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LETTER • OPEN ACCESS

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## Letter

# Microfluidic angle of repose test for Pickering emulsions

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**Abstract**

Pickering emulsions are appealing systems for droplet-based microfluidic technology. However, to date, their implementation in experiments is limited by their intrinsic characteristics: they present a strong gel-like behaviour and their flowability is lower than their surfactant-stabilized counterpart. Measuring the rheological properties of Pickering emulsions is therefore of interest but very few methods provide measurements using low volumes (<1 ml). Here, we propose a microfluidic version of the angle of repose method to study the flow behaviour of fluorinated Pickering emulsions adapted to small volumes of the sample. We observed a strong link between the nanoparticle level of fluorination and the flow behaviour of the water-in-oil (w/o) emulsions, obtaining a dramatic change from an empirically very poor flow behaviour to a good one by increasing the particles wettability by the fluorinated phase. Our method combines the advantages of microfluidic rheometers, such as low sample consumption and visual monitoring of the complex fluid elements, and allows the study of emulsions with a strong level of aggregation between the droplets.

Keywords: emulsions, droplet-based microfluidics, nanoparticles

(Some figures may appear in colour only in the online journal)

**1. Introduction**

Pickering emulsions are liquid dispersions stabilized by solid particles [1, 2]. They differ from surfactant-stabilized emulsions [3, 4], with, for example, an enhanced stability against coalescence related to the dynamics of the particles at the interface. They are of interest in a wide range of emerging applications [2] from the controlled release of substances for drug delivery [5, 6] to the templating of new materials [7]. Recently, fluorinated Pickering emulsions have been combined to droplet-based microfluidics [8–10]. Droplet-based microfluidics is a powerful technology for the miniaturization and automation of biochemical assays at high-throughput

[8, 9, 11, 12]. It is based on the controlled manipulation in the microchannels of droplets of emulsions as assemblies of independent microreactors. The control of emulsion formulations to be used in these devices is crucial, due to the confinement imposed by the microchannels and the specific requirements of biochemical assays. As a result, the family of molecules usable for droplet-based microfluidics is still limited and the most promising molecules are based on fluorinated compounds and formulations [10, 13, 14].

Three main properties of Pickering emulsions are of interest for droplet-based microfluidics. First, the adsorption of the particle to the interface is an irreversible process. The free-energy of desorption is several thousands of  $k_B T$ , which prevents desorption of the particles [2]. After stabilisation of the emulsion, it is therefore possible to deplete the continuous phase from the stabilizing agent without destabilizing the emulsion. It is not possible to do so with surfactants: chemical

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equilibrium determines the concentration of molecules at the interface as a function of molecules in the bulk [15]. As a consequence, removing surfactant molecules from the continuous phase affects the emulsion stability. On the other hand, reducing the concentration of the surfactant in the continuous phase would certainly be of interest to improve the performance of the encapsulation process [16], since surfactants were shown to promote the transport of small organic molecules between droplets [16–18]. Pickering emulsions have the properties to reduce these transport processes [19] and, therefore, constitute a very promising alternative to surfactant-stabilized emulsions. Second, Pickering emulsions provide a rigid layer, allowing cells to bind at the the droplet interface [20]. As a result, it becomes possible to extend the range of assays performed at high-throughput in the droplet format [21–23] to adherent cells. Third, the possibility to graft functional groups at the nanoparticle interface provide additional features, such as molecular recognition [20, 24] increasing interface functionalities.

However, fluorinated Pickering emulsions introduce new challenges not previously encountered with surfactant-stabilized systems. For example, the non-specific adsorption of enzymes on the nanoparticle surface leads to a loss of enzymatic activity. PEG-functionalized nanoparticles have been recently proposed as a solution to this issue [25]. Another potential limiting factor of Pickering emulsions is their flow properties. Pickering emulsions often exhibit the classical behaviour of adhesive suspensions. This behaviour directly results from strong attractive interactions between the droplets. Such a drop adhesion can result from particles that tend to aggregate, even in the dispersed state or from bridging between the droplets [26, 27].

