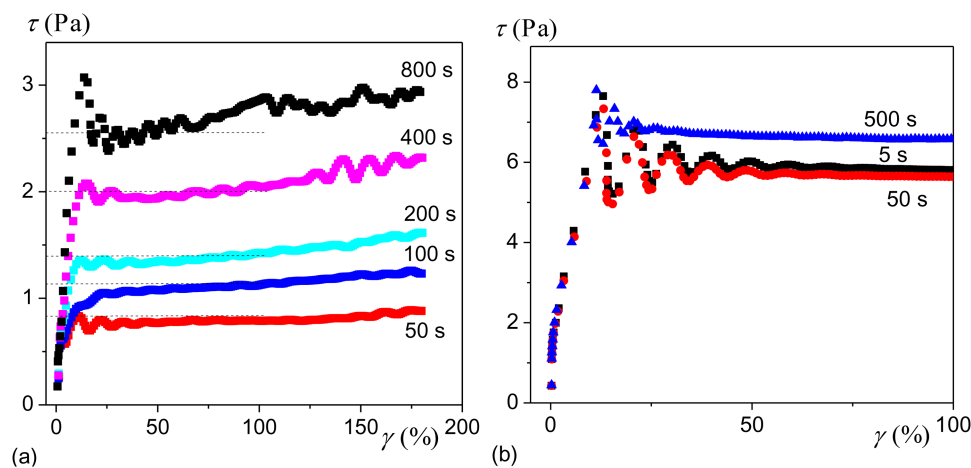


FIG. 7. Shear stress as a function of shear strain while imposing a shear rate $\dot{\gamma} = 0.01 \text{ s}^{-1}$ to (a) a direct emulsion B and (b) an inverse emulsion (82%) after different times of rest (indicated in the graph close to the corresponding curves) prior to the experiment on a smooth surface; the dashed lines indicate the assumed level of τ'_c .

stress fluids [2]: after an increase the stress reaches a plateau; note, however, that there are some oscillations at the beginning, which likely result from the fact that the stress controlled rheometer imposes a constant low shear rate with the help of a feedback loop. Since the imposed shear rate value is around the critical shear rate value below which flow stops with smooth walls in our other tests (see Figs. 3 and 4), we can consider that the stress plateau level (taken in the initial horizontal part, before the slight increase) here observed would correspond to the wall slip yield stress. Under these conditions, it is remarkable that this slip yield stress increases significantly with the time of rest [see Fig. 7(a)], approximately with the square root of the time of rest. A second remarkable observation is that the increase of the stress during the flow is smaller than that resulting from the rest over a similar duration [this may be seen from the curves for the smallest times of rest (smaller than the creep test duration, i.e., 180 s)]. This means that the wall slip yield stress essentially evolves when the material is at rest, and only slightly evolves over the typical time of flow of creep tests. This proves the validity of our series of creep tests for consistently determining the behavior of the materials below the yield stress: we impose successively increasing stress levels; the material starts to flow for some critical stress associated with the flow history from the beginning; since (i) the next tests are carried out at larger stress values, they also induce a flow, during which the wall slip yield stress does not increase much, and (ii) the tests are carried in a vapor saturated air, which considerably limits the drying so that the wall slip yield stress even increases less during our series of creep tests and, finally, can be considered as constant.

From the above analysis, we conclude that withdrawing τ'_c from the stress should reveal the shear stress solely associated with the wall slip along the area of contact between the sample and the solid surface. And indeed, we observe an excellent superimposition of the curves of $\tau - \tau'_c$ vs $\dot{\gamma}$ for the different sample diameters [see inset of Fig. 6(a)], showing that removing the edge effects give a unique wall slip flow curve. We call the stress strictly associated with wall slip, τ_S ,

and define it as $\tau_S = \tau - \tau'_c$. Then V_S as a function of τ_S can be considered as the wall slip law of the material over a given surface. It appears that for the tested emulsion this law is linear [see inset of Fig. 6(a)], i.e., $\tau - \tau'_c$ is simply proportional to $\dot{\gamma}$, and thus to the slip velocity $V_S = h\dot{\gamma}$. We deduce that we can write $\tau_S = \alpha V_S$, and expressing α as $\alpha = \mu/\delta$, where μ is the viscosity of the interstitial liquid and δ a characteristic length, we get

$$\tau_S = \mu V_S / \delta. \quad (1)$$

Under these conditions, δ has a physical meaning: if we assume that the slip occurs as a result of the simple shear of a uniform layer of (pure) interstitial liquid along the wall while the bulk remains rigid, δ is the thickness of this layer. Moreover, from Eq. (1), we deduce the slip law expressed as a relationship between dimensionless parameters:

$$\tau_S / \tau_c = (1/\delta)(\mu V_S / \tau_c), \quad (2)$$

which, in particular, allows one to proceed to a relevant comparison of results obtained with materials with different interstitial liquid viscosities.

2. Inverse emulsions

This origin of the wall slip yield stress, i.e., an edge effect due to the adherence of the material around the line of contact as a result of evaporation, can hardly apply to inverse emulsions. Indeed, the water droplets are covered with an oil layer, which considerably slows down evaporation, and even if they finally evaporate, this will increase the local concentration of oil, which should *a priori* foster wall slip. Actually, we effectively do not see lateral tracks of the bulk material when a drop is moved over the smooth surface [see Fig. 5(b)]: the dark areas appearing in the photo along the edges of the drop trajectory have apparently the same thickness as the extremely thin oil layer covering the rest of the surface and left behind the drop. Moreover, we observe that there is no significant impact of the time of rest on the value of τ'_c for inverse emulsions [see Fig. 7(b)], in strong contrast

659 with direct emulsions [see Fig. 7(a)]. These observations
 660 confirm that for inverse emulsions, the main origin of the
 661 wall slip yield stress is not an edge effect.

662 Two other aspects distinguish the wall slip yield stress for
 663 inverse emulsions: τ'_c is larger for direct emulsions, and its
 664 value fluctuates widely, as appears from reproducibility tests
 665 [see Fig. 6(b)]. Although we can suspect that the origin of this
 666 effect is the exact history of the surface cleaning before each
 667 test, we were unable to distinguish a clear trend, except one
 668 point: the standard procedure involves cleaning the surface
 669 with acetone, then blowing it with compressed air; smaller τ'_c
 670 values were generally obtained when before set up the solid
 671 surface is rubbed with a lens paper. Finally, it does not seem
 672 possible to distinguish an increase of τ'_c with the decrease of
 673 the sample diameter, the flow curves in the slip regime are
 674 scattered in the range of variations obtained for a single diame-
 675 ter [see Fig. 6(b)], without specific trend. This confirms that
 676 for inverse emulsions, the wall slip yield stress does not find
 677 its origin in an edge effect. As a consequence, this is an effect
 678 which takes place along all the surface of contact between the
 679 material and the solid surface, typically some slight interaction
 680 between the droplets and the solid surface.

681 This interaction apparently takes the form of an adhesion
 682 force, whose level is very sensitive to the exact preparation
 683 of the surface, which implies that we have to present the
 684 results as a set of flow curves illustrating the range of varia-
 685 tion of τ'_c . If we now withdraw the value for τ'_c obtained in
 686 each of these tests, so as to represent $\tau - \tau'_c$ vs $\dot{\gamma}$, we again
 687 find that all the data fall along a single master curve [see the
 688 inset of Fig. 6(b)]. This means that, for inverse emulsions,
 689 the wall slip law (in terms of shear stress) is the sum of a fric-
 690 tion term, very sensitive to exact conditions, plus a constant
 691 function of the shear rate.

