Title: Microgels at interfaces, from Mickering emulsions to flat interfaces and back

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Abstract

In this review, we cover the topic of p(NIPAM) based microgels at interfaces, revisiting classical studies in light of the newest ones. In particular, we focus on their use as emulsifiers in the so-called mickering emulsions, also called Pickering emulsion stabilized by soft particles. Given the complexity of the experimental characterization and simulation of these soft particles at interfaces, the review is structured in progressive complexity levels, until we reach the highly interesting and promising responsiveness to stimuli of mickering emulsions. We start from the lowest level of complexity, the current understanding of the behavior of single microgels confined at a flat interface. Then, we discuss their collective behavior upon crowding, their responsiveness at interfaces, and their macroscopic properties as microgel films. Once we have the necessary characterization tools, we proceed to discuss the complex and convoluted picture of responsive mickering emulsions. The way is rough, with current controversial and contradicting studies, but it holds promising results as well. We state open questions worth of being tackled by the Soft Matter community, and we conclude that it is worth the trouble of continuing after the master theory of microgel interfacial activity, as it will pave the way to widely adopt responsive mickering emulsions as the worthy Pickering emulsion successors.

Keywords: Microgels; Interfacial tension; Visco-elasticity; Responsiveness; Mickering emulsions; interfacial rheology

Contents:

1. Introduction and background

Microgels are colloids that can be swollen in a good solvent, as described for the first time more than 70 years ago [1]. The thermo- and pH-responsive hydrophilic microgels that are a Swiss knife in Soft Matter, gaining popularity in a steady fashion, were synthesized for the first time more than 30 years ago [2]. This steady increase in popularity is largely due to the broad range of responsiveness to stimuli that they exhibit both in aqueous bulk and when adsorbed at interfaces. In bulk, Poly-N-isopropylacrylamide p(NIPAM) based microgels are known for their lower critical solution temperature (LCST) around 32 ºC, being swollen in water below, and collapsed above it [3]. Microgels can also exhibit a pH-responsiveness in the same fashion if a co-monomer able to protonate/deprotonate is used, as it is the case of methacrylic acid (MAA), becoming P(NIPAM-co-MAA) microgels, already synthesized in the first report on p(NIPAM) microgels [2,3]. Other responsiveness, e.g. to magnetic fields [4], can be engineered when the proper co-monomers and functional smaller parts are incorporated to the polymeric network. Thus, the reason for this rich responsiveness resides at the fundamental characteristic of microgels: they are very soft polymeric particles with solvent present inside the particle due to the solubility of the uncross-linked polymer chains, and therefore cross-linking is necessary to provide structural integrity to the particle, differing from hard polymeric particles (e.g. PS or PMMA particles [2]), and allowing for reversible spatial reconfiguration when the responsive functional parts are triggered by the corresponding stimuli. Moreover, microgels synthesized via standard precipitation polymerization present a core-shell morphology with a denser core and a loosely cross-linked shell, with dangling polymers in the outermost part. Nevertheless, this shell might be very thin due to similar reactivity of all monomers involved in the polymerization [5]. In Fig. 1a, a Transmission Electron Microscopy (TEM) image of the first 2D crystalline microgel hexagonal-packing array deposited on a substrate is shown [2]. 30 years ago, the authors correctly hypothesized that the separation between microgels in Fig. 1a was due to their swollen size in water. Nevertheless, it was too early for them to check the monolayer with Atomic Force Microscopy (AFM), as the Nobel Prize for its precursor was awarded the same year. Otherwise, they probably would have found that these microgels were in fact in shell-shell contact, even after deposition on the TEM substrate, as we will discuss.

In 2011, a new term was coined: mickering emulsions, referring to emulsions stabilized by microgels, in contrast to Pickering emulsions, which are generally stabilized by hard particles [6]. For a mickering emulsion to form, microgels need to adsorb at water/oil interfaces. Therefore, we need to pay close attention to their behavior at interfaces in comparison to the one they exhibit in bulk. In fact, microgels are interfacial active in most cases, spontaneously adsorbing to water/air and water/oil interfaces, enabling the formation of mickering emulsions.

There are already comprehensive review studies describing mickering emulsions, which summarize relevant investigations providing valuable insight in understanding the behavior of microgels at interfaces [7–9]. Some of them focus on microgels as stabilizers of food emulsions [10–13]. Also, there have been particular applications of mickering emulsions as stimuli-responsive nanocarriers in storage and release systems [14,15], in the release of the model drugs from colloidosomes [16,17], for the development of droplet-based microsystems as microreactors and microdetectors [18], and in the formulation of new oxidation-responsive emulsions [19].

Furthermore, as a clear example of the accelerating pace on this topic, during the peer-review of this work a review on microgels at liquid-liquid interfaces as stabilizers of emulsions was published [20].

In this review, each co-author comes from a different background, approaching the topic of microgels at interfaces from different perspectives. On one hand, the fundamental understanding at the level of single microgels, aiming to first understand to then engineer the pair potential between neighboring microgels confined at interfaces. This perspective is detailed in recent reviews on this topic, particularizing to flat interfaces [21–23] and further deposition of the microgel monolayers on substrates for further uses as lithographical masks [24–26]. On the other hand, the interfacial behavior of charged microgels in the form of adsorbed layers and spread layers comprises the other viewpoint [27,28]. This is undertaken by combining macroscopic interfacial expertise [29–31] and fundamental interactions between microgels [32]. Indeed, a major achievement covered by this review is addressing the macroscopic characterization of microgel films, including the rheological properties and its implications on the stability of mickering emulsions and their responsiveness. We believe that the combination of these different points of view provides an original approach to tackle controversial topics with a non-biased fresh view.

One of the hot topics around mickering emulsions concerns their thermo- and pH-responsiveness, probably the most attractive characteristic of such systems, inherited from the responsiveness of the microgels used for their preparation [33]. A responsive emulsion is with no doubt an advantage. However, at present, the understanding of the mechanisms underlying such responsiveness is far from reaching consensus, in particular related to the stabilization and destabilization on demand. A question that seems easy to answer remains untapped: *Do microgels desorb from interfaces upon destabilization of mickering emulsions?* The fact that no clear answer is available exemplify the two sides of this topic, i) it is difficult to experimentally characterize and simulate such systems to the extent of knowing what happens to individual microgels in mickering emulsions, and ii) there are open questions in the field that should serve as an incentive to keep on track. These answers will help to unravel the intricate behavior of such soft particles at interfaces, with promising rewards in the form of truly responsive emulsions with tailored properties on demand. We envisage that such answers will serve as a significant next step in expanding the mickering emulsions as the natural successors of Pickering emulsions.

It is tempting to extrapolate the behavior of microgels in bulk to explain the findings at interfaces, but reality unravels much more subtle as we will discuss in the coming sections. Particularly controversial up to today is the understanding of the stabilization/destabilization of pH-responsive mickering emulsions at extreme pH values, with no consensus and with explanations that often contradict each other as we will discuss. Therefore, we embrace in this review the ambitious objective of bringing together the up-to-date knowledge on the fundamental understanding of the behavior of microgels confined at fluid-fluid interfaces, and correlating this knowledge with the engineering of mickering emulsions stability. For such endeavor, we start describing the behavior of single microgels at interfaces, only then going on to collective effects upon crowding of microgels at flat interfaces. We then proceed to include the responsiveness ingredient, focusing at flat interfaces but also sneak peaking in the implications of highly curved interfaces. Finally, we step into the macroscopic characterization of microgel films, by interfacial tension and interfacial rheology, to have all the tools in hand before correlating the accumulated evidence with the stability of mickering emulsions. In the second part of the review, we start paying attention to the role of visco-elasticity of individual microgels, often referred as their deformability, in the emulsion stability. Then we enter the controversial domain of trying to understand the role of electrostatic charges in relation to pH-responsive microgels in pH-responsive mickering emulsions, covering also the responsiveness to temperature. Finally, we focus on the less explored but very promising field of correlating the characteristics of microgel interfacial films with the final behavior and responsiveness of mickering emulsions.

2. Fundamentals on microgels at the fluid-fluid interface

Since p(NIPAM) microgels were first synthesized 30 years ago, a great deal of attention has been paid to describe their properties in bulk, mostly due to their softness and responsiveness to external stimuli [3]. After realizing that they are the main ingredient of mickering emulsions, more and more attention has been paid to their behavior when confined at fluid-fluid interfaces. In the following subsections we will cover the current understanding of the behavior of single microgels at interfaces, their collective behavior upon crowding, their responsiveness to stimuli, and their macroscopic behavior as part of microgel films.

2.1. Single microgel at the interface

The interfacial activity of microgels is due to their ability to lower the surface tension via decreasing the energetically unfavorable area of contact between water and oil [34], or air, when at water/air interfaces [35]. Therefore, microgels adsorbed at interfaces will stretch as much as possible, even more than doubling their diameter in bulk, to decrease the interfacial tension, and this will be counterbalanced by the internal elasticity of the polymeric network, acting as a recovery force, which increases with the cross-linking density of the microgel [34,35]. On the other hand, the portion of the microgel immersed in water keeps being solvated and swollen below the LCST, forming a *fried-egg* shape [34,36]. Both effects work together to enhance the core-shell morphology of the microgels, when they adsorb at interfaces from bulk. A recurring problem in the characterization of microgels adsorbed at interfaces is that the portion spread at the interface is typically a few nanometers thick, which it is the reason why the shells are not visible in Fig. 1a. Typically, the spread shells can only be imaged ex-situ via AFM measurements in dry conditions, after deposition on a substrate [23,37–40]. The spread shells can be seen in situ via conventional cryo-Scanning Electron Microscopy (cryo-SEM) of emulsions or by Freeze-Fracture Shadow-Casting (FreSCa) cryo-SEM of interfaces and emulsions [6,41,42], although the shells are not always visible via cryo-SEM [34]. Fluorescent marking of the microgels allow for in situ localization of the microgels, which is quite useful when characterizing the stability and time evolution of mickering emulsions (see Fig. 1b-e). However, only the inner portions of microgels are fluorescent, while the outer part usually cannot be marked with dye, a problem that increases for the dangling polymers in the outermost part of the microgel. For this reason, the microgels appear not to be in shell-shell contact in Fig. 1b-e. The difficulties in characterizing experimentally the microgels adsorbed at interfaces have drawn attention into simulations of such systems. Nevertheless, the real system involving millions of p(NIPAM) molecules, for a single microgel, is out of reach with the current computation capabilities. Luckily, simplified versions of in-silico microgels can reproduce the fried-egg morphology of microgels at interfaces, with the swollen portion immersed in water, as seen in Fig. 1f, and the correlation between cross-linking density and maximum spread, and even the height of the microgels after deposition on a substrate [34]. On the other hand, diamond-like networks representing microgels require less computational power and are useful to describe the portion spread at the interface [43], but they tend to underestimate the swelling of the part immersed in water (see first panel in Fig. 1g), while the addition of charged co-monomers in the polymeric network help to recover this swollen shape, as can be seen in Fig. 1g. From these images, also a reduction in the diameter of the portion of microgel adsorbed at the interface is visible as the microgel becomes more charged. As we will see, this fact will impact on the behavior and stability of pH responsive microgel-laden interfaces against pH changes. The examples discussed above involve pure polymeric microgels, while a hard core and polymer shell particle adsorbed at the interface introduces a new ingredient in the adsorption physics, with the relative size of the core and the shell dictating the position at which the hard core will sit at the interface, or below it, but with the stretching of the shell happening as in the case of pure polymeric microgels [44,45]. In the extreme case of low fraction of oil, recently it has been predicted that single microgels can scavenge oil inside their polymeric matrix, as can be seen in Fig. 1h, reducing the contact area between water and oil, and upon increasing the oil fraction, the picture of emulsion formation is recovered [46]. We foresee that an experimental proof of this oil-scavenging prediction would have potential implications in the oil recovery industry, and emphasizes how useful these simulations are to help bridge the gap between experimental limitations and high potential of tailoring the responsiveness of mickering emulsions.