Furthermore, both surfactant stabilized emulsions and solid-stabilized emulsions exhibit elastic behaviours over a critical droplet volume fraction,  $\phi_c$ , from which its osmotic pressure,  $\Pi$ , and shear modulus,  $G$ , increase as  $\phi - \phi_c$  [28, 29]. However, Arditty *et al* showed that  $G$  and  $\Pi$  values are higher for solid-stabilized emulsions, due to different droplet deformation processes between these two emulsion types. While surfactant stabilized emulsions are controlled by the capillary pressure of the non-deformed droplets, solid-stabilized emulsions are controlled by the 2D yield stress of the droplet surface [30].

Emulsions reinjection and droplets sorting [31], two basic functions of droplet-based microfluidics, have so far not been demonstrated reliably. Measuring the flow properties of these emulsions and choosing their optimal formulations is essential to demonstrate a full compatibility of these systems with the wide range of modules of droplet-based microfluidics. The most widely used method to characterize the flow behaviour of complex fluids, such as Pickering emulsions, is the rheometric measurement of steady shear viscosity [32]. Lately, a broad range of microfluidic viscometers with various working principles have been developed to overcome typical limitations of macroscale rheometers which are limited by sample volumes, access to high shear rates, hydrodynamic instabilities and interfacial artifacts [33–35]. Since the microstructure of a fluid strongly influences the

flow behaviour, the capability of microfluidic viscometers to simultaneously characterize rheology and microstructure through microscopic visualization distinguishes them from macroscale rheometric methods [32].

The rheological behaviour of complex fluids can range from viscoelastic fluids to soft solids, and is strongly dependent on shear rates. Similarly, the flowing properties of granular materials exhibit non-trivial transitions between static, quasi-static and dynamical states, behaving like a solid or a fluid according to the applied stress [36]. We believe well-known techniques used to characterize the flowing properties of granular materials could potentially bring an additional insight to complex fluids' flow behaviour. The angle of repose test is a well-known method utilized to characterize granular materials flow behaviour; as described by Lumay *et al* [36], it consists of placing the studied granular material on top of a circular support until a conical heap naturally develops. The angle of repose  $\alpha_r$  is the angle of the isosceles triangle which has the same surface area as the heap formed. Typically,  $\alpha_r < 36^\circ$  indicates good to excellent flow properties, whereas  $\alpha_r > 57^\circ$  indicates very poor flowability.

In this paper, we propose a microfluidic adaptation of the angle of repose test to characterize the flow behaviour of fluorinated Pickering emulsions. The angle of repose test is very sensitive to the method used to create the heap, needing a defined initialization protocol. Droplet-based microfluidics provide such a versatile system, since the droplets—our equivalent to the particles of a granular material—are produced and deposited in a controlled manner by using a simple droplet maker device. Our method provides a quantitative reference on the flow properties of fluorinated Pickering emulsions, and aides in selecting optimal formulations for droplet-based microfluidics applications.