692 3. Conclusion concerning the origin of the wall slip 693 yield stress

694 The above observations for two types of emulsions
 695 provide two different situations leading to an apparent wall
 696 slip yield stress.

1. An edge effect: some material is stuck along the periph- 697
 eral line of contact, which induces a shear along a small 698
 surface at the periphery, leading to an apparent yield 699
 stress at low velocity; the characteristics of this effect are: 700
 a thin bulk deposit along the lateral edges of a drop dis- 701
 placed along the solid surface, an increase of this effect 702
 with the time of rest, and an increase of this (edge) effect 703
 for decreasing sample radius. In addition, the order of 704
 magnitude of this effect may be estimated from the above 705
 rough approach: the sheared surface is typically of the 706
 order of $200\ \mu\text{m}$ (as deduced from our observations with 707
 emulsions), during current tests (with no times of rest 708
 exceeding 100 s), which induces a ratio τ'_c/τ_c of the order 709
 of $3e/R \approx 0.6/R$ (with R in millimeters). 710
2. A surface effect: the elements of the material tend to adhere 711
 onto the solid surface, and some critical stress is needed to 712
 break these links; the characteristics of this effect are: no 713
 thin bulk deposit along the lateral edges of a displaced 714
 drop, no increase of this effect with the time of rest, and no 715
 impact of the sample radius. For the inverse emulsion, it 716
 also appears that the value of the wall slip yield stress 717
 widely fluctuates, which will in fact appear as a general 718
 characteristics of surface effects in the following. 719

Note that these two types of behaviors, i.e., negligible and 720
 significant (with regard to τ_c) wall slip yield stresses, were 721
 already observed with emulsions, respectively, over a well- 722
 controlled non-adhering and a weakly adhering surface [37]. 723
 However, in the latter case, a quadratic variation of the slip 724
 velocity with $\tau - \tau'_c$ was observed, in contradiction with our 725
 results. 726

Determining whether we are dealing with an effect of 727
 type 1 or 2 is not so easy in practice. The conclusion can be 728
 immediate if one observes a ratio τ'_c/τ_c significantly larger 729
 than $0.6/R$, since then it is unlikely that edge effects could 730
 induce such a high stress. When this is not the case, i.e., the 731
 two values are of the same order of magnitude, the diagnosis 732
 requires a full enquiry, such as the tests described above. It 733
 may also happen that both effects play a role, an even more 734

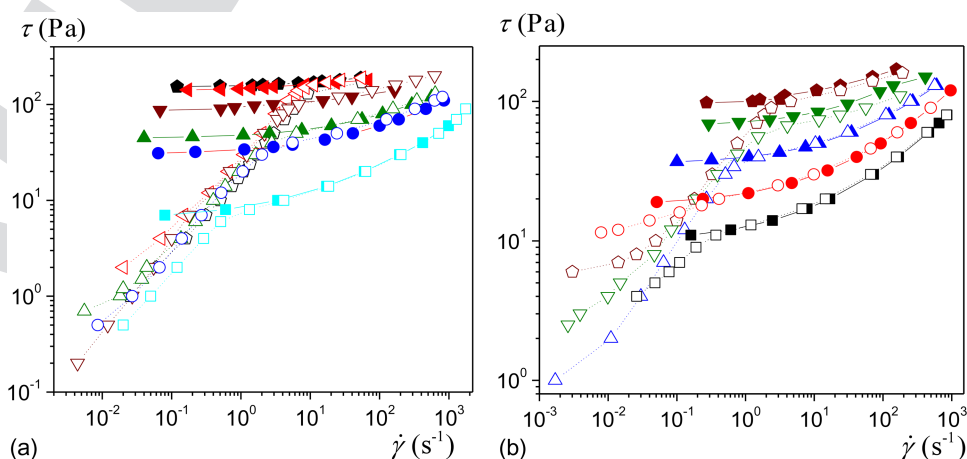


FIG. 8. Flow curves, as deduced from steady state flows in creep tests, for (a) direct emulsions (composition B) at increasing concentrations: (from bottom to top): 72%, 78%, 82%, 86%, 90%, 92% and (b) inverse emulsions at increasing concentrations: (from bottom to top) 72%, 74%, 78%, 82%, 86%. Open symbols correspond to smooth bottom surface, filled symbols to rough surfaces.

735 complex situation, for which it might be ultimately extremely
736 difficult to conclude.

737 C. Impact of concentration

738 The flow curves, deduced from steady states in creep tests,
739 for the direct emulsion at different concentrations and for
740 smooth or rough surfaces are shown in Fig. 8(a). As
741 expected, the yield stress increases with the concentration
742 but, remarkably, the flow curves in the presence of wall slip
743 below the yield stress appear to essentially follow a master
744 curve independent of the concentration, except at the
745 approach of τ'_c , which takes different values below 1 Pa. Note
746 that the data for the 72% emulsion correspond to a slightly
747 higher slip velocity. We do not have an explanation for that
748 trend, this may be either due to the fact that the concentration
749 is close to the critical concentration beyond which jamming
750 occurs and a true yield stress is clearly observed (around
751 70%) or to the uncertainty on data, or both.

752 This means that both the slip yield stress and the wall slip
753 law are independent of the concentration. Thus, the part of
754 flow curve with wall slip of an emulsion at some concentra-
755 tion may be directly deduced from a measure of wall slip at
756 another concentration. As expected from the flow curves, it
757 appears that, for the direct emulsions, the wall slip laws at
758 different concentrations fall along a single master curve (see
759 Fig. 9), indicating that, if concentration has some effect, it is
760 weaker than the uncertainty on measurements. This master
761 curve is linear, which means that the slip velocity is propor-
762 tional to the slip stress.

763 For the inverse emulsions, it is more difficult to appreciate
764 the impact of concentration on the wall slip flow curve, due
765 to the large scattering on the slip yield stress [see Fig. 8(b)].
766 However, the slip yield stress remains in the same (wide)
767 range observed for a series of tests at the same concentration

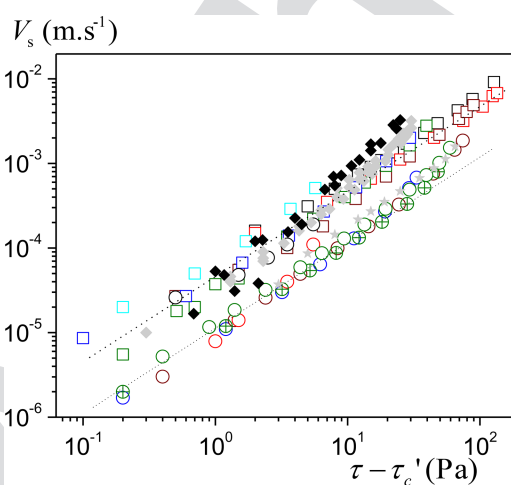


FIG. 9. Slip velocity (over smooth surface) as a function of the slip stress for direct emulsions at the different concentrations presented in Fig. 8(a) (squares, same colors) and for inverse emulsions at the different concentrations presented in Fig. 8(b) (circles, same colors). The upper dotted line corresponds to the function $\tau_s = \mu V_s / \delta$, with $\mu = 0.89$ mPa s and $\delta = 35$ nm, and the lower dotted line to the same function with $\mu = 1.36$ mPa s and $\delta = 15$ nm. Data for Teflonlike surface (filled grey symbols) and Black Silicon surface (black filled symbols) are also presented for the direct (diamonds) and the inverse emulsion (stars).