2.2. Collective effects

When considering the collective behavior of microgels at interfaces, a key factor to design mickering emulsions, we need to disentangle the huge variety of microgel architectures, compositions, and external stimuli, as temperature, pH, ionic strength, etc. Thus, we start with the case of conventional microgels at interfaces at room temperature and neutral pH. Comparing smaller and bigger microgels adsorbed at water/oil interfaces, some of us found that the big ones tend to aggregate at zero surface pressure due to capillary forces, with interfacial deformation in the range of a few nanometers, as the corona is stretched thin at the interface [25]. A similar explanation was found at the same time for microgels at the water/air interface by Keal et al. [47]. Furthermore, the cross-linking density plays a major role in their collective behavior when microgels start to be in shell-shell contact. In Fig. 2a-b, the conventional picture of a microgel monolayer with 5% cross-linking density, deposited from a water/decane interface to a substrate is shown, where microgels are apart at zero surface pressure while they form a 2D crystalline hexagonal-packing, with all microgels in shell-shell contact, upon compression of the monolayer [5], similar to the monolayer in Fig. 1a. Although the shells cover all areas in the hexagonal-packing, we can identify the more cross-linked cores with larger heights in AFM images. Nevertheless, when microgels are synthesized without cross-linker, the NIPAM self- cross-linking limited ability produces Ultra Low cross-linked (ULC) microgels. Upon crowding, as shown in Fig. 2c-d, ULC microgels virtually entangle into a flat polymer layer indistinguishable from linear molecular p(NIPAM) [5,38]. Further compression of the monolayer recovers the core-shell morphology, being a reversible process. This is in good agreement with recent simulations of diamond-like network microgels at water/oil interfaces, where high (Fig. 2e-f) and low (Fig. 2g-h) cross-linked microgels present a similar trend as the ones in Fig. 2a-b and 2c-d [48], respectively. In fact, these simulations showcase an open question: *Do microgels in shell-shell contact repel through steric interactions or interdigitate each other through their dangling polymers?* Experimentally this is still an open question because of the aforementioned difficulty in tracking and imaging the outer part of the shell or dangling polymers, where dyes could not be attached. Even in the case in which microgels were synthesized with functional groups to attach fluorescent dyes added to the shell, there was an outer part of the shell with dangling polymers where they were absent [49]. On the other hand, also from the Fig. 2e-h, there is a hint on a possible way to discriminate to which extent steric repulsion or interdigitation is dominating. Fig. 2f shows a honeycomb pattern devoid from polymers which forms from the steric repulsion between shells, while interdigitation tends to blur such pattern. Moreover, a general experimental finding is that once the hexagonal-packing is formed, the capillary attraction and steric repulsion freezes the monolayer, which can be compressed until buckling but not rearranged [25,26,37]. Nevertheless, recently it was predicted that sufficiently small microgels adsorbed at interfaces will exhibit reentrant dynamics upon compression of the monolayer [50], i.e. fluidification and therefore rearrangement of the monolayer. Experimental proof of such prediction is missing, and it will add an extra degree of control on the self-assembly of microgels at interfaces. Once the 2D crystalline hexagonal-packing is formed, with all microgels in shell-shell contact, the monolayer can be further compressed until the shells start to fail and the microgels randomly aggregate into core-core contact. This aggregation process takes place earlier in the compression isotherm for higher cross-linking densities [51], and can be suppressed for small microgels [25] or low cross-linked and ULC microgels [5,52]. As shown in Fig. 2i, once this transition finishes, a new hexagonal-packing forms with all microgels in core-core contact, which can be compressed to a much lesser extent before failure of the monolayer [37]. This is slightly different for smaller microgels, where a continuous transition between the hexagonal-packing in shell-shell contact and a disordered packing in core-core contact is found [25]. This finding at flat interfaces naturally translates into curved surfaces in mickering emulsions, where microgels can be also compressed to the extent in which core-core contact is achieved, as shown in Fig. 2j-l. We see room for experiments to explore the bridge between crystallinity of the monolayer, impact of the shell-shell to core-core transition, and mickering emulsion stabilization. Other architectures as hollow microgels, or hard core-shell microgels, add an extra layer of complexity to tailor the pair potential of interaction between microgels adsorbed at interfaces, worth of investigating and connecting to the stability of mickering emulsions [53].

2.3. Responsiveness of the microgels

The next complexity level comes from the responsiveness of the microgels. Mickering emulsions that can be stabilized or destabilized on demand, with pH or temperature, are consistently reported [33,54]. As shown in the left panel of Fig. 3a, oil-in-water emulsions tend to destabilize when microgels are heated above their LCST, when they collapse in size. This is in agreement with the slowing down of microgel adsorption dynamics at interfaces with the temperature, which suggests less interfacial activity above the LCST [55]. While the microgel adsorption kinetics is important for the formation of emulsions, studying the collective behavior becomes more important as the interface becomes crowded [23]. On the other hand, in the right panel of Fig. 3a the responsiveness of microgels to charged co-monomers is shown, although in this case charged-swollen microgels seem to be less interfacial active than uncharged ones [54]. Interestingly, the charged groups of the microgels used in Fig. 3a come from chitosan, which provide amine groups that are positively charged at low pH and neutral at high pH, but the authors report an unexpected for us overall swelling with increasing pH [33], opposite to other microgels functionalized with amine groups [38,55]. In any case, the destabilization, with the temperature or pH, of Mickering emulsions is a general finding that needs to be confronted with the current knowledge of what happens to microgels adsorbed at interfaces upon triggering the responsiveness to temperature or pH. Adding up the two responsiveness seems counter-intuitive as temperature-swollen microgels below the LCST are more interfacial active, but charged-swollen microgels are less interfacial active, according to the studies presented so far. In fact, as we will see in following sections, different studies contradict each other regarding the role of pH in the stabilization of mickering emulsions. Therefore, it is not straightforward to relate swelling to interfacial activity, and careful separate analysis needs to be done before generalizing results. Maintaining the pH constant and changing temperature, it is found that isolated polyelectrolyte microgels spread to the same extent at water/oil interfaces below and above the LCST, while the portion protruding into oil is collapsed, and the portion immersed in water keeps being thermo-responsive, as shown in Fig. 3b [38,40]. Considering only that fact, no differences should be expected in their collective behavior at interfaces upon temperature change, and mickering emulsions should be very stable, and not exhibit the destabilization observed upon heating. Nevertheless, the portion immersed in water affects the collective behavior of the microgels upon crowding. Thus, below the LCST, the behavior is the one described in Fig. 2i, which was obtained at room temperature, below the LCST, while above the LCST the portion of the core immersed in water is collapsed and this brings different collective behavior. Above LCST, microgels in shell-shell contact that fail into core-core contact cannot be compressed anymore, as their cores are already in the collapsed state. This is signature that the 3D swelling of microgels adsorbed at interfaces has to be taken into account to describe their 2D phase behavior. It is also reasonable to think that at curved interfaces, especially when their size is comparable to the microgel size, as it is the case in Fig. 1d-e, the influence of the portion exposed to the water phase will differ from the one at flat interfaces, with a hindering of such mechanisms for higher curvatures, at a given swelling state. In the extreme case of microgel and droplet being of comparable size, the microgel will not be able to deform to the point of stabilizing the droplet in a mickering emulsion. This comparison between collective behavior of microgel-laden flat and curved interfaces is another field that appears open to be explored thanks to these recent studies. Another study was published considering the pH-responsiveness of polyelectrolyte microgel-laden water/oil interfaces, analog to the one just discussed above for the temperature responsiveness [43]. In this case the picture is more complex, for example small microgels were predicted to slightly decrease their spread diameter at the interface upon being charged, as it was discussed in Fig. 1g. This was recently experimentally found for small microgels [39], as depicted in Fig. 3c, where the onset of the increase in surface pressure was delayed for charged microgels, due to their lesser spread at the interface compared to when they are uncharged, and therefore the interface needs to be further compressed before they become in shell-shell contact. For bigger microgels this effect is hindered due to the increasing relevance of the portion immersed in bulk, scaling with the hydrodynamic diameter as d_H^3, in comparison to the portion spread at the interface, scaling as $d_{interface}^2$, recovering consistency with previous cryo-SEM pictures that show polyelectrolyte microgels that spread to the same extent at different pH [41], as shown in Fig. 3c for large microgels. Moreover, although the part protruding into the oil phase is expected to be less responsive, limited by the water trapped and effectively displaced into the oil phase for microgels with low solubility in the oil phase, there is still room to elucidate the role of such protrusion, especially when the oil phase starts to be a good solvent for the microgel, even producing much less explored inverse water-in-oil emulsions, as it is the case when using octanol, dichlorobenzene, or fatty acids as the oil phase [6,56]. Therefore, we will focus on the much more explored case of oil-in-water emulsions. For this purpose, FreSCa cryo-SEM, despite being a cryo-SEM technique, distorts less the interface and might elucidate the role of this protrusion into the oil phase. Focusing again on the collective behavior of charged microgels at interfaces, at high compression states when the shell-shell contact starts to fail into core-core contact, the charged-swollen portion in water starts to interact earlier with their neighbors both via electrostatic interaction and via steric interaction. Therefore, upon compression of the monolayer, the collapse into core-core contact happens earlier and can be further compressed less before the collapse, compared to the case of the same uncharged microgels. Moreover, the authors showed that this electrostatic interaction can be screened and thus tuned at will through the ionic strength of the water phase [39].

We look now at mickering oil-in-water emulsions, for now only focusing on the geometrical confinement to spot the differences that we can expect as we go from flat to highly curved interfaces. Therefore, interfacial tension considerations will be discussed in the next section. In Fig. 3d, two different microgel architectures were added to the emulsion, both uncharged at low- and charged at high-pH. Both are p(NIPAM-co-MAA) microgels, one termed dense-core (DC) with MAA in the core, and the other termed dense-shell (DS) with MAA in the shell. The low pH-uncharged MAA binds to fluorescein but expels it when it is charged, at high pH. Therefore, at pH 3, the bright dots are DC and hollow particles are DS microgels. In this uncharged state both DC and DS microgels are adsorbed with equal probability at the droplet interface. At pH 11, dark spots are DC and dark rings are DS microgels, and in this charged state the DC microgels are predominantly adsorbed at interfaces while the DS microgels still can provide emulsion stabilization even if not adsorbed at oil droplets through steric repulsion of emulsion droplets at sufficiently high fraction, or in other words, when non absorbed swollen microgels become so numerous and ubiquitous that they can stabilize the droplets even if they do not adorb at their interface. The preference of adsorption of DC microgels in the charged state points out to their stabilization at interfaces thanks to the shell devoid from MAA monomers, that keeps the microgel less swollen and softer than the DS microgel counterpart. Both studies, at flat interfaces in

Fig. 3c, and in emulsions in Fig. 3d, suggest the same broad conclusions: charging microgels upon pH change can be used to modify the interaction between microgels at interfaces and their adsorption energy. The parallelism goes even further, as in Fig. 3c and 3d all are p(NIPAM-co-MAA) microgels, where the small microgels in Fig. 3c are synthesized with conventional precipitation polymerization, resulting in a DC-like structure, while the large microgels are synthesized with the MAA added at a later step in the shell of a pure p(NIPAM) core, resulting in a DS-like structure as in Fig. 3d. As can be seen the picture becomes more and more convoluted, as for example this pH responsiveness mechanism is actually present also for conventional Pickering emulsions where hard colloids exhibit a change in wettability with a change in pH [57]. And some of us found recently that also charging of microgels adsorbed at interfaces can be found via heating instead of adjusting the pH [28], recovering the behavior exhibited by small microgels discussed in Fig. 3c. These comprehensive studies provide proof that the adsorption of charged-swollen microgels to interfaces is more difficult, analog to collapsed microgels above the LCST, especially when such collapse brings charge to the microgel. However, as we will see in following sections, this mechanism is contested and under debate. Moreover, the desorbing mechanism once they are adsorbed remains not fully elucidated.

2.4 Microgel films and interfacial rheology

The deformation of microgels upon adsorption onto fluid interfaces is driven by the reduction of the free energy, i. e. of the interfacial tension. This deformation is only counterbalanced by their intrinsic visco-elasticity, directly related to their cross-linking density [34]. Microgels flatten at interfaces upon adsorption in order to spread and maximize the amount of surface active polymer chains at the interface. The degree of deformation depends on the internal elasticity of the microgel as explained above. Hence, the conformation adopted by microgels at interfaces results from a balance between the free energy and the internal elasticity, which can be assessed by changes in the interfacial tension and on the interfacial rheology of the interfacial films. These interfacial characteristics can be measured in Gibbs or Langmuir microgel films. Gibbs films are formed by spontaneous adsorption of microgels and characterized macroscopically by adsorption dynamics, equilibrium values of interfacial tension or by interfacial dilatational rheology [12,13,58,59]. Langmuir monolayers are obtained by spreading microgels at liquid interfaces and highlight the interfacial interactions upon lateral compression [27,28,42,51,60]. These techniques can be combined with shear rheology, to gain insight into intermolecular associations at macroscopic level [58,61]. As a middle term between the macroscopic and microscopic characterization of the visco-elastic properties of the microgel adsorbed layers, microdisks operated via external magnetic fields serve to study rheological properties of the adsorbed layer at the mesoscale, in the range of hundreds of microns [37,62–64]. This might be a helpful tool to bridge between macroscopic and microscopic characterizations of the visco-elastic behavior, of the adsorbed layer and of single microgels at interfaces, respectively. Finally, AFM can also be used to measure the mechanical properties on a local scale providing nanorheology of microgels [65].