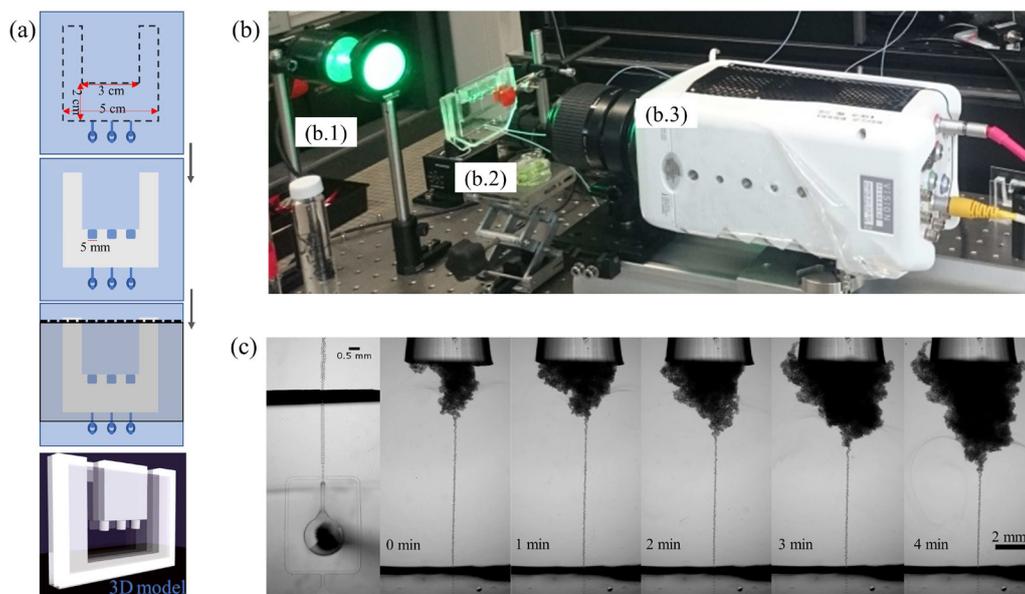
## 2. Materials and methods

### 2.1. Fluorination of silica nanoparticles

Pristine silica nanoparticles (Si-NPs) ( $D = 94$  nm) were synthesized in house, following the protocol described previously by Hartlen *et al* [37].

Surface functionalization of these nanoparticles was performed following a similar protocol as the one reported by Pan *et al* [19]: first, Si-NPs were dispersed in absolute ethanol (99%) at  $10 \text{ mg ml}^{-1}$ . Ammonium hydroxide solution (30%) was added to reach 2% v/v. Finally, 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOTES) was added in the required amounts to reach the degree of surface functionalization desired ( $\phi_{wt}$ ), which, in this paper, we defined as the weight relation of PFOTES versus Si-NPs in the final dispersion.

The reaction was left mixing at 250 rpm for a reaction time of two days to guarantee a time independent functionalization. Afterwards, the dispersion was centrifuged at 15000 rpm for 30 min during three washing cycles. After removing the supernatant, the particles were desiccated overnight and redispersed in the fluorinated solvent HFE-7500 (3 M) using 15 min of sonication followed by vortex mixing.



**Figure 1.** Angle of repose measurement device fabrication and set-up. (a) Sketch side view of device fabrication steps: First, the indicated area of PDMS-PDMS microfluidic device is cut and retrieved; then, 5 mm cylindrical PDMS supports are fixed and aligned with microfluidic outlet; furthermore, glass slides are plasma bonded on both sides of the microfluidic device and extra PDMS is cut. Finally, a 3D projection of the finished device. (b) Microfluidic angle of repose measurement set-up: (b.1) back-light; (b.2) angle of repose microfluidic device held in place by a clamp on a support; (b.3) high speed camera with photo lens. (c) Pickering emulsion production and heap formation recorded at 24 fps.

All of the experiments were done with a fixed concentration of Si-NPs of  $6 \text{ mg ml}^{-1}$  and  $\phi_{\text{wt}}$  values ranging from 3.6 to 10.5 (PFOTES (mol)/ Si-NPs ( $\text{m}^2$ )) ranging from  $1.13 \times 10^{-5}$  to  $3.29 \times 10^{-5}$  values).

## 2.2. Angle of repose microfluidic device design and fabrication

A standard microfluidic droplet maker device with a flow-focusing junction was designed and moulded in polydimethylsiloxane (PDMS) using the soft-lithography techniques of replica moulding of a SU-8 master [14, 38]. A 0.5 cm PDMS stamp was obtained and its inlet ports were punched with a 0.75 mm-diameter biopsy. Then, it was bonded to a 0.5 cm patternless PDMS substrate through oxygen plasma activation. Afterwards, an area of the bonded PDMS was cut and removed, as shown in the figure 1(a), where the edge of the removed area coincides with the ending of the micropattern outlets that are between the two PDMS substrates. A 5 mm-diameter biopsy needle was used to obtain PDMS circular bases, which were fixed 1.5 cm away from the microfluidic device outlets, and, finally, a glass slide was bonded on each side of the PDMS device through oxygen plasma activation; the remaining PDMS was cut and removed. The microfluidic channels were hydrophobized using a commercial coating agent (Aquaapel, PPG industries).

It is important to remark that, due to the density differences between the aqueous phase (droplets) and the heavier fluorinated solvent ( $\rho = 1.614 \text{ g cm}^{-3}$ ) used as continuous phase, the droplets deposition in our device occurred upwards and the cylindrical PDMS support worked as an upper limit for the droplets.