[see Fig. 6(b)], a range once again typically 1 order of mag-
768 nitude larger than that observed for τ'_c for direct emulsions at
769 different concentrations [see Fig. 8(a)]. Moreover, after with-
770 drawing τ'_c , the shear stress appears to be also proportional to
771 the slip velocity but with an apparent thickness of the slip
772 layer smaller than for direct emulsions (see Fig. 9). One may
773 also note that the data tend to depart from the line of slope 1
774 in logarithmic scale for large stress values, indicating a faster
775 increase of the slip velocity as a function of the stress.
776

777 D. Impact of surface characteristics

778 The detailed impact of surface roughness or surface inter-
779 action between the fluid and the solid has been studied
780 through detailed measurements of the flow characteristics at a
781 local scale, by few authors [38–40], in the yielding regime.
782 These works were carried out essentially in the frame of con-
783 fined flows, i.e., with characteristics flow length (typically,
784 the gap between the two solid boundaries) not very much
785 larger than the element size. It was, in particular, found that
786 in this context, the roughness or the hydrophobicity may alter
787 wall slip properties. It was also shown from internal velocity
788 measurements that the surface–fluid interaction has a long
789 range action, leading to some unexpected shear at some dis-
790 tance from the wall [37]. These different results were inter-
791 preted within the frame of the fluidity model.

792 Here, we focus on the impact of surface characteristics on
793 wall slip under conditions for much larger gap sizes so that
794 possible confinement effects *a priori* have a negligible influ-
795 ence, and we focus on the slip regime below the yield stress.
796 In that aim, we first look at the behavior of direct emulsions
797 in contact with Black Silicon surfaces, which have an appar-
798 ent roughness of the order of the droplet size (see Sec. II A).
799 Such a roughness can thus be considered as intermediate
800 between the smooth silicon surfaces and the rough (serrated)
801 surfaces. From creep tests at different stress levels (see
802 Fig. 10), we see that the material reaches a steady flow for a
803 stress larger than the yield stress, but can also reach a steady
804 flow between a lower stress (τ'_c) and the yield stress. It does

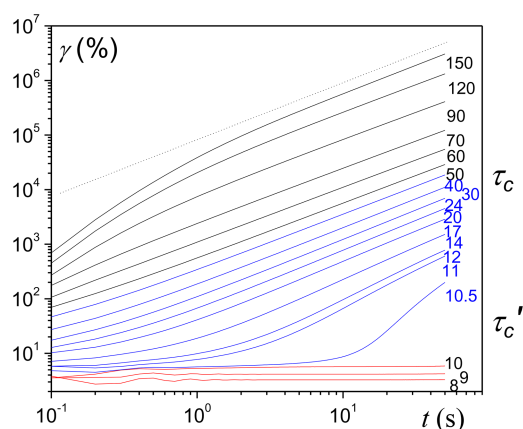


FIG. 10. Creep tests for emulsion B on Black Silicon surface (shear stress values applied are mentioned in Pascals); red curves correspond to the solid regime, blue curves to the slip regime, and black curves to the liquid regime; the slip yield stress τ'_c is situated between 10 and 10.5 Pa. The sample diameter here is 5 cm.

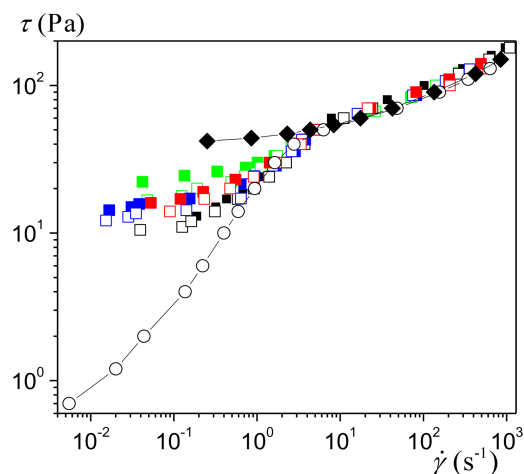


FIG. 11. Flow curve deduced from creep tests for emulsion B (82%) with rough (serrated) surfaces (diamonds), bottom smooth surface (open circles), and bottom Black Silicon (squares) with different sample diameters: (green) 3 cm; (black) 5 cm; (blue) 6 cm; and (red) 9 cm. Empty/filled symbols distinguish two different tests under the same conditions.

move out the droplet from this potential well and allow for a steady state motion. Note that there might remain some edge effects as for smooth surface, but its level is much lower than the apparent value for τ'_c so that it does not induce significant variation of τ'_c (it might, nevertheless, become significant for a small diameter, which could explain the apparent larger τ'_c value for 3 cm diameter in Fig. 11). Finally, it is interesting to compare the relationship between the additional wall slip stress (i.e., $\tau_s = \tau - \tau'_c$) and the slip velocity with the same relationship for smooth surface. It appears that the slip velocity with the Black Silicon surface is similar for that for smooth surface for low stress but tends to be significantly larger (see Fig. 9), by a factor about 2, for larger stress.

With Teflonlike surface, the flow curve of direct emulsions now also exhibit a fluctuating τ'_c , but anyway much larger than that observed over silicon surface [see Fig. 12(a)]. This situation is similar to that observed for inverse emulsions over silicon surface, which suggests a similar physical origin, i.e., some kind of (provisional) adhesion of the droplets onto the solid surface. The impact of Teflonlike surface on the wall behavior of inverse emulsions is stronger. Now, wall slip may completely disappear [see Fig. 12(b)]: a 74% emulsion flows without wall slip with rough or Teflonlike surface.

These observations suggest that, for a given material, a solid surface induces a given adhesion effect associated with some particular stress value, which may be smaller or larger than the material yield stress. In the former case, wall slip will occur, in the latter case, wall slip will not occur since the minimal stress needed to induce wall slip is larger than the yield stress and thus induces bulk flow. This is confirmed by further tests with a very concentrated inverse emulsion, with a yield stress much larger than the 74% emulsion [see Fig. 12(b)]: with the same Teflonlike surface, we now have a wall slip regime, with a τ'_c value smaller than the yield stress but larger than the yield stress of the 74% emulsion for which no wall slip was observed with Teflonlike surface.

Let us finally mention that we also tested PMMA and glass surfaces on bottom plates, for direct and inverse emulsions, but the results did not offer sufficiently significant

not flow for a stress below τ'_c . This means that the roughness is not sufficient to avoid any type of wall slip, and some wall slip effect can develop, which leads to an apparent flow curve situated between the flow curve of the material and the wall slip flow curve over a smooth surface (see Fig. 11).