In general, interfacial tension approaches are experimentally easy and accessible but can be difficult to interpret due to the complex physical chemistry underlying the behavior, which needs to consider interactions within the interfacial layer and coupled with the bulk [58]. There are recent reviews in the literature devoted to discuss in detail some of the main interfacial characteristics of microgel particles [7,10,12,13,58,59,66]. Also, in section 3.3 the works correlating explicitly interfacial tension and rheology with emulsion behavior are discussed in more detail. Therefore, in this section, a summary on the general characteristics of Gibbs and Langmuir films formed by microgel particles is given as regards of changes in interfacial tension and interfacial rheology. Interfacial layers of microgel particles share common features with proteins, polymers and particles but do not completely match any of them [58]. Hence, the interfacial behavior of microgels particles highlights some unique features arising from their soft, porous and deformable structure.

2.4.1 Gibbs adsorbed microgel films

As it has been previously discussed, microgels adsorb spontaneously onto fluid interfaces lowering the interfacial tension in a similar way to proteins and polymers do. Also, this process is irreversible as microgels do not spontaneously desorb from the interface once the interfacial film has been formed [28,42,67]. This has been proven by analyzing the change of interfacial tension by subphase exchange of bulk solution which provided no change upon removal of excess bulk microgels [68]. This again, similarly occurs with proteins owing to the conformational changes undergone by proteins upon adsorption [69,70]. Chains of linked polymers retain some of the hydrophobicity of the original monomers as chains of unfolded proteins and hence remain anchored at the interface to decrease the free energy of the system. Particles also adsorb irreversibly onto liquid interfaces [10,12].

The dynamic process of adsorption for microgels has been only recently addressed in the literature [55,67,71,72] and although there is a certain agreement in the general picture, there are still some unknown features [12,13]. Most literature works show three distinct kinetic regimes for the adsorption of microgel particles which are analyzed by changes in the time dependence of the interfacial tension [55,67,71]. A first period, characterized by a negligible change in the interfacial tension which appears for low concentrations or highly cross-linked systems [55,67]. This regime requires a minimum interfacial coverage to affect the interfacial tension which decreases as the concentration increases in bulk [42,67,71,72]. This critical microgel concentration increases with cross-linking and is higher for charged microgels and will be a decisive parameter later in the stabilization of emulsions. The second regime, is characterized by a steep reduction of the interfacial tension. The reduction of interfacial tension in this regime is related to the presence of hydrated dangling chains in the microgel. Microgel flatten upon adsorption, as has widely discussed in the previous sections. In this flattened structure, less cross-linked microgels have more density of loose chains and therefore should be more efficient in covering the interface, decreasing the interfacial tension. Collapsed microgels have a lower degree of dangling chains and are less surface active. The rate of change of interfacial tension in this second regime depends on concentration and conformation of microgels. Most authors claim that the initial adsorption is a diffusion controlled process, as deduced by a square root variation of the adsorption time with the protein concentration [13,55,58,71]. However, some others state that the sharp evolution of the adsorption time with concentration can only be explained by a cooperative phenomenon [67,73]. In the third and final regime, the interfacial tension reaches an equilibrium value and remains unchanged. The time required to reach the equilibrium interfacial tension value is again affected by various factors as the time needed to begin the reduction of interfacial tension in the second adsorption regime. Lower concentrations, increased cross-linker content and highly charged systems take longer times to reach equilibrium interfacial tension [42,67,71,72]. Interestingly, the equilibrium value of interfacial tension reached upon spontaneous adsorption of microgels onto fluid interfaces seems to be practically independent of the bulk concentration of microgel as reported elsewhere [7,74]. This constitutes a major difference with respect to protein layers, in which the final value depends on the concentration of microgel in bulk as the protein adapts to the available area [75–78]. Moreover, this suggests that the interfacial coverage is very similar in all cases and dominated mainly by the presence of dangling chains anchored at the interface from flattened microgels. In fact, as it will be shown later, the equilibrium interfacial tension does not seem to provide practical information on the performance of the interfacial layer in emulsified systems.

The adsorption of thermo-responsive microgels displays some special features which deserve attention. The first adsorption regime is shorter for swollen microgels, hence the critical concentration needed to reduce the interfacial tension is lower below their LCTS [55,71]. In the second regime, the rate of change of the interfacial tension is non monotonous. Below the LCST the interfacial tension decreases faster as the temperature increases, whereas above the LCST, the interfacial tension decreases slower as the temperature increases. Accordingly, the time needed to reach the equilibrium interfacial tension is longer as the microgel collapses above the LCST while the final interfacial tension reached depends on the swelling state [55]. There is a slight variation in the final equilibrium interfacial tension reached as a function of T, reported repeatedly, which shows a minimum equilibrium interfacial tension located around the LCST [7,13]. This minimum is more noticeable for charged systems [79]. The origins of the increase in interfacial tension above the LCST are still not fully understood. Electrostatic repulsion between charged groups seems to play a role [62,79] but also particle aggregation [80] and desorption [55,71] are seen responsible for this apparent reduced interfacial coverage. The correlation of this minimum with emulsion stability is complex and will be developed in section 3.3. Anyway, the variations of equilibrium interfacial tension are in general very subtle and suggest that the interfacial coverage remains practically unaltered. Cross-linking density and temperature possibly promote conformational changes of absorbed particles, rearrangements within the interfacial layer, formation of multilayers, changes in the interparticle associations and overlapping of dangling chains. These are not detected by equilibrium interfacial tension but required the use of rheological tools.

The dilatational interfacial rheology is obtained by analyzing the response of the surface pressure (Δπ) of an interfacial layer to a small perturbation of the interfacial area. The general response can be simplified to:

$$\Delta\pi = -\left[\varepsilon + \eta_s \frac{d}{dt}\right] u(t)$$

Where the deformation of the interface is given by the relative change in interfacial area. For small sinusoidal deformation (linear regime) it reads:

$$u(t) = \frac{\delta A(t)}{A_0} = u_0 e^{i\omega t}$$

In this case, the response of the surface pressure follows the imposed deformation with a lag phase (ϕ) and the interfacial dilatational modulus E* is a complex quantity which depends on the oscillation frequency ω.

$$E_S^*(\omega) = E'_s(\omega) + iE''_s(\omega) = \varepsilon + i\omega\eta_s$$

The real part is the dilatational storage modulus accounts for the surface dilatational elasticity. The imaginary part is the dilatational loss modulus accounts for the viscous dissipation. deskmuth2015 [58,81]. The dilatational modulus contains information on the intra and intermolecular interactions within the interfacial layer and relates to different phenomena underlying formation and stability of foams and emulsions [82]. There seems to be an agreement in the influence of temperature on the dilatational modulus concerning concentrated interfacial films. The storage modulus E' is always higher than the loss modulus E'' indicative of a solid-like behavior of the interfacial film in a concentrated state [42,55]. Also, the storage modulus (interfacial elasticity) shows a minimum as a function of temperature, located at the LCST, again in concentrated systems [55,64,71]. This suggests the existence of different interacting regimes between microgel particles below and above the LCST for concentrated interfacial films. In general, the values reported for the elastic moduli in these references are low [55,64,83] and this is possibly related to the high bulk concentration used. The dilatational rheology is strongly dependant on the interfacial coverage [42,59,84]. This was first evidenced by Pinaud et al. who reported a steep maximum in the dilatational elasticity of adsorbed layers as a function of surface coverage (adsorption time). In the initial state of adsorption, as the microgels reach and flatten at the interface, the dilatational elasticity is maximum and then diminishes rapidly as the interfacial film is further condensed and the flattened particles compress [42]. More recently, Akentiev et al. have studied in great detail the surface dilatational elasticity of p(NIPAM) films obtaining two maxima as a function of surface coverage. The first maximum is related to the interaction of shells while the second maximum corresponds to the interaction of cores [84].

2.4.2 Langmuir spread microgel films

The two dimensional organization of microgels has been most extensively studied for spread microgel particles at the interface by means of Langmuir films. These provide the interfacial pressure as the particles spread at the interface are compressed hence highlighting the interaction between particles. It is also generally accepted that the interaction between microgels lies in between that of solid particles and soft polymers in Lagmuir films [10,12]. Analysis of Interfacial Pressure-Area (π-A), or compression isotherms, highlights new features arising from their softness and responsiveness nature of microgels [25,37,41,85]. In general, as the interface is compressed and the microgel particles become closer, the monolayer undergoes different interaction regimes as already commented above. The microgels undergo a continuous transition from a highly flattened state, at low surface coverage where the maximal amount of dangling chains are anchored at the interface, to entangled flattened microgels and eventually the formation of a dense layer of compacted microgels. These transitions are reflected in changes in the slope of the π-A isotherm as illustrated in Fig. 4a for charged p(NIPAM-co-MAA) microgels [37]. It is now generally accepted in the literature that microgel monolayers undergo 5 interaction regions upon lateral compression [23,45,51,60]. Region I corresponds to a negligible surface tension characteristic of a gas of non-interacting particles. Region II shows a steep rise corresponding to the interaction of the shells followed by a pseudo-plateau corresponding to the shell-core interaction in region III. Region IV shows another sharp rise in surface pressure corresponding now to core-core interaction ending in region V which marks the collapse of the monolayer, as seen in Fig. 4a.

Figure 4b shows the shear viscoelastic properties of the monolayer depicted in Figure 4a as measured by interfacial microdisk rheology. This technique creates a miniaturized version of a surface viscosimeter. Interfacial shear rheology uses similar concepts to bulk rheology. Hence, the interfacial shear modulus can be obtained as the ratio of the stress response of the monolayer (σ_{xy}) to the applied strain (u_{xy}):

$$\sigma_{xy} = \left[G + \eta_s \frac{d}{dt}\right] u_{xy}$$

In response to small amplitude shear deformations, the interfacial shear modulus is a complex magnitude, which depends on the oscillation frequency ω:

$$G_s^*(\omega) = G'_s(\omega) + iG''_s(\omega)$$

The real part is the storage modulus and accounts for the elastic component. The imaginary part is the loss modulus and accounts for the viscous component. deskmuth2015. This experimental technique shed new light into the nature of the interaction found in each compression state [37]. The storage modulus of the monolayer appears always higher than the loss modulus, confirming the elastic nature of the interface in agreement with results of Gibbs monolayers of spontaneously adsorbed particles reported elsewhere with macroscopic shear and dilatational rheology [42,55,61,83]. Also, the trend reported for the surface shear rheology deformation as a function of surface coverage in Fig. 4 is completely similar to the trend reported by Akentiev et al with surface dilatational rheology, who also showed a first maximum related to a phase-coexistence region and a second one due to particle percolation,,as commented above for adsorbed Gibbs layers [84]. Fig. 4b allows further interpretation of these maxima in terms of interparticle interaction. The visco-elasticity increases owing to the compression of the shell-shell hexagonal lattice which bears high shear forces (Region II). The elasticity saturates, and then diminishes owing to the melting of the shell-shell phase (Region III). This is followed by a steep increase upon the formation of a percolating network of the core-core contacts (Region IV).

The influence of a solid core and of the cross-linker content on the compression of microgel particles at water/oil interfaces on the compression isotherms was investigated by Geisel et al. [60]. Core-shell particles with different cross-linker and the corresponding hollow microgels where compared showing that the removal of the core produced an increase of the surface pressure at low compression states, similar to the effect caused by decreasing the cross-linker content, as shown in Fig. 4c. Hence, lower cross-linker content promotes the flattening of the microgel at the interface as the isotherms appear displaced to higher areas. Upon higher compression states, the presence of a solid core promotes a steeper transition into regime IV owing to core-core interactions. The transition to close hexagonal packing is hindered as the cross-linker content decreases. Geisel et al. also reported the compression modulus (C^{-1}) of the monolayer as a function of the surface pressure. This is also known as Gibbs Elasticity (ε_0) and defined as $\varepsilon_0=C^{-1}=-A(d\pi/dA)$ [28,60]. The compression moduli of microgel monolayers depicted in Fig. 4d shows two maxima corresponding to regions II and IV of the compression isotherm. In region II, the elasticity of the monolayer decreases as the cross-linker content increases in the microgel. In this regime the microgels are highly flattened at the interface and the maximum elasticity is reached at the maximal number of adsorbed contacts, which is higher as the cross-linker content decreases and the chains are looser. As the compression of flattened microgels proceeds, chain entanglement is accompanied by reduced number of interfacial contacts. The energy required to reduce the number of contacts during compression will be higher in the case of weakly cross-linked microgel owing to the higher spreading and adsorbed chains. Hence, the elasticity of the monolayer is higher as the deformability of the microgel increases for low cross-linked particles. Further compression induces higher chain entanglement and the elasticity decreases accordingly. This continues until the monolayer enters in regime IV where the monolayer elasticity increases rapidly. Microgels are now laterally jammed and the high cross-link density or the presence of a solid core produces higher values of the elasticity, owing to higher stiffness of core-core contacts [60].