## 2.3. Angle of repose measurement set-up

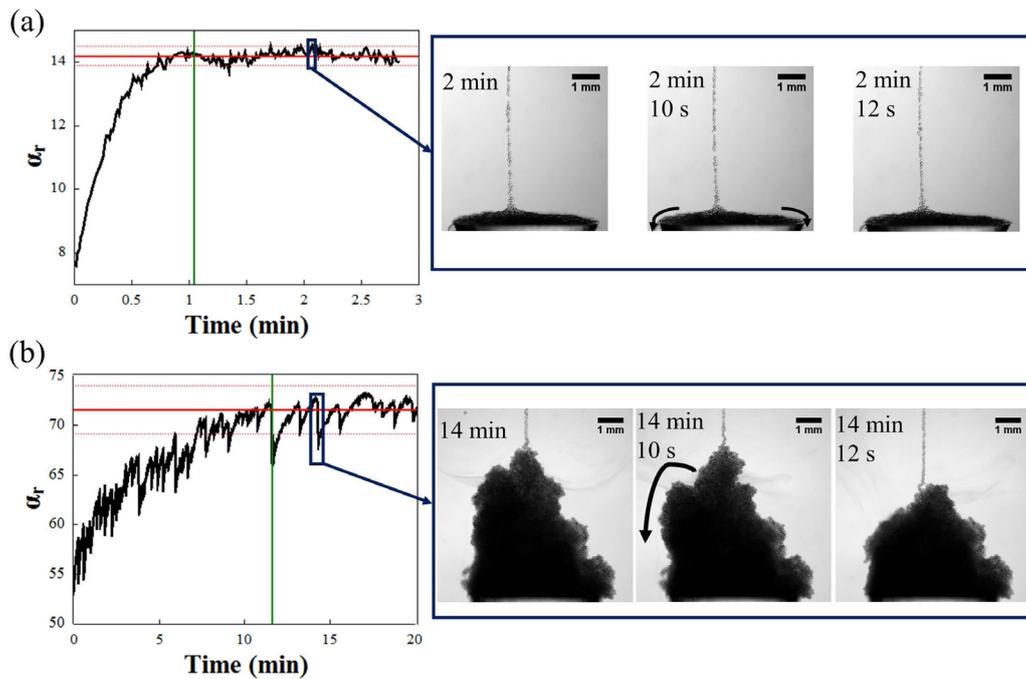
In figure 1(b), the set-up used for all the angle of repose measurements is shown. A phantom 4.2 high speed digital camera was mounted on a horizontal rail and connected to a Canon macro photo lens (MP-E 65 mm), as shown in figure 1(b.3).

The angle of the repose device was fixed on a support and filled with clean fluorinated solvent (figure 1(b.2)). Before each trial, the correct alignment of the device was verified using air bubbles injected from the microfluidic device. For illumination, a flash light and filter were placed behind the device, as shown in figure 1(b.1).

The microfluidic inlets were connected to syringes through Peek tubing of 0.75 mm inner diameter and the fluids flow rates were controlled using syringe pumps (Nemesys, Cetoni). For all of the trials, unless stated otherwise, the flow rates were fixed as  $10 \mu\text{l min}^{-1}$  for the fluorinated phase, and  $5 \mu\text{l min}^{-1}$  for the aqueous phase. Obtaining monodispersed droplets of  $\sim 80 \mu\text{m}$  diameter. Droplet production is shown in figure 1(c), as well as the particle-stabilized droplets deposition on the cylindrical base, which was monitored and recorded at a frame rate of 24 images per second. Droplet size variations were not observed with the controlled parameters studied (pH of aqueous phase and particle wettability).

## 2.4. Image processing and data analysis

The image processing was performed with ImageJ software [39]. All of the images were flipped  $180^\circ$  before processing. The contour of the pile formed on the PDMS base was extracted as coordinates ( $x$ - $y$ ) per each frame. This data was processed with a homemade script using Matlab, obtaining an angle of repose value as a function of deposition time.