The apparent wall slip obtained with the Black Silicon surface has some specific characteristics. First of all, we notice that, in creep tests, the transition between the solid state and the wall slip is rather abrupt (see Fig. 10), precluding any steady state flow at an apparent shear rate lower than 10^{-1} s^{-1} . Moreover, here, considering the large value of τ'_c , the wall slip yield stress is undoubtedly due to a surface effect. This is confirmed by the tests at different diameters (see Fig. 11), τ'_c varies in the range 10 to 20 Pa, but there is no clear correlation between its value and the sample diameter. It is likely that the micro roughness of this surface tends to block, at least provisionally, some droplets, as in a small potential well so that some minimum stress is needed to

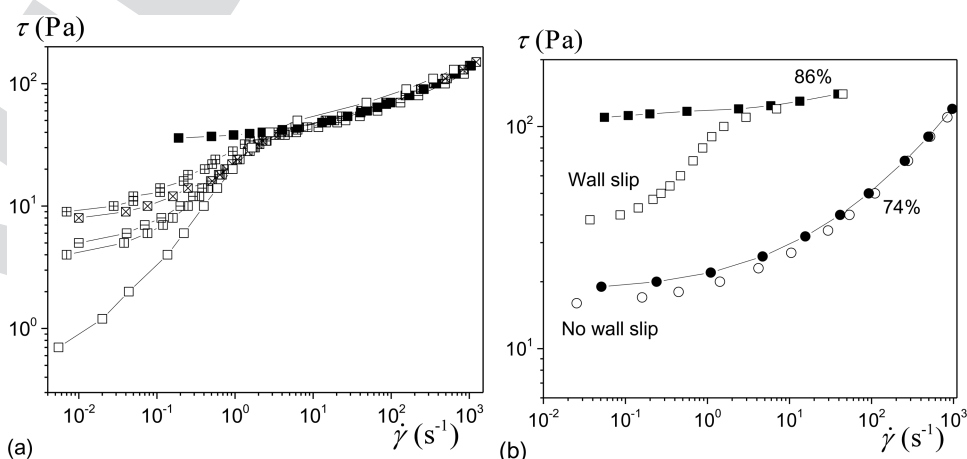


FIG. 12. Flow curves, as deduced from steady state flows in creep tests, for (a) emulsion B (82%) with rough surfaces (filled squares), smooth surface (open squares) or Teflonlike surface (cross-squares), and for (b) 74% (circles) and 86% (squares) inverse emulsion with rough surfaces (filled symbols) or Teflonlike surface (open symbols).

862 differences with those observed with silicon surface. In some
863 cases, a slightly larger value for τ'_c than with silicon surface
864 was observed, but it is not possible to definitely conclude
865 about a possible different physical process.

866 E. Impact of material structure

867 We may look at the impact of a change of the material
868 structure by varying the droplet size distribution of emul-
869 sions. The flow curves of direct emulsions with different
870 droplet sizes with rough or smooth surfaces are shown in
871 Fig. 13(a). We observe that, in addition to the increase of τ_c
872 with $1/r$ discussed in Sec. II A, all the emulsions exhibit
873 wall slip on the silicon wafer. However, we do not obtain a
874 clear, unique master curve for the stress vs shear rate in the
875 slip regime for the different droplet sizes. At first sight, there
876 seems to be some slight increase in the slip velocity with the
877 droplet size for a given stress. These observations are con-
878 firmed by the results represented in terms of slip velocity vs
879 rescaled slip stress [see Fig. 13(b)]. As for the above emul-
880 sions, we find that the data follow a straight line of slope 1,
881 but we also observe a slight tendency to departure from this
882 line at the approach of the yield stress. Actually, this depart-
883 ure occurs earlier for increasing droplet size [see Fig. 13(b)].
884 Moreover, there seems to be a slight evolution, larger than
885 the usual noise on such data, when the droplet size increases:
886 the slip velocity, or equivalently the apparent slip layer thick-
887 ness, fitted to data [see inset of Fig. 13(b)] increases by a
888 factor about 2 when the (average) droplet size increases from
889 1.1 to 11 μm . However, this value (i.e., 2) is still relatively
890 low with regards to the general scattering on such data so
891 that we can hardly consider that we here evidenced a clear
892 trend.

893 By the way, we see that with this rescaling, the data fall
894 along the same master curve as the data for emulsion B of
895 viscosity smaller by a factor about 5 [see Fig. 13(b)].
896 This confirms the generality of the expression for the slip law
897 [Eq. (2)].

898 F. Impact of flow conditions

899 Previous works essentially focused on wall slip properties
900 when the fluid is constrained between two solid tools (in a

rheometer) and without particularly controlling the normal 901
stress. Here, we intend to evaluate the wall slip properties 902
under different flow conditions with two aims: possibly some 903
better understanding of the physical mechanisms at work in 904
wall slip, and test of the applicability of the slip law deduced 905
from rheometry to different flow conditions. 906

907 1. Impact of normal stress

908 In order to get a further insight into the physical origin of 908
wall slip, and in particular, to test the possibility of some 909
balance between attractive and repulsive forces, it is interest- 910
ing to test the impact of a normal force on the wall slip. 911
According to the concepts of Princen [22], Le Merrer *et al.* 912
[19], and Meeker *et al.* [11,16], the slip layer would be gov- 913
erned by a balance between repulsive and attractive forces, 914
the latter resulting from the repulsion between the compo- 915
nents of the material which, in a microgel suspension, an 916
emulsion or a foam, is related to the mechanical properties of 917
the material. There thus exists a kind of osmotic pressure, 918
tending to push the droplets against the solid surface (“attrac- 919
tive force”), and which can be related to the elastic modulus 920
of the material [41]. Now, if additional external forces also 921
tend to push the droplets against the wall are applied, the 922
balance of forces should be displaced, leading to a change in 923
the slip layer thickness. We can test this effect by imposing a 924
nonzero normal stress difference to the system (with a force 925
applied along the sample axis). The interesting point is that 926
such yield stress fluids are able to support some normal stress 927
difference (below a critical value) without flowing. As a con- 928
sequence, the structure is only slightly deformed but this 929
structure is pushed against the wall with this additional force. 930

931 We carried out rheometrical tests under our standard condi- 931
tions in simple shear but now imposing larger normal 932
stresses. More precisely, we varied the normal stress in the 933
widest range over which this stress does not induce an elon- 934
gational flow of the material in its liquid regime (i.e., yield- 935
ing in elongation). For a direct emulsion (82%, $\tau_c = 45$ Pa), 936
we did not observe any significant effect (difference less than 937
1.5%) on the slip velocity when the normal stress was varied 938
in the range $-200 + 200$ Pa. Note that we do not have a clear 939
explanation of what sets this maximum stress amplitude 940

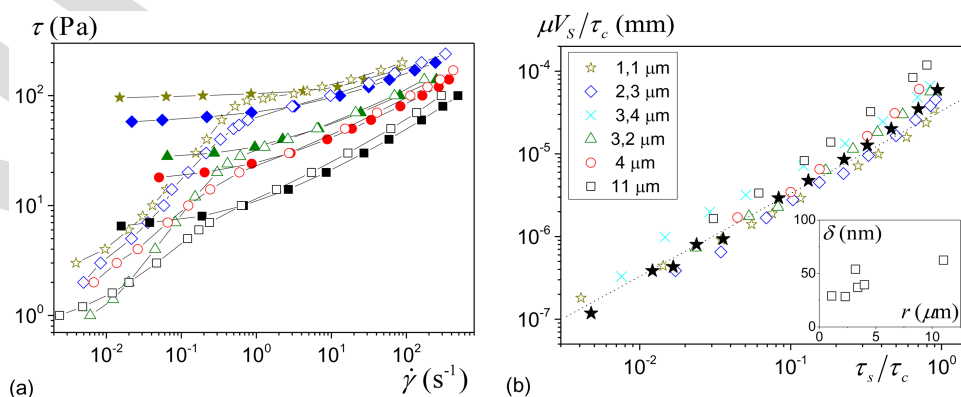


FIG. 13. (a) Flow curves for emulsions A with different mean droplet sizes (from top to bottom: A1 to A5) with rough (filled squares) or smooth bottom surface (empty squares); (b) slip velocity as a function of slip stress rescaled by the yield stress. Filled stars correspond to emulsion B (2 μm). The oil concentration of the emulsions is 82%. The inset shows the apparent slip layer thickness fitted to the data as a function of the mean droplet radius.