Accordingly, the presence of two maxima in the interfacial elasticity of the interfacial layer is reported with different rheological tools validating the existence of different interaction regimes as shown in Figure 4. However, the specific characteristics of these regimes will depend on structural aspects of the microgel. The cross-linking content has a strong impact on the shape and location of compression isotherms as commented by Geisel and also by other authors [42,51]. Also, the temperature can induce changes in the compression isotherms as the it impacts the swelling of the microgels [27]. Indirectly, the electrostatic charges can modulate the interaction as they change with the swelling state of the microgel [28]. Although the specific role played by electrostatics is still a matter of debate as will be further commented [51]. In any case, the interfacial tension and rheology complement the understanding of the visco-elasticity, or deformation of microgels providing mechanical information of the state of the interfacial film and the strength of the interactions. This in turn, will have an impact on the formation and stability of emulsions as will be further analyzed in following sections.

3. Correlations with emulsion stability

Quoting Tatry et al.: "*although the microgels abilities to adsorb at an interface and to stabilize emulsions are known, many questions remain about*". In particular, they pointed out three major aspects that they considered had to be taken into account to characterize the mickering emulsions: i) reversibility, ii) the role of impurities on the microgel adsorption, and iii) the role of the monomer electrostatic charges on the adsorption kinetics [67]. The accumulated evidence points out to several other key factors that need to be taken into account for a proper mickering emulsion characterization. These key factors should include the effects of intrinsic microgel visco-elasticity, i.e. deformability, and size, as well as the monomer structure of microgels on the ability to stabilize emulsions, thoroughly explored in the literature. The majority of significant studies up to the year 2013 concerning the impact of electrostatic charges, interfacial packing, and visco-elasticity, on the stability of mickering emulsions were comprehensively reported and discussed by Schmitt and Ravaine [7]. Therefore, we will focus in more recent investigations related to these interesting key parameters, and referring to past ones to provide continuity with the accumulated evidence. In the following subsections, we will analyze those studies that attempt to fill the gap, correlating the fundamentals of microgels at the interface, with the stability of mickering emulsions. We divide these studies into the following categories: *i*) role of the visco-elasticity, *ii*) role of electrostatic charges and responsiveness, and iii) role of microgel films and interfacial rheology.

3.1 Role of the visco-elasticity of microgels

The role of the intrinsic visco-elasticity of microgels when confined at an interface, i.e. their deformation at the interface, on the emulsion stability was first studied by synthesizing kinetically stable emulsions using both neutral p(NIPAM) and p(NIPAM-co-MAA) charged microgels [86]. These emulsions were tuned by varying the internal cross-linking density of the microgels or the temperature of the emulsions, and characterized via cryo-SEM. According to their observations, water/alkane emulsions (hexadecane, dodecane or heptane), obtained with the most deformable microgels were kinetically stable at rest and remained stable against centrifugation or mechanical disturbances, such as compression and shear. In contrast, emulsions fabricated with the less deformable microgels exhibited more instability. They found that 2D-connected networks were formed for the case of deformable microgels, correlating microgel visco-elasticity and emulsion stability. They hypothesized that these elastic structures were characterized by significant overlapping of the microgel shells, impacting on the interfacial elasticity of the monolayer and thus, on the resistance of the thin liquid films to coalescence. On the other hand, increasing the cross-linking density, or the temperature of the emulsion, would reduce the deformability of the particles as well as their emulsion stabilization efficiency. These results were subsequently complemented with the study of the impact of microgel cross-linking density on the formation of adhesive films between oil-in-water drops [87]. Analyzing the dynamics resulting when two of these droplets approach each other, they found that the lateral overlapping of the microgels as well as their coverage density appeared as key parameter on the emulsion stability. Once more, they found that increasing cross-linking densities resulted in increasing droplet flocculation, and decreasing stability of the emulsions against mechanical stresses. Moreover, mickering emulsions prepared by Schmidt et al. with two types of oils with different affinities with the microgels, an alkane and an alcohol (n-heptane and 1-octanol), corroborated that no stable emulsions were formed when the microgels were less deformable [6]. In contrast, when the swelling ratio of the microgels, and therefore their deformability, was enhanced, stable emulsions were obtained. As previously shown in Fig. 2j-l, cryo-SEM images of low cross-linked p(NIPAM-co-MAA) microgels adsorbed on droplets of n-heptane-in-water stable emulsions, at pH 9, show very deformed microgels, covering efficiently the interface. Moreover, they experimentally observed the existence of interconnecting filaments between deformable microgels in Fig. 2l [6]. Additionally, the impact of microgel size on its capacity to stabilize mickering emulsions was also studied [88]. Since small microgels present a more homogeneous cross-linking distribution and less pronounced core-shell morphology, the deformation gradient of adsorbed microgels is less pronounced as the microgel size decreases. Therefore, smaller microgels cover the water/oil interface more uniformly and with a higher density. Moreover, since smaller microgels exhibit a higher interfacial mobility at the interface and less capillary attraction [25], they are more likely to better rearrange in the film as a response against mechanical stresses. As a consequence, smaller microgels seem to lead to less flocculated and better performing mickering emulsions.

While the previous results focused on the final state of mickering emulsions, the microgel instrinsic visco-elasticity also seems to play a role on mickering emulsion formation through the adsorption kinetics [67]. This effect was studied for neutral p(NIPAM) and charged p(NIPAM-co-MAA) microgels, using a co-flow microfluidic device that enabled to demonstrate that microgel deformability, as well as higher particle concentrations, favors their adsorption. As has been already mentioned and will be also discussed in the next section, Tatry et al. found the existence of a critical microgel concentration above which microgels spontaneously adsorb to cause a sufficient decrease of the interfacial tension to allow the mickering emulsion formation. This concentration is lower as the deformability of the microgel increases and for uncharged systems. As a consequence, microgels in excess, compared to the droplet interfacial area, are required to produce the emulsions via the microfluidic device. While cryo-SEM in itself has been proven a good tool to study mickering emulsions, FreSCa cryo-SEM allowed for the first time to go deeper into the in situ imaging of the deformation of microgels at water/oil interfaces [41]. This procedure, introduced in section 2.3, provides additional quantitative information on the protrusion of each individual microgel from the water phase into the oil phase. Although this method seems to distort less the interface during its vitrification, there seems to be consensus in the invasive nature of cryo-vitrification and fracturing of the samples, prior to observation via cryo-SEM (either from the oil or the water side). Thus, some authors claim that these sample preparation steps might introduce unknown effects into the samples [13].

In view of the results discussed in this section, the importance of the visco-elasticity/deformability of microgels on their ability to stabilize mickering emulsions is evident. Nevertheless, the stabilization mechanism of mickering emulsions for the case of strongly deformed microgels needs to take additional parameters in consideration which will be presented in the following sections.

3.2 Role of the electrostatic charge and responsiveness of microgels

Responsive emulsions stabilized by stimuli-responsive microgels were first and thoroughly studied by Ngai et al. [55,89,90]. These authors synthesized both thermo- and pH-responsive p(NIPAM-co-MAA) microgels to form octanol-in-water mickering emulsions, also responsive to temperature and pH. As can be seen in Fig. 5a, stable emulsions were reached at high pH, even at high temperature above the LCST, where the microgels were highly charged, whereas the same emulsions could be broken upon demand with low pH values and heat [89]. It is tempting to assume their hypothesis, considering that both heating and pH reduction results in microgel shrinking, and even possible partial desorption, of the increasingly hydrophobic interfacially adsorbed microgels. Nevertheless, as stated in section 2.3, the full picture seems to be more complicated, depending on many other parameters as the affinity of the microgels towards the oil phase, higher for alcohols than for alkanes, with even some of the same authors reporting in a recent study the opposite behavior of low mickering emulsion stability for highly charged microgels, as described in Fig. 3d. Remarkably, their first reported emulsions were stable at pH 9.4, even at 60°C [89]. This suggests that highly charged microgels remain at the water/oil interface and prevent droplet coalescence, opposite to what it is described in Fig. 3d, also by Ngai and coworkers, where highly charged microgels at high pH are less capable of adsorbing at interfaces. Furthermore, they hypothesized that the destabilization of the octanol-in-water emulsions at low pH (less charged) and T > LCST was due to the true desorption of microgels towards the octanol phase. This hypothesis would not be possible in the case of microgels at water/alkane interfaces with a much lower affinity towards the oil phase, even in its collapsed state. On the other hand, no direct evidence of microgels desorption from the water/oil interface during mickering emulsion destabilization was found for similar dual stimuli-responsive microgels [83,91]. Instead, they observed formation of clusters by aggregation of microgels at the interface, which seems more in line with the results described in section 2.3 at flat interfaces upon monolayer collapse [91]. Therefore, they concluded that emulsion destabilization is mainly due to a variation in the intrinsic visco-elasticity of the microgels confined at interfaces. Furthermore, according to rheological and cryo-SEM experiments, well-ordered interfacial layers of microgels at low pH were found, while clustered crystalline patches with voids covered by polymer chains were found for high pH [86]. Thus, the clustering of microgels might be in fact responsible of the stabilization of the oil-in-water emulsions at high pH, when the microgels are charged. They concluded that the stability and the responsiveness of the mickering emulsions reported by Ngai et al. depended on the polarity of the oil used (alcohol vs alkane), and pollutants such as unreacted monomers and small oligomers or copolymers. In the case of thermo-responsive mickering emulsions, the destabilization via desorption mechanism was also ruled out in favor of the stability being controlled by modifications on the microgel interfacial mechanical properties [79]. Moreover, in light of these new ingredients, we can revisit the studies of microgel deformability discussed in the previous section, where charged microgels p(NIPAM-co-MAA) were reported to be less deformable than their neutral counterparts [86]. According to this study, the presence of charges induced a reduction in the compressibility and deformability of charged microgels at interfaces, due to Coulombic interactions as well as the osmotic pressure of counter-ions. At this point, one can only envisage the difficulty in trying to extract meaningful and general findings to predict the stability of mickering emulsions solely based on the behavior of microgels in bulk. For example, one would expect that the clustered microgels at interfaces with voids reported to enhance the emulsion stability [86] would result rather in the opposite, since the clustered microgels are expected to be less deformable as they become more compressed, and the voids should play in favor of coalescence. However, one can try to relate this fact to the studies at flat interfaces [38,39] and then additional info seems to be available to understand the experimental results: highly charged microgels at interfaces offer both a higher interfacial coverage for small microgels as discussed in Fig. 3c and overall a more deformable microgel. The next logical step is to think on the formation of smaller and smaller emulsion droplets upon mechanical energy input, where microgels start to be more and more crowded with an isostructural shell-shell to core-core transition [5,24–26,37]. This transition will proceed to larger extent before the monolayer collapse the more deformable, i.e. swollen, the microgel is. More precisely we refer here to the portion of the microgel immersed in the more affine phase which it is still thermo- and pH-responsive [38,39]. This seems a plausible but anyways speculative way to reconcile the variety of results presented so far. Thus, as we discussed before there is room for new master experiments and simulations that should univocally discriminate which are the leading factors in the mickering emulsion stabilization/destabilization mechanisms.

More recently, the impact of electrostatics on the adsorption of microgels at the water/oil interface of mickering emulsions was specifically studied by systematically varying p(NIPAM) microgels loaded with different numbers of charges by incorporating pH-sensitive monomers of acrylic acid (AAc) or vinyl acetic acid (VAA) [92]. Although decreasing the charge density of microgels led to unstable emulsions, in line with what Ngai et al. reported in Fig. 4a [89], the inter-microgel spacing in the hexagonal lattice at the interface of drops became independent of the number of charges and range of electrostatic interactions, in line with results reported at flat interfaces via FreSCa cryo-SEM [41]. Thus, the microgel morphology and packing was affected mainly by the interfacial activity of the polymer chains at the interface and electrostatic charges were not required to ensure emulsion stability, and the number of charges, or their spatial distribution across the core-shell structure, did not affect the adsorption of the microgels at the water/oil interface. As a consequence, charges would not impact the way in which microgels stabilize oil-in-water emulsions, which once more is precisely the opposite finding reported by Ngai et al., who claimed that microgel need to carry a certain amount of charges to be efficient stimuli-responsive emulsion stabilizers [8,89]. At this respect, hydrogen bonding between adjacent carboxylic groups or between carboxylic and amide groups were hypothesized to play the role of additional cross-linking within the microgels [92], which would go in the direction of reduced emulsion stability with higher cross-linking density, resulting in less deformability, as discussed in section 3.1 [86].