**Figure 2.** Angle of repose evolution over time, with indicated stabilization time  $t_{ss}$  (|), steady state angle  $\alpha_{ss}$  (—) and cohesiveness  $\sigma_{ss}$  (· · ·). (a) Emulsion stabilized by Krytox (2% wt) where droplets slide off the edge of the support. (b) Fluorinated Pickering emulsion with consecutive avalanches events (all pile images are tilted 180°).

Time zero was set as the moment the entire surface of the base was completely covered by droplets. The total monitored time was between 3 and 20 min, depending on the time required for the specific system to reach a steady state.

### 3. Results and discussion

#### 3.1. Angle of repose test versus microfluidic adaptation for complex fluids

Our microfluidic adaptation of the angle of repose test brings along inherent differences with the method described by Lumay *et al* [36]. Rather than a fixed amount of material left on the support to reach a static equilibrium, in our system, the continuous deposition of droplets on the cylindrical support builds up a heap that eventually reaches a dynamic equilibrium, where the amount of droplets that falls off the base is equivalent to the amount that comes on it. The droplets are regarded as individual grains—since their interface is stabilized against coalescence through the use of surfactants or NPs—and monodisperse droplets are obtained by keeping the same flow rate conditions in the droplet maker microfluidic device.

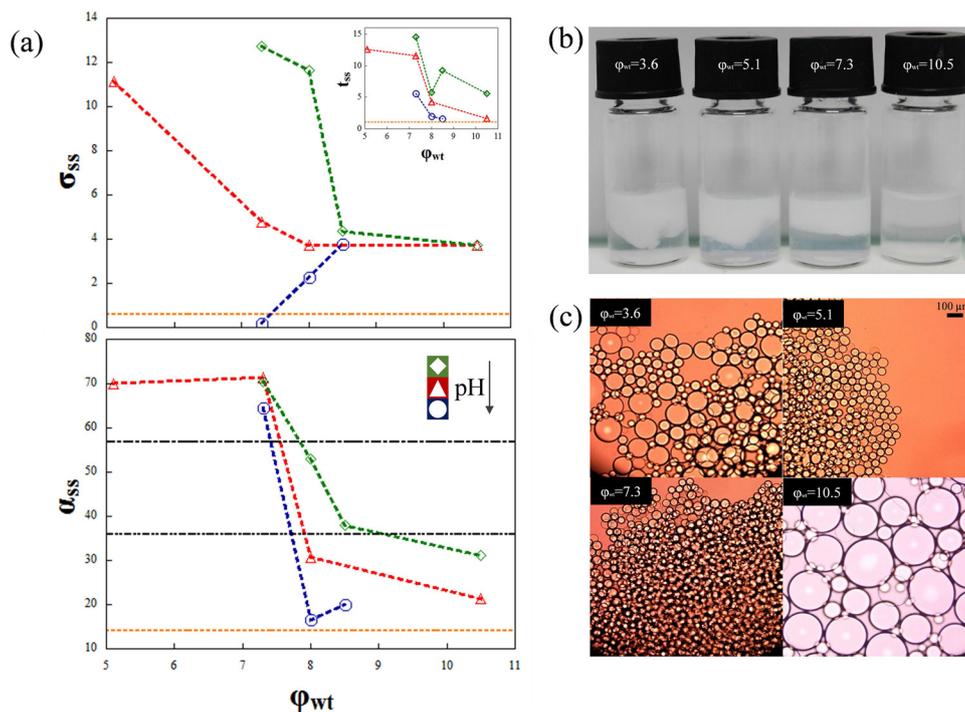
In figure 2, the evolution over time of the angle of repose is shown for droplets stabilized by a fluorinated surfactant (figure 2(a)) and droplets stabilized by fluorinated Si-NPs (figure 2(b)). There are clear differences between both systems: the stabilization time ( $t_{ss}$  green vertical line in figure 2) required to reach a steady state is ten times smaller for a flowable emulsion stabilized by surfactant, since the final steady state angle reached ( $\alpha_{ss}$  red horizontal line in figure 2) is significantly smaller. Additionally, instead of droplets sliding off

the edge of the support with the continuous feeding stream in the middle, in the poorly flowable Pickering emulsion, droplets aggregate with each other until the weight difference is enough to promote an avalanche event, which consists of chunks of aggregated droplets falling from the top of the pile, as shown in figure 2(b).