941 below which there is no elongational flow. We can just note
 942 that if the two walls were smooth, we would expect a bulk
 943 flow (elongation) in the liquid regime for a stress equal to
 944 117 Pa (i.e., $1.5\sqrt{3}\tau_c$, according to [42]), but here the bound-
 945 ary conditions are more complex (smooth and rough walls).
 946 For an inverse emulsion (82%, $\tau_c = 65$ Pa), we did not either
 947 observe more significant variations than the standard scatter-
 948 ing in data of the slip velocity when a normal stress ampli-
 949 tude was varied up to 300 Pa, either in the positive or the
 950 negative range.

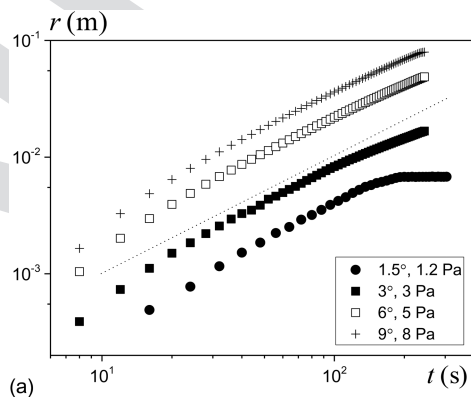
951 Let us now compare the value of this additional stress to
 952 the osmotic pressure of the material. On the basis of mea-
 953 surements on monodisperse emulsions [41] and generaliza-
 954 tion (in particular, for polydisperse materials) [43], we can
 955 estimate the osmotic pressure to be of the order of 5000 Pa
 956 for the 82% emulsions. As a consequence, the impact of a
 957 normal stress, even close to the largest value before yielding,
 958 should be negligible compared to the osmotic pressure.
 959 Finally, within the frame of the models assuming some
 960 balance between repulsive and attractive forces (see above), it
 961 is thus not surprising that such normal forces do not affect
 962 wall slip.

963 2. Wall slip in unconfined flows

964 When a drop of emulsion is put on the inclined silicon
 965 wafer, it may slightly slump due to its own weight [44,45] if
 966 its volume is large enough (typically larger than 0.4 ml),
 967 whereas for smaller volumes, the drop apparently does not
 968 slump. Besides, the weight component parallel to the surface
 969 tends to move the sample downward. When this occurs, the
 970 shape reached by the drop after a possible initial slump
 971 remains constant, indicating that the bulk material is in its
 972 solid regime and slips along the solid surface. Finally, the
 973 drop advances faster for larger slopes [Fig. 14(a)] and larger
 974 volumes [Fig. 14(b)].

975 We can compute the mean shear stress τ acting on the
 976 sample along the solid surface according to the shear stress
 977 derived from the momentum balance:

$$\tau = \rho\Omega g \sin i/S. \quad (3)$$



From Eq. (3), the observed variations of slip velocity with
 volume and slope appear consistent.

When this stress becomes larger than the yield stress, typi-
 cally for too large drop volumes, the drop starts to flow over
 the plane, in that case it now significantly spreads. We did
 not study this case.

Figure 14 shows that generally the curves of displacement
 vs time have a slope 1 in log-log scale, meaning that a
 steady motion has been reached. In that case, we can con-
 sider that wall slip occurs, since we have a constant motion
 of the rigid bulk along the wall. For too small angles of incli-
 nation or volumes, the curve slope may slowly decrease and
 finally, the sample stops moving at long time (see Fig. 14).
 This is a situation similar to that of the deformation then
 stoppage of a sample in rheometrical tests for a stress lower
 than the slip yield stress. Here, the edge effects (side depos-
 its) might again be at the origin of this effect. However, the
 critical stress associated with edge effects is more difficult to
 determine than in rheometry. Indeed, here the additional fric-
 tion associated with some fluid flow at the edge acts over a
 fraction of the perimeter which may vary from one test to
 another depending on the sample shape, which in addition
 may vary slightly due to some sample deformation during
 the flow initiation. As a consequence, for the inclined plane
 tests, we simply represent the wall slip velocity as a function
 of the total stress (and not after withdrawing some residual
 value). We did the same for tests with a Teflon-coated
 surface. Besides, note that with the silicon wafer we varied
 the drop shape in some tests, which did not appear to change
 the results in terms of slip law.

It appears that the data obtained at relatively high stress
 (typically larger than 5 Pa) again fall along slope 1 (see
 Fig. 15) and are similar to the data obtained from rheometri-
 cal tests. This demonstrates that the process at the origin of
 wall slip when the fluid is constrained between two solid sur-
 faces works in the same way under unconfined conditions.
 At smaller stress, say for $\tau < 5$ Pa, some deviations from this
 law appear, which is likely due to the impact of the slip yield
 stress not taken into account here.

In order to get more insight into this process, we carried
 out the same test [with emulsion B (82%)] but now after

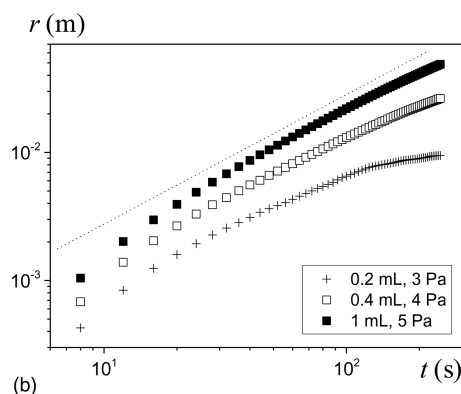


FIG. 14. Tests over smooth inclined planes with emulsion B (82%): position vs time for (a) different angles of inclination (for a volume of 1 ml) and (b) different sample volumes (for an angle of inclination of 6°). The corresponding wall shear stress is indicated in the caption. Dotted lines of slope 1 are showed in both figures as guides for the eyes.

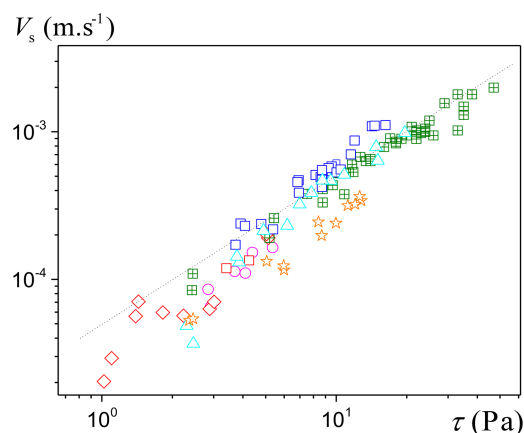


FIG. 15. Slip velocities of emulsion B (82%) in the steady state motion over smooth inclined plane surface, for various drop volumes and surfaces: 0.2 ml (pink circles); 0.4 ml (red diamonds); 1 ml (green cross-squares); 2 ml (blue squares); 1 ml on a Teflonlike coated surface (light blue triangles); and 1 ml on a silicone oil covered surface (orange stars). The dotted line is the slip model fitted to the direct emulsions at different concentrations [see Fig. 8(a)].

1019 having covered the smooth plane by a thin layer of oil (vis-
1020 cosity 0.35 Pa s). The thickness of this layer could not be
1021 controlled, and it continuously decreased in time during the
1022 test, as the oil flowed downward, but it is order of a few hun-
1023 dreds of micrometers when the emulsion drop is placed
1024 above it. However, this does not affect our qualitative obser-
1025 vations: as the sample moves downward it seems to “clean”
1026 the plane, i.e., there does not seem to be oil behind the
1027 sample along its path; the slip velocity is not significantly
1028 affected by the presence of this oil layer: it is about two
1029 times smaller than without oil (see Fig. 15).