Now we particularize on the impact of addition of salt to mickering emulsions to try to elucidate the true impact of electrostatic charges, and corresponding screening, into the emulsion stability. Ngai et al. looked deeper into the impact of electrostatics on the stability of mickering emulsions formed by their pH-responsive microgels by adding salt to the mickering emulsions [90]. As the addition of salt to aqueous dispersions of both thermo- and pH-responsive p(NIPAM) has an impact on their swelling behavior [93], they expected that such influence could be transferred in the case of responsive mickering emulsions. The addition of NaCl to stable octanol-water emulsions prepared at pH 9.4 screened the electrostatic repulsive interactions between chains and rendered the microgels more hydrophobic. Above 100 mM NaCl, the emulsion composed of large and polydisperse droplets phase separated. Therefore, it follows that the interfacial activity of microgel particles at the interface is significantly reduced at high salt concentrations, leading to emulsion droplets being unprotected [90]. Once more, disagreement was stated as it was demonstrated that there exists an important difference between neutral microgels without charged monomers, screened polyelectrolyte microgels by the addition of salt, and neutral polyelectrolyte microgels by pH decrease [92]. In such study, the instability of emulsions in the presence of salt was attributed instead to the formation of hydrogen bonds that would reduce the microgel deformability as it was previously pointed out.

All in all, electrostatic repulsion does not seem to be primarily responsible for emulsion stability, or at least it is a controversial and contested idea. Nevertheless, the relative position of electrostatic charges on the microgel could control the type of emulsion [10]. Indeed, this feature was explicitly studied recently as previously discussed in section 2.3 with the carboxylic dense shell (DS) and dense core (DC) microgels, when analyzing the pH-responsiveness of the emulsion at T < LCST [54]. The morphology of the microgels and spatial distribution of the polyelectrolyte carboxylic monomers resulted in unstable mickering emulsions in both acidic and alkaline conditions, for an adequate concentration of particles and through different mechanisms as already discussed. The stability of emulsions stabilized by DS and DC microgels was very similar at low pH. On the contrary, DS microgels lost most of its interfacial activity at high pH and therefore, the resulting emulsions were less stable. In this case, the results could be considered as a case of significantly big microgels upon swelling, where the microgel is no longer able to deform enough to adapt to small droplets in comparison to their size, this might be a plausible way to reconcile with contradicting previous studies.

The same authors recently re-analyzed the influence of MAA monomer content on the thermo-and pH-responsiveness of p(NIPAM-co-MAA) microgels, and its impact on the stability of the corresponding mickering emulsions [94]. Interestingly, they built an emulsion stability phase diagram, as a function of MAA content, temperature and pH, as can be seen in Fig. 5b [94]. Smaller carboxylic group content (MAA-10) leads to low pH-responsiveness. However, above pH 10, carboxylic groups completely deprotonated are highly charged, and the emulsions are stable for a greater range of temperatures, recovering the initial picture of high stability for high pH described at the beginning of this section. Concerning the thermal behavior, they found a critical temperature about 40 °C from which the phase separation begins and the emulsion breaks. Since this temperature was above the LCST of p(NIPAM), they expected a reduced microgel surface area, an idea contested at flat model interfaces [38]. For temperatures above 50 °C, the emulsions were unstable as a consequence of severe microgel aggregation. Similar stability diagrams are found for emulsions stabilized with higher MAA content, MAA-50 and MAA-150, as shown in Fig. 5b. Stronger pH-responsiveness compared to MAA-10 is observed and the resulting mickering emulsions show higher resistance against heating, once more going in the direction of their original work where polyelectrolyte microgels greatly enhance the mickering emulsion stability against high temperature well above the LCST. This feature is in stark contrast to previous discussed studies in which the role of the charge of microgels is reported to be negligible.

After such enumeration of studies contradicting and contesting each other, spanning almost 20 years, with finer and finer experimental characterization tools, still this debate seems far from ended and calls for new master experiments trying to reconcile the different evidence and points of view. One arising common fact is that the description of the microgel behavior and responsiveness in bulk only partially and indirectly applies when considering them confined at interfaces [38,39].

3.3 Role of microgel films and interfacial rheology

Brugger et al. authored the first explicit relationship between interfacial activity and emulsion properties regarding changes in interfacial tension and macroscopic visco-elasticity of the monolayer [83]. Since then, not many works addressed explicitly this link, which hence still offers many open questions and space for innovation. We have already stated that measurement of interfacial tension and rheology are in general easier and more accessible than other experimental techniques which combine microscopic characterization tools or imaging. However, the experimental results are difficult to interpret as intra-particle structure, inter-particle interactions and interactions with bulk phases and interfacial region need to be considered. Also, the production of comparable emulsion (or foam) requires a careful manipulation of the emulsion procedure to match the situation at the interface. As we will detail in this section, the works found in the literature regarding stability of emulsions correlate in general with interfacial rheology and microrheology of adsorbed layers [42,61,62,83,91] while dynamic interfacial properties appear more related to emulsion formation [67,73]. In general, charged and uncharged microgels have been studied separately and none of them have addressed specifically the link between interfacial characteristics and thermo-responsive mickering emulsions.

Brugger et al. addressed the link between emulsion stability and interfacial rheology for (charged) p(NIPAM-co-MAA) microgels showing stable emulsions at high pH and low temperature, and unstable systems at low pH and high temperature [83]. This agrees with the previous discussion indicating that in general, only swollen microgels stabilized emulsions [89]. Brugger et al. showed that the interfacial tension of the adsorbed microgels was lower at low pH, indicative of higher interfacial coverage, and/or to the formation of a thicker interfacial layer. These results seem to contradict the reduced stability of emulsions formed at low pH values. A reason for this behavior could be originated in the increased particle charge at high pH which could induce an adsorption barrier as later demonstrated for charged microgels [43], but this fact was not specifically discussed by Brugger et al. [83]. The impact of temperature on the interfacial tension was not reported either in that work. Conversely, the trend obtained for the interfacial dilatational rheology of adsorbed microgels at the water/heptane interface provided a useful correlation with emulsion stability and it was studied in more detail as a function of pH and temperature. Lower pH values provided lower elastic moduli in agreement with the less stable emulsions formed with collapsed microgels (at low pH). The interfacial dilatational elasticity decreased also with temperature and this was attributed to a reduced inter-particle interaction due to reduced hydrophilicity of p(NIPAM) in the collapsed state (at high T) [83]. An enhanced interfacial elasticity of the adsorbed layer for swollen microgels (at low T) has since then been reported in the literature and attributed to an increased interfacial coverage and increased interaction between dangling chains residues as discussed extensively in previous reviews [7,13,58]. The absolute values reported for the dilatational elasticity by Brugger et al. are very low owing to the high concentration used as was later established [42]. In a later work, Brugger et al. reported the interfacial shear rheology of the same p(NIPAM-co-MAA) microgel particle at the same water/oil interface [61]. Interfacial dilatational rheology provides combined information on both intra and intermolecular associations within the interfacial layer, whereas interfacial shear rheology highlights the inter-particle associations [58,95–97]. The shear elasticity values reported by Brugger et al. demonstrate the formation of a more elastic interfacial layer at higher pH, possibly resulting from increased inter-connection between swollen microgels with more dangling segments. At lower pH, the shear elastic modulus decreases as the inter-particle association is reduced. Swollen microgels (highly charged) display a soft gel-like behavior while collapsed (less charged) form brittle surfaces with a solid like behavior. In fact, it is here recognized, that at low pH the microgels form a densely packed monolayer owing to the reduced electrostatic repulsion in the collapsed state [61]. In emulsions, both dilatational and shear deformations take place at the same time and hence the phenomena cannot be directly related independently to the behavior of emulsions, and as suggested by Brugger et al. it is important to combine both experimental methods.

Concerning the thermo-responsive behavior of mickering emulsions and how it relates to interfacial characteristics of adsorbed films it was studied first by Monteux et al. [79]. The presence of a minimum interfacial tension at a temperature matching the LCST of the microgel was linked to emulsion stability. The origins of this minimum in interfacial tension were well known, as have already been discussed in section 2.4. p(NIPAM) microgels were prepared in the presence and absence of dimethylamino ethyl methacrylate (DMAEMA) in order to investigate also the role of charge. In both cases, the surface tension showed a minimum around the LCST. However, the minimum is more significant for charged p(NIPAM-DMAEMA). As discussed widely in previous works [8,71], below the LCST swollen microgels form a dense adsorbed layer owing to decreased excluded volume interactions and interaction of dangling chains which maximize the interfacial coverage. Above the LCST, the interfacial tension increases owing to subtle reorganizations in the surface layer as the microgel collapses which promote the formation of a loosely packed interfacial layer. The changes in interfacial tension are very subtle, especially in the case of non-charged p(NIPAM), and therefore imply a similar surface coverage. It is rather correlated to the formation of a heterogeneous adsorbed layer with aggregates and precipitate in which some unprotected interfacial areas appear. This interfacial conformation can promote droplet coalescence in emulsions in agreement with the reduced stability encountered as temperature increases. This work has been extensively commented in the literature as particle aggregation appears responsible for the formation of a less stable emulsion at higher temperature [7,13,98]. Unfortunately, the visco-elasticity of the microgel films was not measured by Monteux et al. [79]. The correlation of the minimum surface tension of microgels at the LCST with foam stability at different temperature has been recently revisited at the water/air interface and completed with ellipsometry and microrheological tools [62]. The p(NIPAM) microgels used by Maestro et al. carried a slight negative charge. Foams made from microgels showed a similar stability behavior as emulsions. Below the LCST, swollen microgels produced more stable foams while increasing temperature lead to less stable foams formed by collapsed microgels. Maestro et al. find a maximum surface pressure around the LCST of microgels, which is equivalent to the minimum interfacial tension reported by Monteux et al. Ellipsometric tools show that below the LCST, swollen p(NIPAM) microgels adsorbed at the surface layer by anchoring the external dangling chains while above the LCST the microgel particle collapsed, both in the vertical direction and within the surface, reducing the thickness and the surface coverage. Also they speculate that this is also result from the higher surface charge density of collapsed microgels which enhanced electrostatic repulsion within the surface layer [62]. Some of us reported similar charge dependence in p(NIPAM) monolayers [28]. Hence, the degree of swelling of the p(NIPAM) microgels at the surface layer alters the surface organization and film thickness, and this impacts the stability of the resulting foams. Maestro et al. used particle tracking to asses microrheology of the adsorbed layers as a function of temperature reporting a transition from solid to liquid behavior of the interfacial film as temperature increased [62]. Accordingly, above the LCST adsorbed layers composed of swollen microgels behave like an amorphous solid, which is able to resist deformation while around the LCST the collapsed microgels behave like a liquid film which rather flows under stress and these determine foam stability. These findings advance in the picture given by Huang et al. [63] who reported a solid like behavior of p(NIPAM) at the water/oil interface and that of Cohin et al. [64] who also showed a limited diffusivity in adsorbed microgel layers at temperatures below the LCST. Another recent example shows a more drastic dependence with temperature for uncharged p(PNIPAM) as stable foams are only formed by uncharged p(NIPAM) below the LCST while no foam could be formed with microgels above the LCST [80]. Moreover, the foam formed below the LCST rapidly disappeared upon heating. Similarly, the surface tension of microgels below the LCST decreased with temperature while above the LCST the surface tension could not be measured because the collapsed p(NIPAM) formed aggregates and then precipitated. This provides an interesting simple correlation between foaming and surface tension [80]. Uncharged p(NIPAM) in the swollen state adsorb onto the surface anchoring the dangling external chains which facilitated foam formation by decreasing surface tension. The smaller size of the p(NIPAM) microgels used in this work (< 50 nm) possibly facilitated its aggregation and apparent desorption. The behavior of aqueous foams stabilized by microgels compared to other systems such as polymers and proteins has been recently reviewed by Braun et al [99]. This work underpins the importance of interfacial viscoelasticy and surface deformation of microgels in the resulting foam stability. Braun et al also suggest that investigation of single foam films should provide additional information. The drainage of foam films stabilized by microgels has been very scarcely studied in the literature. However, it appears useful to look into bridging and adhesion of films, with application to emulsion systems and to explore the role of electrostatics [47].