We consider that the system reaches a steady state after the consecutive cycles of aggregating droplets, followed by an avalanche event with a mean angle variation smaller than 1% between cycles. Then, an additional parameter can be extracted by taking four times the standard deviation ( $\sigma_{ss}$  pointed red horizontal lines in figure 2) of the mean angle of repose after reaching a steady state ( $\alpha_{ss}$ ).  $\sigma_{ss}$  will be directly related to the aggregation level of droplets, since the stronger the aggregation, the less disrupted the pile by gravitational stress [30]. Consequently, the stronger the aggregation, the bigger the maximum angle reached before each fall and the bigger the aggregated chunks falling per cycle. Lumay *et al* quantified a similar parameter by relating cohesiveness between grains—originated from interactions, such as liquid bridges, electric charges and van der Waals forces—with the deviation of the irregular contour of the pile in repose formed from the ideal isosceles triangle shape expected for non-cohesive materials [36].

#### 3.2. Formulation parameters

The wettability of the particles is a key element in the formulation of Pickering emulsions, similar to how the hydrophilic-lipophilic balance (HLB) is for emulsions stabilized by surfactants. In both cases, these parameters directly influence the emulsion type and stability [40]. In our system, we monitor this variable by changing the Si-NPs surface coverage,  $\phi_{wt}$ ,



**Figure 3.** (a) Degree of surface functionalization  $\phi_{wt}$  effect on the steady state angle ( $\alpha_{ss}$ ), aggregation level ( $\sigma_{ss}$ ) and stabilization time ( $t_{ss}$ ):  $pH = 3$  ( $\cdots \circ \cdots$ ),  $pH = 6.8$  ( $\cdots \triangle \cdots$ ) and  $pH = 9.5$  ( $\cdots \diamond \cdots$ ). Emulsion stabilized by surfactant is also indicated ( $\cdots$ ), as well as empirical upper  $\alpha_r$  limit for a good flowability ( $-\cdots-$ ), and lower limit  $\alpha_r$  for very poor flow behaviour ( $-\cdots-$ ). (b) Pickering emulsions collected in vials for different  $\phi_{wt}$ . (c) Observed collected Pickering emulsions on a glass slide after one week of production (original droplet size 80  $\mu\text{m}$ ).

which is the weight ratio of the reacted fluorinated compound on the Si-NPs surface (PFOTES) and the Si-NPs weight. When we increase  $\phi_{wt}$ , the wettability of the particles for the continuous fluorinated phase increases.

In figure 3(a), we show how by increasing  $\phi_{wt}$ , we can effectively improve the flowability of the Pickering emulsion obtained. In particular, going from  $\phi_{wt} = 7.3$  to  $\phi_{wt} = 8.0$  dramatically decreases  $\alpha_{ss}$  from  $70^\circ$  to  $30^\circ$ , going from an empirically very poor flow behaviour to a good one. This effect is also apparent in figure 3(b), where the interface line of the collected Pickering emulsions with the organic phase becomes more irregular the smaller the  $\phi_{wt}$  value is.

The ability to improve the flow behaviour by increasing the degree of Si-NPs coverage,  $\phi_{wt}$ , provides a very useful parameter to control when selecting the optimal formulation of Pickering emulsions for droplet-based microfluidics applications. However, increasing  $\phi_{wt}$  to extreme values, renders the particles too hydrophobic and limits their ability to stabilize collected emulsions, as shown in figure 3(c), where microfluidic made emulsions with the same droplet size (80  $\mu\text{m}$  diameter) were observed after one week of collection, showing significant coalescence for small and high values of  $\phi_{wt}$ .

pH is another commonly studied variable affecting Pickering emulsions behaviour, particularly when the particles involved are pH responsive, meaning that its surface chemistry undergoes some type of modification in response to changes in proton concentration [41]. We used hydrochloric acid or sodium hydroxide to vary the pH of the aqueous phase. In figure 3(a), we show how this parameter affects the flow

behaviour of our system more significantly for intermediate values of  $\phi_{wt}$ . When  $\phi_{wt} = 8.0$ , we can effectively vary  $\alpha_{ss}$  to empirically flowable or non-flowable emulsions by decreasing or increasing the pH of the aqueous phase, respectively. For  $\phi_{wt} = 7.3$ ,  $\alpha_{ss}$  is not affected by the change of pH; however, a significant effect can be observed on the aggregation level of droplets reflected on the magnitude of the avalanche events ( $\sigma_{ss}$ ).