1030 Under these conditions, considering that there remains an
1031 oil layer of thickness of the same order as the usual slip
1032 layer, due to the much larger viscosity of the oil, its contribu-
1033 tion to slip will be much weaker (for the same stress) than
1034 that of water, and we can conclude that wall slip is still gov-
1035 erned by a slip layer roughly similar to the standard one
1036 (without oil).

1037 More surprising is the removal of the oil layer between
1038 the emulsion and the wall. Indeed, as a first approximation,
1039 we can describe the process as the squeeze flow of a fluid
1040 layer between two disks of radius R situated at a distance b
1041 and approached to each other with a normal force F . This
1042 normal force is the sample weight, i.e., typically 0.01 N.
1043 Following the lubrication assumption (see [2]), we can
1044 compute the velocity of approach, $V = 8Fb^3/3\pi\mu R^4$. For an
1045 initial distance b of the order of 300 μm , we find
1046 $V \approx 0.5 \mu\text{m s}^{-1}$, which could explain the disappearance of
1047 the oil layer over the test duration (typically 100 s), but as
1048 long as b decreases V strongly decreases so that it is already
1049 1000 times smaller for $b = 30 \mu\text{m}$. This means that the oil
1050 layer cannot be removed by this simple effect. This suggests
1051 that there is a kind of attraction between the elements (drop-
1052 lets) of the material and the solid surface, which tends to
1053 further push away the oil. This implies that in any case, some
1054 droplets will be positioned at a very short distance from the
1055 wall, and this effect plays a critical role in wall slip.

G. Wall slip beyond yielding

1056

Our different techniques above limit the wall slip measure-
1057 ments to the slip regime, where the bulk remains in its solid
1058 regime. We used NMR velocimetry to probe the slip velocity
1059 when the bulk material is flowing, either in a capillary or in a
1060 Couette cell. 1061

Typical velocity profiles obtained in the capillary are
1062 shown in the inset of Fig. 16. The integration of each profile
1063 is in quantitative agreement with the corresponding flow rate.
1064 As expected from the shear stress decrease from the wall to
1065 zero along the central axis, the material is essentially sheared
1066 near the wall, while the central region remains unsheread,
1067 indicating that the shear stress τ is now below τ_c . We esti-
1068 mate the slip velocity V_s from the intersection of the wall and
1069 the profile extrapolated to the wall. The uncertainty (shown
1070 by error bars) comes from the uncertainty on the exact posi-
1071 tion of the wall and the dispersion of data point at the
1072 approach of the wall. Besides, as we could not obtain at the
1073 same time reliable measurement of the pressure drop inside
1074 the capillary, the shear stress τ along the wall is estimated
1075 from the shear rate value observed along the wall by using
1076 the constitutive equation measured independently through
1077 standard rheometry. 1078

The corresponding values for V_s and τ are reported in
1079 Fig. 16 along with the data obtained from rheometry. The
1080 data for different capillary diameters are consistent though
1081 scattered. Although they correspond to stress values signifi-
1082 cantly larger than the yield stress, they seem to be in continu-
1083 ity with the effect of a faster increase of the slip velocity at
1084 the approach of the yield stress, and the data appear to
1085 approximately follow a quadratic variation. 1086

Data with a Couette cell allow a more complete view of
1087 the evolution of flow characteristics as the velocity is
1088 increased. At sufficiently low rotation velocity of the inner
1089 cylinder (i.e., $V < 0.4 \text{ cm/s}$), we do not observe any signifi-
1090 cant shear of the material: essentially, there is an approxi-
1091 mately similar slip velocity along both walls, and the velocity
1092

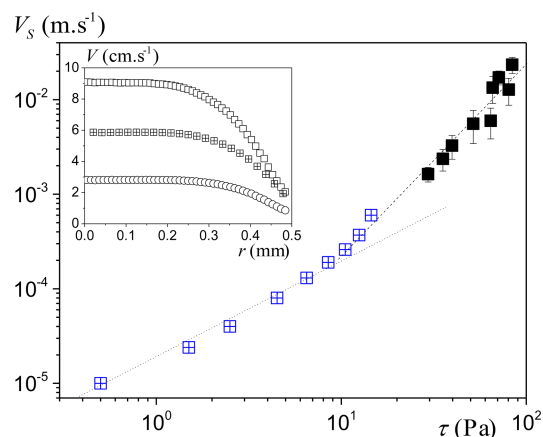


FIG. 16. Slip velocity deduced from velocity profiles in capillaries (black symbols) and deduced from rheometrical tests (blue cross-squares) as a function of the shear stress, for an inverse emulsion (74%). Straight lines of slope 1 (dotted) and 2 (dashed) in log-log scale are plotted as a guide for the eye. The inset shows a set of typical velocity profiles for different flow rates (from bottom to top, 1, 2, and 3 ml/min) in a 1-mm diameter tube.

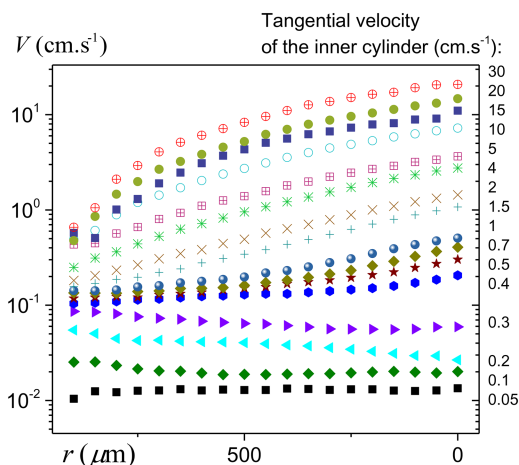


FIG. 17. The NMR velocity profile for the inverse emulsion (82%) in the Couette geometry: tangential velocity as a function of the distance from the inner cylinder wall, for different tangential velocities of the inner cylinder.

profile is a plateau (see Fig. 17). Note that in the slip regime, the material turns as a plug with a rotation velocity Ω so that the tangential velocity in the bulk slightly increases from Ωr_1 along the inner cylinder to Ωr_2 along the outer cylinder, which leads to a total increase by a factor about 1.1 in our case. Here, in some cases, we observe a (nonphysical) more significant increase of the velocity toward the outer cylinder which *a priori* reflects the uncertainty on NMR measurements. For larger rotation velocities, the evolution of the velocity profiles is completely different: there is now a sheared region along the inner wall, which grows in size as the velocity is increased, while the unsheared region progressively disappears; at the same time, there is still some wall slip along each wall (see Fig. 17), which may be appreciated from the difference between the last value in the profile and the wall velocity (indicated in the graph).