Uncharged p(NIPAM) microgels were also used by Pinaud et al. in one of the most complete interfacial characterizations, explicitly comparing with emulsion stability, including adsorption kinetics, compression isotherms and interfacial dilatational rheology [42]. The authors used uncharged p(NIPAM) microgels in order to focus on structural aspects excluding electrostatics and also provided visualization of the microgels in emulsions. To produce comparable emulsions, the limited coalescence process was used, which allows also measuring the diameter of adsorbed microgels. In this way, Pinaud et al., can draw the compression isotherm as a function of the center-to-center distance of microgels and compare with the size in solution and adsorbed at emulsion interfaces, as shown in Fig. 6a. This representation provides a direct comparison between the deformation and packing at the planar interface with the state in emulsified systems as a function of the interfacial pressure. The various stages of the evolution of the microgel at planar interfaces correspond to regimes I to V as discussed in section 2.4 at flat interfaces. In regime I, the interfacial pressure increases as the external shells of the flattened microgels come into contact and interpenetrate. In regime II the interfacial pressure increases as the flattened microgels are compressed until reaching the diameter of non-flattened swollen microgel ($d_{HT=25^{\circ}C}$). In region III, the density of adsorbed chains remains constant as microgels deform perpendicularly to the interface. Region IV marks the contact of collapsed microgels ($d_{HT=50^{\circ}C}$) which finally desorb or form multilayers at the highest compression stage. It is a remarkable finding that the diameters measured for the microgels directly in emulsions lie all within region II. In emulsions, the local inter-particle distance varies from low local microgel concentration where the shells do not overlap and the microgels are flattened ($d_{CC(emulsion)}$) to a higher local concentration where the microgels are in closer packing and the shells are compressed ($d_{Core(emulsion)}$). This finding comprises important advances in the correlation between interfacial and emulsion properties of microgels. An estimate of the surface dilatational elasticity can be obtained directly from the compression isotherms through the Gibbs limiting elasticity

$$\varepsilon_0 = -\frac{1}{A}\left(\frac{d\pi}{dA}\right)_T \quad (\ldots.)$$

This Gibbs Limiting elasticity exhibited a marked maximum as a function of surface pressure. The curve can also be also be plotted against the inter-particle distance, as shown in Fig. 6b. It can be appreciated that the maximum elasticity of the interfacial film corresponds to the flattened conformation of microgels. Interestingly, this maximum also matches the conformation of microgels found in emulsions. Hence, emulsions form with flattened microgel conformations providing a maximum elasticity of the interfacial film. This is further confirmed by analysis of the dynamic adsorption of microgels to compare the properties of microgels spontaneously adsorbed at model interfaces to their forced adsorption during emulsification. Microgels spontaneously adsorb in a compressed state while they are highly flattened at the interface of emulsion droplets at high shear rates. Furthermore, the interfacial elasticity of adsorbed layers was maximum at the beginning of the adsorption and decreased with the concentration of the adsorbed layer, again highlighting its role in emulsion stabilization [42]. Further investigation hence, should concentrate on the properties of flattened microgels at interfaces since the more concentrated regimes do not seem to be reached for the microgels adsorbed in emulsified systems, at least using high shear emulsification and limited coalescence methods (Destribats2013). This fact is striking when comparing the surface elasticity corresponding to the flattened conformation of microgels in emulsions in Fig. 6b, exhibiting 1 maximum, with the 2 maxima found at higher compression states reached upon spontaneous adsorption in Fig. 4, with micro- and macro-rheology. This, together with the pictures shown in Fig. 2j-l seems to go indeed in the direction of non-accessible regimes in mickering emulsions. Realization of mickering emulsions that exploit the unexplored compressed regimes might bring along new visco-elastic properties and responsiveness of the already promising mickering emulsions. In this sense, Destribats et al proposed that emulsification energy determines the interfacial conformation of microgels Emulsions produced with high shear rates showed highly flattened microgels whereas low shear rates lead to dense monolayers of compressed microgels. Interestingly, the resulting emulsions have opposite behavior in terms of flocculation in agreement with our reasoning. However, they do not explicitly compare with interfacial viscoelasticity in their study and this remains to be explored yet.

In a recent work, Kwok and Ngai have proposed a new experimental magnitude termed relative interfacial affinity [74]. It allows a direct comparison of the interfacial activity of microgels with different densities but comparable sizes. It is calculated by forming an emulsion with a mixture of two kinds of microgels. The number of microgels of each kind which are located at the water/oil interface is then counted. As the diameters of the microgels are known, the relative interfacial coverage is calculated and termed relative interfacial affinity. Kwok et al. prepared emulsions with different microgels showing that the relative interfacial affinity decreases with the cross-linker density, as shown in Fig. 6c. Hence, softer microgels display a higher relative interfacial affinity; i. e. are more surface active. This parameter, correlates with the adsorption kinetics of microgels. In general, a slower kinetics of microgel adsorption onto a water/air interface is found as the cross-linker density increased in the microgels and the reduction in surface tension is mainly due to the adsorption of microgel fragments [8,67,71]. Kwok and Ngai elaborate this hypothesis by measuring the relative interfacial affinity of microgels with similar cross-linker content, but in which the dangling chains on the periphery of microgels were cross-linked [74]. This surface modification of the particle reduced significantly its surface activity as measured with the relative interfacial affinity, hence validating previous works. An important advance in the work of Kwok and Ngai is the direct correlation proposed between the interfacial affinity and the emulsion stability as quantified by the maximum osmotic pressure after centrifugation. Fig. 6c shows the corresponding images taken of emulsions after centrifugation at 1000 g, were the amount of oil separated is delimited with lines at the top of the emulsions and increases in the same trend. Hence, it can be seen how the stability of the emulsion decreased as the content of cross-linker increased in the microgel particle. This in turn, decreased the relative interfacial affinity. Accordingly, the stability of the emulsion decreased as the surface activity of the microgel decreased. This trend also was found for the surface cross-linked microgels (termed L50A). Again, the presence of looser segments seems to contribute to the stability of mickering emulsions. Microgels with less cross-linker content have higher interfacial affinity and better emulsion stability.

As mentioned above, Tatry et al. examined the kinetics of adsorption of microgels at the water/air interface as a function of charge and cross-linker content as it impacts emulsification by microfluidics [67]. They carried out one of the most complete descriptions of the dynamics of adsorption of microgels to date on the basis of surface tension measurements. Also, their findings show a direct correlation with the emulsifying ability of microgels. Tatry et al. demonstrated that the concentrations in bulk which provide the critical surface coverage correspond to the critical concentration needed to produce emulsions. This critical concentration is lower for neutral and less cross-linked microgels. For charged microgels, interparticle electrostatic repulsion provides an adsorption barrier which can be screened by the presence of salt by increasing the concentration of microgels. The surface activity appears then directly related to the existence of dangling chains with high mobility as compared to cross-linked chains which are blocked. As a result, from this work, Tatry et al. reported a clear between this critical bulk concentration and the stabilization of emulsions [67]. The surface coverage, and the decrease in surface tension, is linked to the adsorption of flattened microgels with high number of contacts adsorbed, which appears crucial for emulsion formation and droplet stabilization. This hypothesis agrees with findings with other type of soft microgels. Saavedra-Isusi et al. studied the interfacial activity and emulsifying properties provided by pectin used as individual polymer chains (pectin polymer) or as a particulate polymer network (pectin microgel) [100]. Pectin polymers decreased the interfacial tension while pectin microgels barely changed the interfacial tension. This is attributed to an increased number of hydrophobic groups adsorbing onto the interface for pectin polymers, which are hidden inside pectin microgels. Pectin polymers provided smaller and controllable emulsion droplet size with lower creaming rates whereas increasing concentration of pectin microgels promoted flocculation and creaming. Another example concerns the behavior of sugar responsive emulsions with saccharide-responsive phenylboronic-modified microgels [73]. The authors correlated the swelling properties of various boronate-functional microgels in aqueous solution, their adsorption dynamics at the water/air interface and the stability of the resulting emulsions. Phenylboronic-modified microgels displayed a much higher swelling ratio in the presence of sugars (fructose and glucose). This is reflected on the properties of emulsion, which are only stable above 5 mM of sugar below the LCST. Again, microgels spontaneously adsorb more rapidly in the presence of sugar possibly due to the presence of more dangling chains owing to increased swelling. The presence of sugar also expanded the monolayer of Langmuir films resembling the behavior of more deformable less cross-linked microgels. Also, in agreement with other works [62,79] no direct correlation is found between emulsion stabilization and equilibrium interfacial tension as this value is not altered by the presence of sugar. The knowledge acquired after extensive investigation of p(NIPAM) model systems was clearly applied here to the development and understanding of more complex microgels responsive to different stimuli by functionalization which can be exploited in future research.

4. Conclusions

We have covered here many works, all concerning the phenomenological and flexible behavior of microgels at interfaces, either at flat model interfaces or in mickering emulsions, which are one of the important uses for such thermo and pH-responsive microgels. Mickering emulsions are thus a promising new system which offers many opportunities with practical applicability. The correlation found with the kinetic adsorption of microgels encourages future investigation of possible links with other surface properties such as the surface tension of saturated films and the interfacial visco-elasticity of the microgel layer. Research is encouraged to unravel the connection of relative interfacial affinity and surface coverage and/or mechanical properties of the interfaces and how they correlate with emulsion stability.

In view of the commented literature works, a complex interplay between microgel interfacial activity and emulsion formation and stability, which relies on the interfacial structure, is widely demonstrated. A condition for the stabilization of emulsions is the generation of a flattened layer of microgels which adsorb rapidly and allows interdigitation of the external regions and high interfacial elasticity. This is favored for deformable microgels with low internal cross-linking, which display many dangling chains in the external shell which anchor at the interface. Unstable emulsions form with microgels with higher degree of cross-linking owing to a reduced surface activity and the formation of loose and heterogeneous interfacial films which display lower elastic modulus. While many works have covered different microgel architecture and composition and their impact in the stability of mickering emulsions, there are still plenty of questions that remain to be answered to reconcile often contradicting results, all of them backed up with finer and finer experimental evidence. For example. experimental proof of the desorption mechanism at the single microgel level would fill the gap, to answer a fundamental question: *Are microgels desorbing from interfaces above LCST and/or upon charge-swelling, and causing in this way the destabilization of the mickering emulsions, or is it a subtler mechanism which results in this destabilization?* At the level of the collective behavior, another open question remains unanswered: *Do microgels at interfaces in shell-shell contact repel through steric interactions or interdigitate each other through their dangling polymers?* Furthermore, at the level of mickering emulsions we could in this review state that there are apparently non-accessible compression regimes, and its experimental achievement might bring new properties to mickering emulsions. The answers to these open questions hold the key to fill the gap in the understanding of how the collective behavior at the inter-particle interactions level impacts at the macroscopic level through the properties of interfacial films and their interfacial rheology. These are many open challenges after 30 years of the first synthesis of p(NIPAM) microgels, where accumulated evidence and experience on microgels adsorbed at interfaces place the Soft Matter community in the perfect spot to try to answer the raised questions. We believe that in their answer relies the key to tailor at will what seems to be the worthy successor of Pickering emulsions: soft, sturdy, responsive, and switchable mickering emulsions.

Acknowledgements

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Figure Captions

Figure 1: **(a)** TEM image of the first 2D crystalline p(NIPAM) microgel monolayer deposited on a substrate. Reprinted from [2], © 1986 with permission from Elsevier. **(b-e)** Confocal laser scanning microscopy images of green-dyed silicon oil emulsion droplets in water, decorated with red-dyed p(NIPAM-co-MAA) microgels, at 20 ºC and pH 12.3. In (b) and (d) only the red dye is observed, in (c) only the green dye is observed, and both dyes are simultaneously observed in (e). Reprinted from [36], © 2020 published by The Royal Society of Chemistry. **(f)** Simulation of in-silico synthesized microgel at a liquid-liquid interface with 42000 monomers and 5% cross-linking, at a water/hexane (blue/yellow) interface, top view from the oil side (top) and side-view of the interface (bottom). Adapted from [34], © 2019 American Chemical Society. **(g)** Simulation of diamond-like network microgel at a water/oil interface, with increasing fraction f of charged monomers from left to right and top to bottom (f = 0, 0.05, 0.2, and 0.3, respectively). Adapted from [43], © 2019 American Chemical Society. **(h)** Simulation of diamond-like network microgel (cross sections) at different concentrations of oil (yellow beads) in the mixture: 0% (top), 10% (bottom). Adapted from [46], © 2020 American Chemical Society.

Figure 2: **(a-d)** AFM images of deposited monolayers in dry state on solid substrates. (a-b) 5 mol% cross-linking and (c-d) ultra-low cross-linked (ULC) at (a,c) zero surface pressure (Π=0) and (b,e) when a monolayer in shell-shell contact is formed ($\Pi_{\text{shell-shell}}$). ULC microgels in shell-shell contact form a homogeneous polymer layer. Depositions at 20 °C and 2 µm-scale bars. Adapted from [5], CC-BY 2020 from Nature. **(e-h)** Simulations of diamond-network microgels adsorbed at water/oil interfaces, as seen from the water phase, and with (e-f) 10% and (g-h) 2.5% cross-linking density at (e,g) Π=0 and (f,h) $\Pi_{\text{shell-shell}}$. Adapted from [48], © 2020 American Chemical Society. **(i)** AFM images of a single substrate where a monolayer of 5 wt% p(NIPAM-co-MAA) cross-linked microgels was deposited at room temperature, forming a gradient on the area per particle, decreasing from left to right as the microgels were compressed at the interface while being deposited on the substrate. After shell-shell contact, the shells start to fail upon compression and the microgels become in core-core contact until a hexagonal-packing with all the microgels in core-core contact is achieved. Adapted from [37], © 2016 with permission from The Royal Society of Chemistry. **(j-l)** 3 wt% p(NIPAM-co-MAA) cross-linked microgels with a p(NIPAM) shell on the droplet surface of n-heptane-in-water emulsions at pH 9. Overview and close-up images. The white circles show the hydrodynamic diameters of the microgels in water at pH 10. The microgels show core-core contact as in (i). Reprinted from [6], © 2011 American Chemical Society.