The aggregating nature of fluorinated Pickering emulsions—evidenced in the irregular interface line (figure 3(b)) and the heap formation during the angle of repose test—suggest the presence of adhesive interactions between the droplets. These interactions, as shown previously by Arditty *et al*, dominate the bulk elasticity of these emulsions for droplet volume fractions below the random close packing and give remarkably high shear modulus for strongly flocculated emulsions [30].

Observing the droplets in our system (figure 3(c)), we can discard the droplets-bridging effect as a possible origin of the adhesive interactions between droplets. As described by Lee *et al*, when droplet bridging is present, a deviation from the clear circular geometry of the droplets is observed [26]. A more likely origin of the observed droplet adhesion could be from the natural tendency of the more hydrophilic Si-NPs to aggregate. When dispersed in the fluorinated phase, this aggregation is not evident, probably because the density of particles is sufficiently low and because Brownian motions helps to prevent the Si-NPs from forming aggregates. The aggregation might, however, be favored at the interface through an increase

of local density of the particles. When the Si-NPs hydrophobicity is raised by increasing  $\phi_{wt}$ , the aggregation should be decreased leading to a decrease in droplet adhesion. It is surprising nonetheless to observe a dependence of the droplet adhesive properties on the pH of the dispersed aqueous phase. When the pH is increased, the dissociation of silanol groups on the surface on to negatively charged silanolate ions renders the surface charge in contact with the aqueous phase more negative, resulting in more hydrophilic NPs and smaller contact angles. This effect is usually employed to destabilize the Pickering emulsion [41] and it has also been used to prevent droplet agglomeration in o/w emulsions [42]. However, it is not obvious why it would cause an effect on particle mediated interactions between droplets for w/o emulsions. One interpretation for such a pH dependence could originate from electrostatic interactions between particles at the oil-water interface [43].

Another effect of special significance above the random close packing volume fraction is droplet deformability. Arditty *et al* showed a solid-stabilized emulsion is dependent on the tension generated by 2D plasticity in the particle layer. They identified three different contributions to the lateral inter-particle attractions: van der Waals forces, capillary forces and the attractive interactions arising from the interpenetration of the hydrophobic chains grafted on the solid particles [30]. In our case, we cannot provide a definitive answer to the origin of the modulation of the mechanical properties of the interface. However, the deformation of the interface involves the deformation of the capillary menisci between nanoparticles. The force required to deform these menisci is presumably a function of the particle wettability and considering the length scale of the menisci—typically the size of the particles—it seems reasonable to consider that the first-order effect in the modulation of the interfacial properties of the droplet comes from capillary effects.

#### 4. Conclusion

In summary, our angle of repose microfluidic adaptation provides a quantitative reference on the flow behaviour of emulsions, combining the advantages that microfluidic rheometers have over macroscopic ones, such as low amounts of samples required (between 45 and 300  $\mu\text{l}$  of emulsion) and the visual monitoring of the fluid behaviour. Additionally, it is possible to study samples that present a very strong gel-like behaviour; a task that could be challenging for microfluidic rheometers previously proposed. With our method, we were able to determine the optimal formulation of fluorinated Pickering emulsions as a function of the degree of surface functionalization ( $\phi_{wt}$ ), as well as flow behaviour changes, due to pH variations in the aqueous phase. Further analysis will be of interest to determine a quantitative link between this method and classical rheological characterization parameters, as well as the effect of additional formulation variables, such as Si-NPs size, droplet size and salt content, to further improve fluorinated Pickering emulsions and implement them into the droplet-based microfluidics toolbox.

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