We can now compare the slip velocity observed in the Couette cell from NMR measurements with those deduced from rheometry in the nonyielding regime. This is done by extracting the slip velocity (at both walls) from the profiles and associate them with the stress along each wall deduced from the torque measured from independent similar rheometrical tests with the same geometry in a rheometer. We see that the slip velocity observed in both cases in the nonyielding regime (at the approach of the yield stress) are

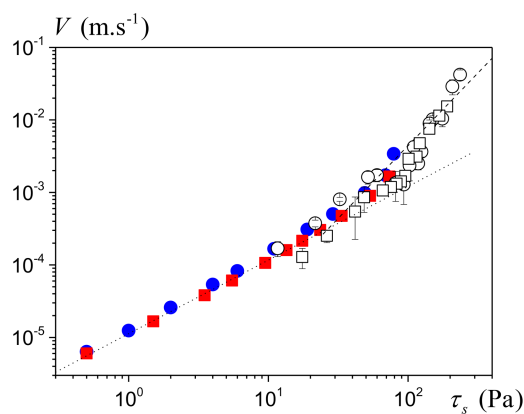


FIG. 18. Slip velocity deduced from the velocity profiles in the Couette cell (open symbols) as a function of the stress, for an inverse emulsion (82%), and from parallel plate tests in rheometer (filled symbols) along a glass surface (squares) or a PMMA surface (circles). Straight lines of slope 1 (dotted) and 2 (dashed) in log-log scale are plotted as a guide for the eye.

consistent (see Fig. 18), although here the smooth surfaces are made of PMMA and glass. In this regime, we again observe the linear variation of the velocity with the stress but at the approach of the yield stress value the velocity increases faster, apparently faster than a quadratic law (see Fig. 18). This confirms the results obtained in the capillary and suggests a change of regime and physical process for wall slip when the yield stress fluid is sheared along the wall.

V. ANALYSIS

Let us now review the different results obtained and interpret them in terms of physical origin of wall slip.

- The wall slip yield stress on smooth surfaces may have two origins: either an edge effect enhanced by evaporation along the line of contact at the sample periphery, or some adhesion between the suspended elements and the solid wall. Usually, edge effects induce a wall slip yield stress of a maximum of a few Pascals, and which tends to increase after some rest.
- Surface effects were observed with inverse emulsions. In that case, the critical stress associated with adhesion, i.e., τ'_c , is very sensitive to the exact surface characteristics.
- From our experiments, it appears that surface effects appear with inverse emulsions on hydrophilic surface and

TABLE I. Compositions, methods of preparation, and characterization of emulsions used in this work.

Emulsion name	Dispersed phase	Continuous phase	Concentration (vol. %)	Surfactant	Emulsifier	Max. rotation speed (rpm)	Mean droplet size in μm (polydispersity in brackets)
A1	Silicone oil	Water (50 wt. %) and glycerol (50 wt. %)	82	TTAB	Couette	600	3.2 (0.8) or 3.4 (0.7)
A2						300	4 (0.6)
A3						150	11 (0.8)
A4					Silverson	6000	1.1 (1.6)
A5						2400	2.3 (0.7)
B	Dodecane oil	Water	72–92	SDS	6000	2 (0.4) for the concentration of 82 vol. %	
Inverse emulsions	Water and CaCl_2	Dodecane oil	72–86	SMO		Not characterized	

TABLE II. Surfaces and contact angles of different liquids.

Surface name	Roughness	Contact angle in ° with 5° uncertainty		
		Silicone oil drop surrounded by water/ glycerol mixture with 3 wt. % TTAB	Dodecane drop surrounded by water with 3 wt. % SDS	Water drop with CaCl ₂ surrounded by dodecane oil with 7.5 wt. % SMO
Silicon	Below 0.3 nm	≈0	≈0	24
Silicon with teflon coating	Below 10 nm	Not measured	≈0	21
Black Silicon	About 6 μm	Not measured	≈0	Not measured

are enhanced (or appear, with direct emulsions) with hydrophobic surface. This suggests that it is due to the attraction and direct contact of water droplets with the wall for hydrophilic surface. We, nevertheless, have no clear explanation for the stronger adhesion effect observed with Teflonlike surface for both types of emulsions.

4. In any case, when τ'_c is removed from the stress, the resulting relationship between stress and slip velocity is linear, as long as the stress is below the yield stress. This relationship appears to apply to a wide range of materials including a variety of structures, element characteristics, and concentrations [23]. In particular, there is no significant impact of the element size, i.e., no clear impact when the droplet size is increased by 1 order of magnitude. And there is no clear impact of the concentration of elements, i.e., no clear impact when the concentration is increased from 72% to 92%, which means that the porosity is decreased by a factor about 4. Moreover, for this range of materials, the apparent liquid layer thickness remains in a rather narrow range, i.e., 35 ± 15 nm. Nevertheless, for inverse emulsions, for which τ'_c could be clearly associated with surface effects, this range is lower: 20 ± 10 nm.

5. This relationship, established for flows inside the geometry of a rheometer, remains valid for flows in the capillary and for unconfined flows, i.e., free surface flows. Thus, for applications, the wall slip law determined from rheometrical tests can be used for describing wall slip of the same material under various other flow conditions as long as the solid surface is sufficiently smooth.

6. In particular, this wall slip law is independent of the normal force applied to the sample, as long as this force does not induce an elongational flow of the material, i.e., as long as the material does not yield. When some elongational flow is induced, a wall slip effect can still occur, with now an apparent liquid layer of thickness several orders of magnitude larger than that for simple shear (see [46]).

7. Experiments of direct emulsion motion over inclined plane, initially covered with oil, show that wall slip then occurs under the same condition, meaning that the material tends to push away the oil layer to reach conditions around the interface similar to those without oil.

8. For a stress larger than the yield stress, the slip velocity appears to increase with the stress faster than below the yield stress, approximately with the square of the shear stress. This is in agreement with previous observations with Carbopol gels [47] and emulsions [48]. However, the general scaling with a power of $\tau - \tau_c$ suggested by Divoux *et al.* [49] for microgels, although it might apply,

cannot here be tested relevantly because of the scattering on our data.

9. The wall slip characteristics are significantly modified with a wall exhibiting a roughness of the order of the droplet size. There is now a significant slip yield stress not due to edge effects, but the additional stress needed for wall slip beyond that point is smaller than with smooth surfaces.

The simplest way to interpret the linear relationship for the slip stress as a function of the slip velocity and its proportionality with the interstitial liquid viscosity is to consider that a uniform and constant liquid layer (of thickness δ) exists between the wall and the bulk (i.e., the homogeneous mixture of elements and liquid). However, such a uniform layer is unrealistic considering the disordered and heterogeneous systems we are dealing with. More likely, we can expect that some elements are closer than others from the wall. It was suggested [24] that, since the suspended elements are jammed in some structure, at the origin of the yield stress, this structure exhibits a roughness, and there is a wide range of distances between the elements along this surface and the wall. This implies that the thickness δ would in fact represent an average apparent thickness. For example, if we assume that the liquid is simply sheared between all the element points and the wall, the mean stress is found by averaging the local resulting force $\mu(V_s/\delta_i)ds_i$ over the surface. Then, the apparent liquid layer thickness is $S(\sum_i (1/\delta_i)ds_i)^{-1}$. In this context, the points for which δ_i is the smallest play a major role. This was already identified by Princen [23], who in fact provided a complete approach of the problem for a relatively simple material, i.e., emulsions. Princen [23] showed that we should expect a fraction of droplets only, squeezed against the wall but separating from it by flat liquid films. In this frame, Princen neglected the impact of the flow of the liquid situated besides, which was considered as “deep oceans” as compared to these films. In the above theoretical approach, this means that δ_i in these regions is more than 1 order of magnitude larger than in the films, which seems realistic if we compare the value we found for δ , typically a few tens of nanometers, to the typical pore size in our emulsions which should be larger than a few hundreds of nanometers. Moreover, in the absence of variation of other aspects, this assumption would be consistent with the observation that the droplet size has no significant impact on wall slip characteristics, since in that case, the pore size varies proportionally to the droplet size. Finally, this

1235 leads to $\delta \approx \delta_0/f$, in which δ_0 is the thickness of the films,
1236 and f the fraction of surface occupied by the films.