Figure 3: **(a)** Isooctane-in-water emulsions stabilized by p(NIPAM-chitosan) microgels showing destabilization with temperature (left panel) and with pH increase (right panel). Adapted from [33], © 2020 with permission from Elsevier. **(b)** Microgel monolayers under compression at 20 and 40 °C. Microgels are schematically illustrated with different shades of blue and red for 20 and 40 °C, respectively. (2D top view) Single microgels and microgel microstructure viewed from above. (2D side view) Illustration of a 2D cross-section of the microgels perpendicular to the interface. Black solid circles

represent the diameter in bulk D_h. Scale bars are 500 nm. Reprinted from [38], © 2019 American Chemical Society. **(c)** Comparison of the behavior of small and large P(NIPAM-co-MAA) microgels at interfaces in their uncharged and charged states, where small microgels show a difference in the onset of the surface pressure increase. Reprinted from [39], © 2020 American Chemical Society. **(d)** Confocal laser scanning microscopy images of decane-in-water emulsions stabilized by a binary mixture of P(NIPAM-co-MAA) microgels with the MAA co-monomers localized in the core (dense core, DC) or in the shell (dense shell, DS), at pH 3 (left) and 11 (right). Uncharged MAA binds to fluorescein and expels it when charged. At pH 3, bright solid dots are DC and hollow particles are DS microgels. At pH 11, dark colloids are DC and dark rings are DS microgels, Adapted from [54], © 2018 with permission from Elsevier.

Figure 4: **(a)** Surface Pressure-Area compression isotherm at the water/air interface. Insets show amplitude sweeps from the microdisk rheometer taken at different compression states. **(b)** Surface storage (G') and loss (G'') moduli as a function of surface pressure measured in the linear regime at a frequency of 0.5 Hz for the microgel monolayer plotted in (a). The inset shows a microscope image of the interface with the microdisk used for the microrheology. Adapted from [37], © 2016 with permission from The Royal Society of Chemistry. **(c)** Surface Pressure-Area compression isotherms of the core−shell (CS, solid lines) and hollow (HS, dashed lines) microgels with different cross-linker content. **(d)** Gibbs Compression modulus as a function of the surface pressure calculated from (d) for core-shell (CS, solid symbols) and hollow (HS, hollow symbols) microgels with different cross-linker content. Adapted from [60], © 2015 American Chemical Society.

Fig. 5: **(a)** Stabilizing efficiency of p(NIPAM) microgels for octanol-in-water emulsions as a function of pH and temperature. ■: Stable, ●: Unstable, ◆: Phase separation. Arrows indicate the probed transitions. Adapted from [89], © 2005 with permission from The Royal Society of Chemistry. **(b-d)** Stability contour map of mickering emulsions stabilized by microgels with different density of carboxylic groups labeled (b) MAA-10 (low), (c) MAA-50 (medium), and (d) MAA-150 (high). Each color represents a stability level for the emulsion, that is: the color blue (1, unstable), green (2), yellow (3), orange (4) and red (5, most stable), respectively. Adapted from [94], © 2019 with permission from Elsevier.

Figura 6: **(a)** Evolution of the surface pressure as a function of center-to-center distance between microgels containing 2.5% BIS at the interface, assuming a hexagonal lattice. Arrows show the microgel diameters in solution, swollen: $d_{H,T=50°C}$≈234 nm, collapsed: $d_{H,T=25°C}$≈632 nm, and the characteristic distances at the water/oil interface, as measured on emulsion drops prepared in the limited coalescence regime, shells compressed: $d_{Core(emulsion)}$≈860 nm, shells flattened: $d_{CC(emulsion)}$≈1100 nm. **(b)** Elastic modulus as a function center-to-center distance for 2.5% BIS (black circle) and 5% BIS (red square) microgels. Adapted from [42], © 2014 American Chemical Society. **(c)** Images of emulsion samples stabilized by microgels with different cross-linking density (L10-L80) after centrifugation at 1000 g. Microgels L50A present a cross-linked surface. The graph shows the relative interfacial affinity of the same microgels. Adapted from [74], CC-BY 2018 Frontiers.