1237 From direct measurements, Princen found that f varies
1238 from about 0.02 for $\phi = 72\%$ to about 0.26 for $\phi = 92\%$.
1239 Assuming a constant value for δ_0 , this should lead to a
1240 decrease of δ by a factor 13 in this range of concentrations.
1241 This is in total disagreement with our data (and those of
1242 Princen, even if he did not withdraw the apparent slip yield
1243 stress), we essentially find no impact of the concentration of
1244 the emulsion. Note that this problem is not immediately
1245 solved by taking into account a possible variation of δ_0 due
1246 to the variation of osmotic pressure with the concentration, as
1247 to maintain a constant δ , we would need here an increase of
1248 δ_0 for an increase of the osmotic pressure, in contradiction
1249 with the natural expectation in the absence of other effects.

1250 On the other side, if we now just consider the standard
1251 models assuming a balance between attractive and repulsive
1252 forces (see above), it is remarkable that for our emulsions,
1253 according to proposed estimations [41,43], we expect varia-
1254 tions of the osmotic pressure by a factor of several tens when
1255 increasing the emulsion concentration between 72% and
1256 92%, whereas we did not notice any impact of concentration
1257 on the apparent slip thickness. This suggests that the slip
1258 layer thickness is imposed by some effect stronger than the
1259 stress resulting from the jamming of the elements.

1260 However, we have also seen that beyond that point, i.e.,
1261 for a stress larger than the yield stress and thus leading to an
1262 elongational flow, the wall slip characteristics change
1263 abruptly: the apparent liquid layer thickness turns to a value
1264 several orders of magnitude larger than that for the shear
1265 flow below the yield stress (i.e., of the order of 10 μm [42]).
1266 This means that in that case there is a kind of irreversible
1267 detachment of the elements from the wall, implicitly
1268 meaning that they were somehow attached in the previous situ-
1269 ation. This kind of attachment is further supported by the
1270 inclined plane tests with an initial oil layer, which is appar-
1271 ently removed by the emulsion sample, as if the droplets
1272 tended to be attracted by the wall.

1273 This suggests that there are significant van der Waals
1274 attractive forces between the droplets and the wall, which
1275 leads to push them to be in contact (in fact, at a distance of a
1276 few molecules) around some point of their surface. Although
1277 we must admit that we cannot fully explain the origin of this
1278 effect, such a scheme would explain most observed trends.
1279 Indeed, the dominant region of liquid shear would be con-
1280 centrated around those points situated at a distance of the
1281 order of a nanometer. As a counterpart, the area concerned
1282 would be rather limited. The resulting apparent liquid layer
1283 thickness would vary with the number of contacts, and thus
1284 would only slightly vary when the concentration is varied in
1285 the range tested. Finally, this scheme would explain that the
1286 elements tend to be able to remove at large distance from the
1287 wall when some critical force has been applied. In contrast,
1288 there should be a significant dependence with the droplet
1289 size, since the number of contact points decreases with r^{-3} .
1290 Note that we indeed observed an increase in apparent slip
1291 layer thickness, but it is much smaller than expected from
1292 this approach, possibly due to the large size distributions of
1293 our samples.

Under these conditions, a change in the wall slip proper-1294
ties will occur when one applies some sufficiently large1295
stress to extract the elements from the wall, i.e., move them1296
at such a distance that the attractive force is now negligible.1297
In that case, the elements would move at a much larger dis-1298
tance from the wall over some distance and possibly get back1299
to it. This would reduce the stress needed to get wall slip,1300
thus explaining the increase in slip velocity (or equivalently1301
the increase of apparent slip layer thickness) observed for all1302
materials (see Figs. 9, 13, and 18) at the approach of the1303
yield stress. This process would tend to develop further, with1304
more and more elements detached from the wall, or equiva-1305
lently spending more time detached, as the stress further1306
increases, which might explain the transition to a new regime1307
of variations of slip velocity with stress at large stresses (see1308
Fig. 18). When this regime is well developed we can con-1309
sider that all elements remain detached from the wall so that1310
their mean distance from the wall could now result from a1311
balance between some lubrication effect and osmotic effect,1312
as assumed in the Meeker *et al.* model [11], thus leading1313
approximately to a quadratic variation.1314

With a surface of roughness of the order of the element1315
size, the elements can also be jammed in the wall structure,1316
from which they can be extracted thanks to a stress larger1317
than a critical value, as for a friction between two solid sur-1318
faces. This explains the appearance of a finite wall slip yield1319
stress in that case. This effect was described in detail in the1320
case of bubbles moving along a rough plane (see [49]). Then1321
the droplets can move along the surface but the contacts with1322
the solid surface are now more seldom, as they have to jump1323
from one contact to another on successive peeks of the1324
roughness. This explains that the (additional) stress *a priori*1325
solely due to lubrication in the total slip stress is smaller than1326
that for a smooth surface for which the contact is maintained.1327
Finally, with such a slightly rough surface, it appears possi-1328
ble to still obtain some wall slip, but now with two opposite1329
effects: a wall slip yield stress, which must be overcome for1330
the flow initiation, and a larger apparent wall slip layer asso-1331
ciated with motion beyond this yielding. This means that we1332
have a kind of aquaplaning effect, in which the elements,1333
after being extracted from the roughness, now encounter a1334
smaller resistance to motion than with a smooth wall.1335

1336 VI. CONCLUSION

The above results finally provided some clues about the1337
physical explanations of wall slip mechanisms, but they also1338
essentially give us a general view of the wall slip characteris-1339
tics. Indeed, if we generalize these results obtained with dif-1340
ferent model materials and some complex materials (from1341
[23]), different surfaces and different flow conditions, we get1342
the following picture:1343

- Pure wall slip (without bulk flow) is observed for a stress1344
between a wall slip yield stress and the material yield1345
stress.1346
- The value of this wall slip yield stress is thus critical, as it1347
determines the ability of a given material volume material1348
to slip over a solid surface, depending on the surface of1349
contact between the material and the solid.1350

- 1351 • This wall slip yield stress may be essentially due to edge
1352 effects.
- 1353 • Alternatively, it may find its origin in some adhesion
1354 between the material elements (composing the jammed
1355 structure of the yield stress fluid) and the solid surface, or
1356 some adherence due to the roughness of the surface.
- 1357 • Wall slip (below the yield stress) disappears when the
1358 adhesion or adherence leads to a wall slip yield stress
1359 expected to be larger than the material yield stress.
- 1360 • The stress minus the wall slip yield stress is generally pro-
1361 portional to the slip velocity so that wall slip may be
1362 described (even if the reality is likely more complex) as due
1363 to the shear of an interstitial liquid layer of given thickness.
- 1364 • Whatever the material type, the thickness of this layer
1365 appears to vary in a rather narrow range, typically around
1366 a few tens of nanometers.
- 1367 • At the approach of the yield stress, the wall slip properties
1368 change, the velocity now tending to increase faster with
1369 the stress.
- 1370 • Beyond the yield stress slip still apparently occurs, but
1371 now the slip velocity clearly varies with a power of the
1372 stress typically of the order of 2.
- 1373 • This suggests that wall slip has a different nature in this
1374 regime, it now likely involves both an interstitial liquid flow
1375 and the displacement of elements unjammed from the bulk.

1376 Further work remains to be done to understand the exact
1377 properties at the origin of the adhesion on the solid surface
1378 below the yield stress and to understand the exact processes
1379 at work for wall slip beyond the yield stress.

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Q6 1383 APPENDIX

Q7 1384 Tables I and II provide ■.

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