Figures

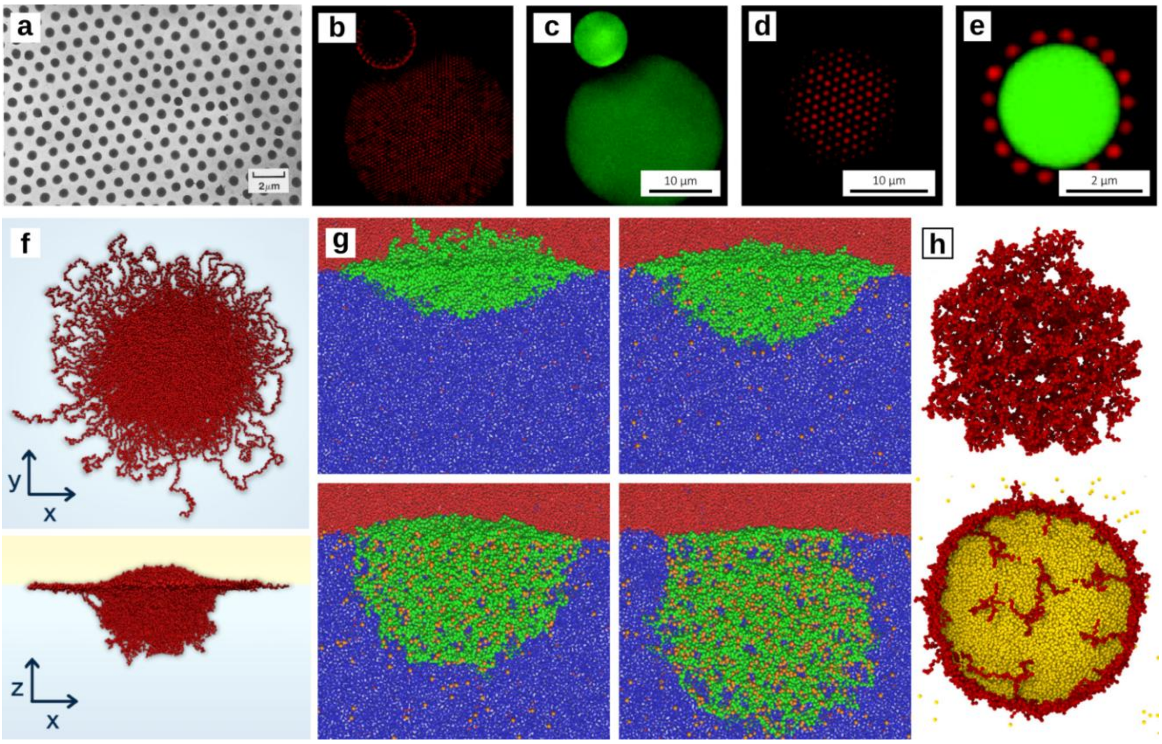

Fig. 1

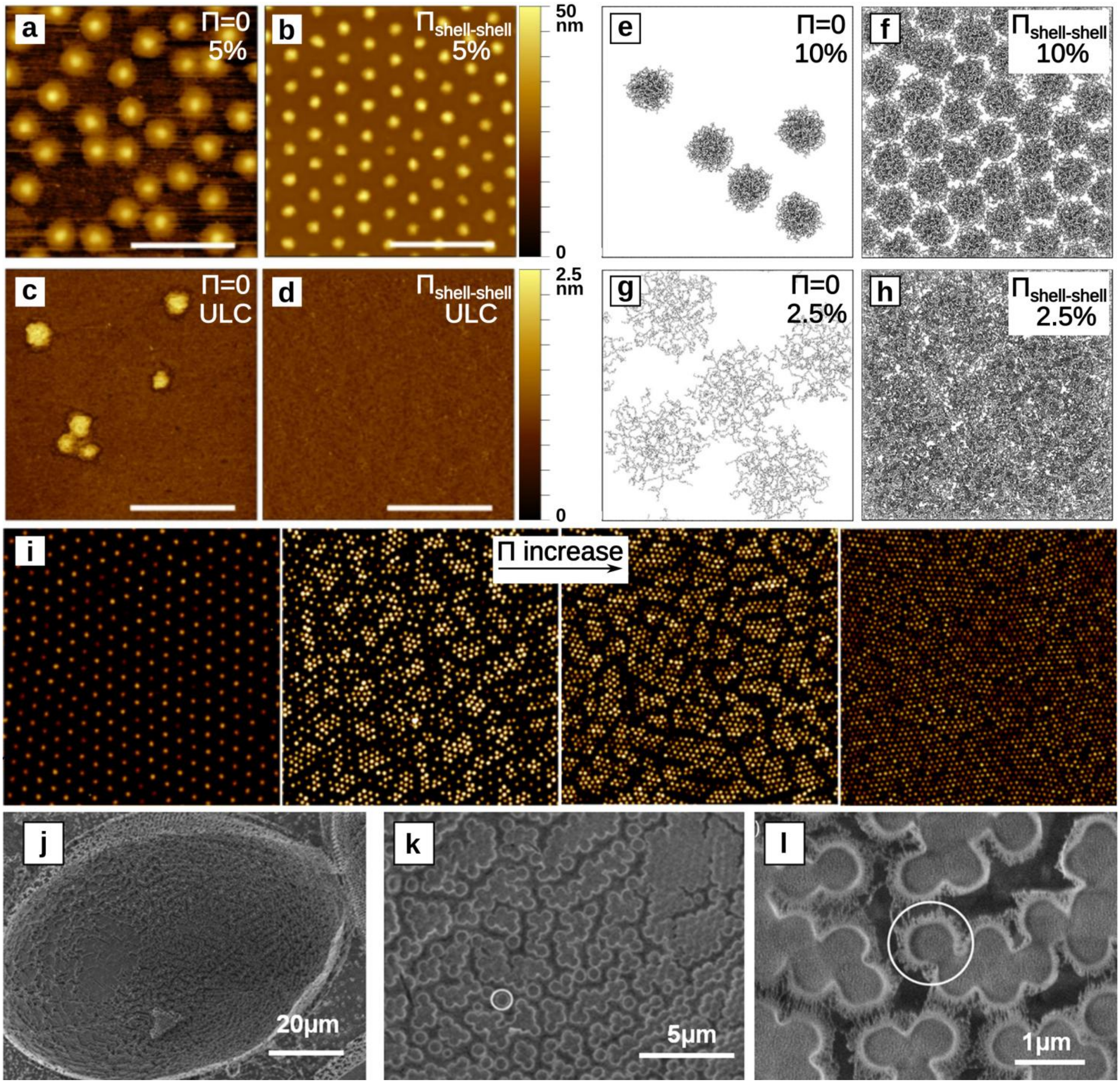
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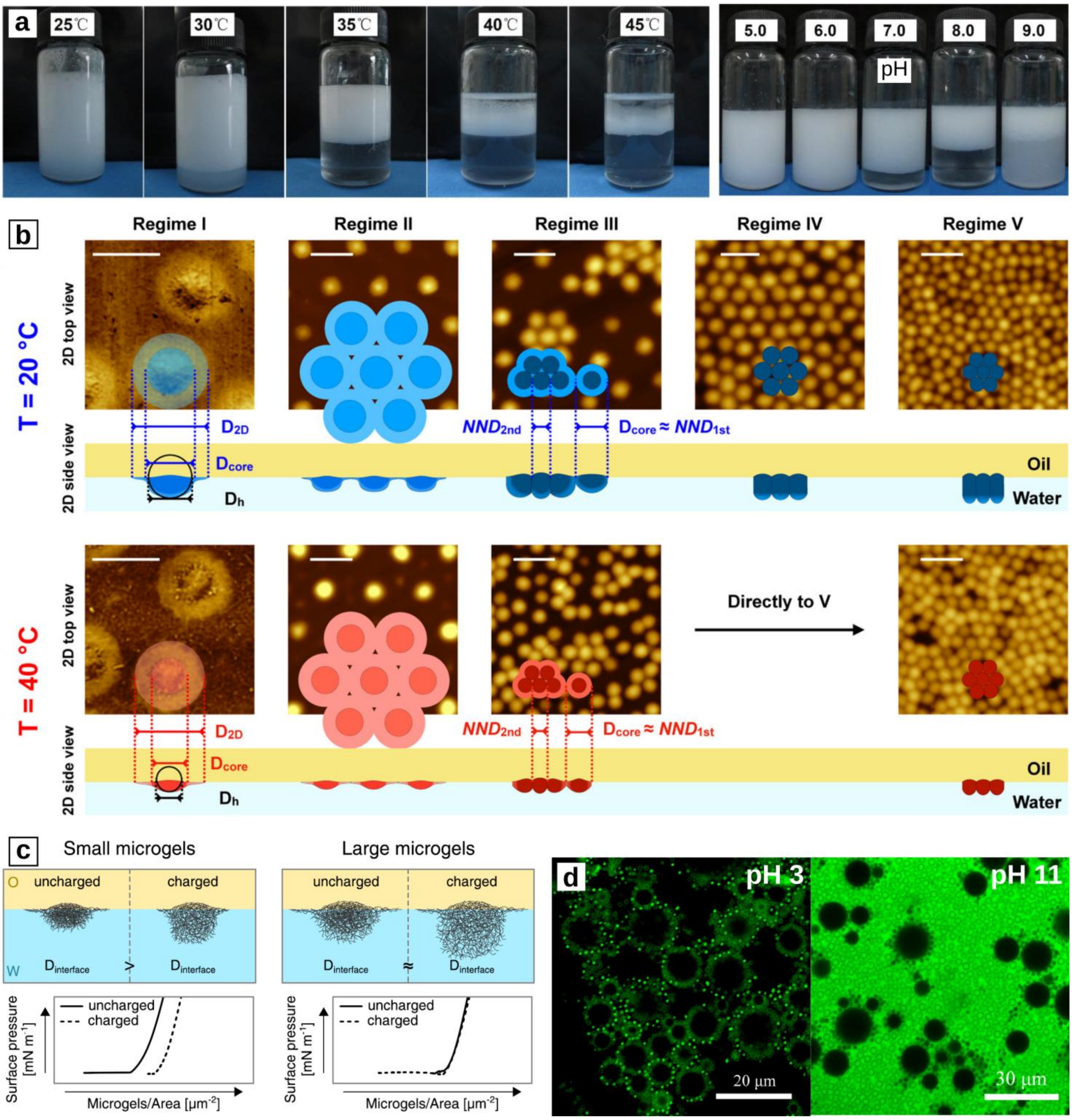
Fig. 2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T = 20 °C
2D top view
2D side view
D2D
Dcore
Dh
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Dcore ≈ NND1st
Oil
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charged
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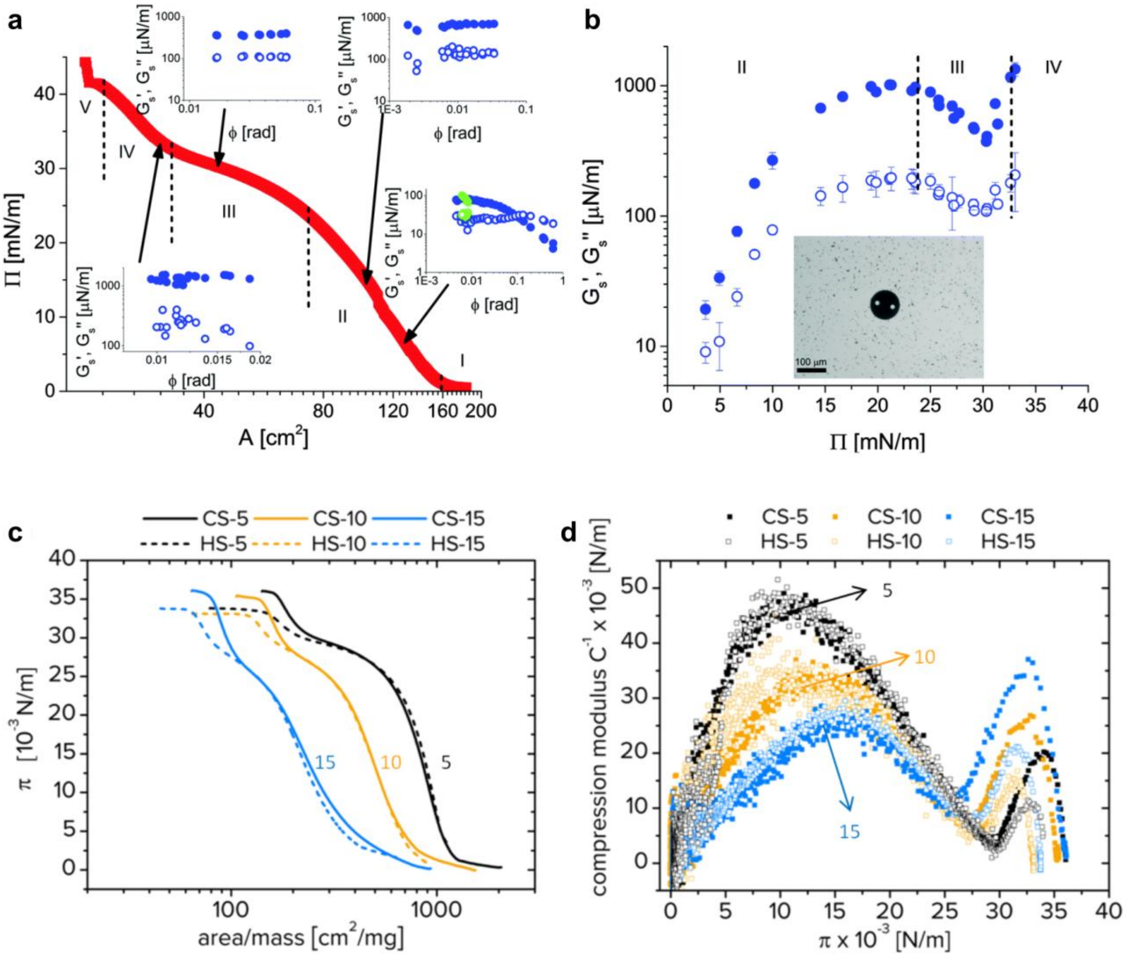
Fig. 3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CS-15
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π [10⁻³ N/m]
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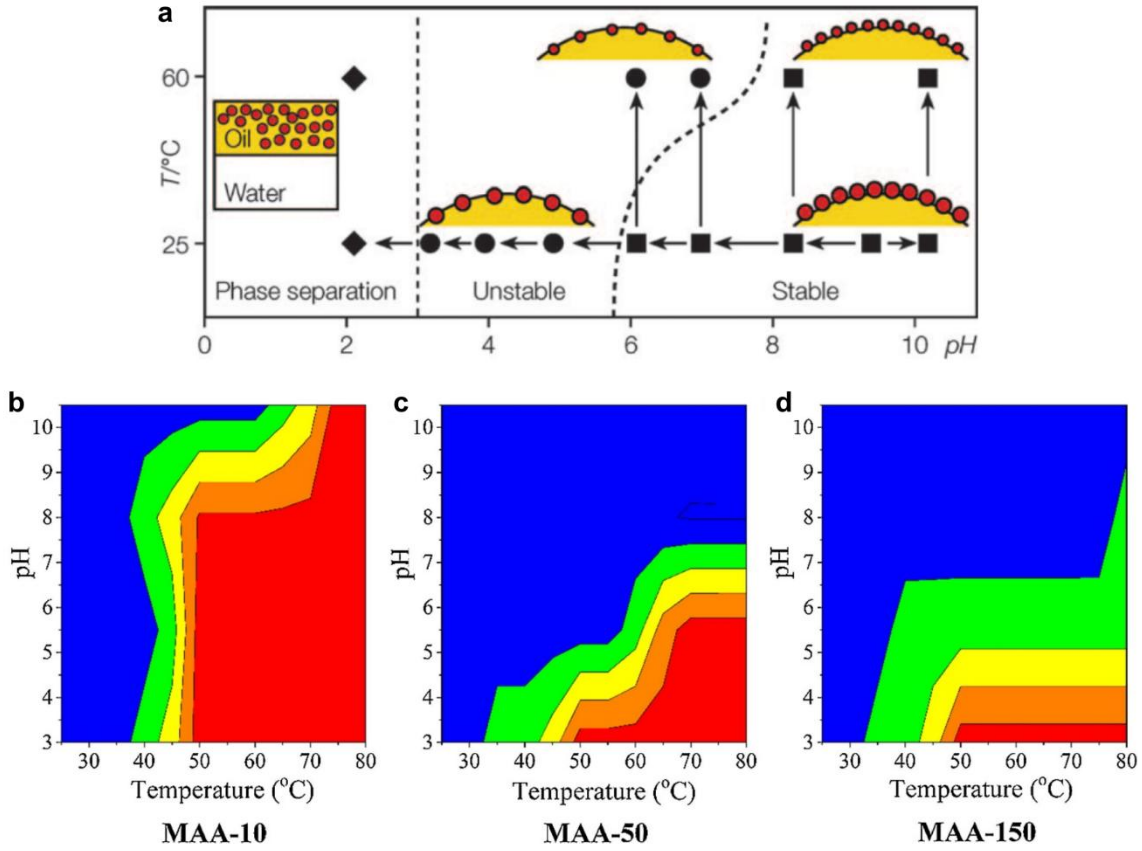
Fig. 4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Temperature (°C)
MAA-10
MAA-50
MAA-150

Fig. 5

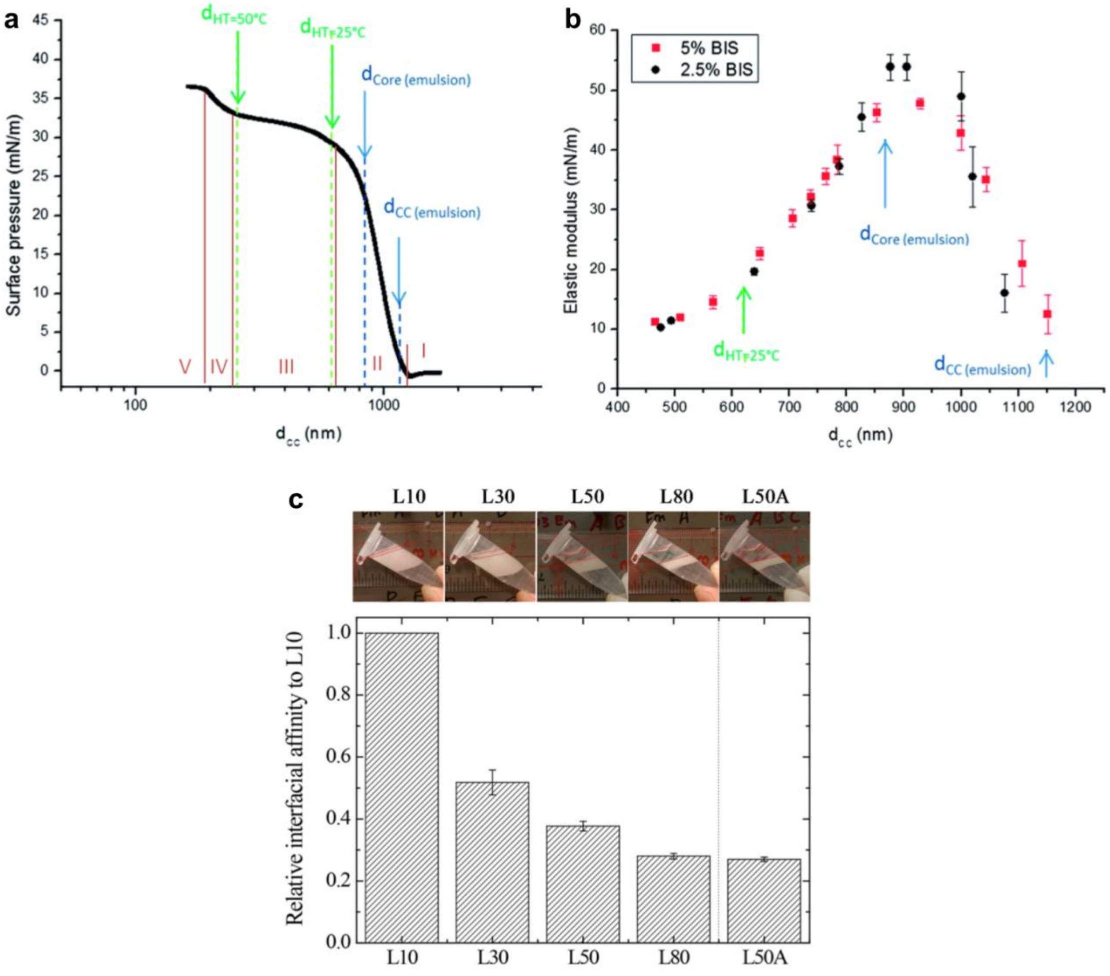
a
Surface pressure (mN/m)
0
5
10
15
20
25
30
35
40
45
100
1000
d_{cc} (nm)
$d_{HT=50°C}$
$d_{HT=25°C}$
$d_{Core\ (emulsion)}$
$d_{CC\ (emulsion)}$
V
IV
III
II
I
b
Elastic modulus (mN/m)
0
10
20
30
40
50
60
400
500
600
700
800
900
1000
1100
1200
d_{cc} (nm)
5% BIS
2.5% BIS
$d_{Core\ (emulsion)}$
$d_{HT=25°C}$
$d_{CC\ (emulsion)}$
c
L10
L30
L50
L80
L50A
Relative interfacial affinity to L10
0.0
0.2
0.4
0.6
0.8
1.0
L10
L30
L50
L80
L50A

Fig. 6

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