

Tracking the interfacial dynamics of PNiPAM soft microgels particles adsorbed at the air–water interface and in thin liquid films

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Abstract We report the behavior of thermosensitive soft microgel particles adsorbed at the air–water interface. We study the effect of temperature on the adsorption, interfacial diffusion, and surface rheology of pure *N*-isopropylacrylamide (NiPAM) microgel particles at the air–water interface. We find that the surface tensions of the solutions are the same as those of polyNiPAM solution; hence, their adsorption properties are dominated by the surface activity of the NiPAM repeat units of the particles. Particle-tracking experiments show that the particles adsorb irreversibly at the interface and form stable clusters at very low concentrations, e.g., $5 \cdot 10^{-3}$ wt%. We suggest that attractions between dangling arms or capillary interaction may be responsible for the formation of these clusters. For concentrations above 10^{-2} wt%, the interface is filled with particles, and their Brownian diffusivity is arrested. The compression elastic moduli—measured using the pendant drop method—are one or two orders of magnitude below those obtained for hard particles and NiPAM chains,

and their value is probably dominated by the intrinsic compressibility of the particles. The thin liquid films made from microgels exhibit a symmetric drainage, consistent with a high surface viscosity, but their lifetime is surprisingly short, illustrating the fragility of the films. We observed the formation of a monolayer of microgels bridging the two interfaces of the film outside the dimple. This zone grows and thins over time to a point where the microgels are highly compressed and stretched, resulting in the rupture of the film.

Keywords Microgel · Thermoresponsive · Adsorption · Surface rheology · Jamming · Brownian motion · Soft particles · Thin liquid film

Introduction

Since Pickering (1907) and Ramsden (1903), we know that solid particles can adsorb at liquid interfaces and be used to stabilize emulsions instead of standard surfactants. Such emulsions, known as Pickering emulsions, are extremely stable because the particles usually adsorb irreversibly at the interface. The two main destabilization processes in emulsions are Oswald ripening and coalescence (Leal-Calderon et al. 2007). In both cases, the surface area of the drops is reduced, and the particles become compressed. Upon compression, the particle layer becomes strongly viscoelastic and resists to coalescence, and ripening is arrested. Moreover, it has been recently shown that colloidal particles can also be used to produce ultra-stable foams (Binks and Horozov 2005; Cervantes-Martinez et al. 2008).

Colloidal particles can also be adsorbed at a liquid interface to probe its microrheological properties by tracking the Brownian motion of the adsorbed particles. This

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Special issue devoted to novel trends in rheology.

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is a very promising field of research because it enables to probe the local mechanical properties of the interface (Ortega et al. 2010). It is interesting to combine such “passive” measurements—no external force is applied on the particles—with “active” surface rheology—where an external force is applied to the interface—to obtain complementary information on the properties of interfacial layers of adsorbed proteins (Lee et al. 2010) or polymers (Maestro et al. 2011). However, the possible interaction between the particles and the adsorbed species may complicate the analysis of the data.

Recently, a new class of particles, the *N*-isopropylacrylamide (NiPAM) thermoresponsive microgels, has emerged as a new way to stabilize interfaces and even tune the stability of the interface with temperature or pH. NiPAM microgels are soft colloidal particles composed of chemically cross-linked thermosensitive polymer chains, poly(*N*-isopropylacrylamide), which exhibit a lower critical solution temperature (LCST). Such particles swell in a suitable solvent, e.g., water, and collapse above their transition temperature as it becomes a poor solvent for the polymer chains. As a consequence, the gel particles shrink when the temperature is increased above the LCST, and their hydrophobicity can be tuned by slight variation of temperature around the LCST. The temperature at which the size of the gel particles collapses is also known as the volume-phase transition temperature (VPTT). Such soft particles have proven to be a very promising system for the modification of the rheological properties of bulk liquids (Saunders and Vincent 1999; Senff and Richtering 1999; Cloitre et al. 2000; Debord and Lyon 2000; Alsayed et al. 2005; Mattsson et al. 2009; Fernandez-Nieves et al. 2011). Although these particles contain a large amount of water, they have been shown to be surface active (Zhang and Pelton 1999a, b) and used for the control of emulsion stabilization (Tsuji and Kawaguchi 2008; Brugger and Richtering 2008; Brugger et al. 2008, 2009; Monteux et al. 2010; Li and Ngai 2010; Destribats et al. 2011a, b).

Destabilization of the emulsions can actually be triggered by increasing the temperature above the VPTT or by varying the pH, depending on the chemical composition of the microgels. Recently, Destribats et al. (2011a, b) have shown that the deformability of the microgels, which can be tuned by varying the cross-link density, has a strong influence on the emulsion stability. Moreover Brugger et al. (2010) found that the surface rheological properties of the interface strongly depend on the electric charge of the particles.

In this article, we report combined measurements of the Brownian motion as well as macroscopic surface rheology of NiPAM microgels at the air–water interface. The originality of our approach is that the probe particles are the microgel themselves. This enables to couple active and

passive surface rheology of the system of interest without using additional probes.

Using micron-sized microgels, we track the Brownian motion of individual particles at the interface using a particle-tracking technique. We found that even at very low concentrations 10^{-2} wt% and above, the microgel particles spontaneously adsorb in a dense layer at the air–water interface where the Brownian diffusion is completely arrested. We were able to track sticking events between several particles at the interface, showing that this aggregation is irreversible. The compressional elastic moduli of microgel-laden interfaces are one or two orders of magnitude below those reported in the literature using hard particles or for solutions of linear polyNiPAM (PNiPAM) chains, because of the high compressibility of the particles. Lastly, we investigate the drainage of thin liquid films made from these NiPAM particles. We find that the drainage exhibits features that are consistent with a high surface viscosity of the layers. However, the lifetime of the films is short, illustrating the fragility of the layers.

Experimental part

Materials

N-isopropylacrylamide, methylene bisacrylamide, and potassium persulfate ($K_2S_2O_8$) were purchased from Sigma-Aldrich and used as received. All samples were prepared using ultrapure deionized water (Milli-Q, Millipore, France).

Synthesis of the microgel particles

Pure NiPAM microgels were prepared by conventional radical cross-linking copolymerization of *N*-isopropylacrylamide in the presence of methylene bisacrylamide (MBA) as cross-linker without surfactant (surfactant-free precipitation polymerization) (Sanson and Rieger 2010; Debord and Lyon 2000). In a typical synthesis, polymerization was carried out in a jacketed round-bottomed flask equipped with a condenser, a thermometer, and a nitrogen inlet and outlet. The monomer NiPAM (1 g) and the cross-linker MBA (53 mg, 3.4 mol%) were dissolved in degassed water (90 mL). The monomer aqueous solution was mechanically stirred at 300 rpm under nitrogen for 45 min to remove dissolved oxygen. After complete dissolution, the reaction mixture was heated up to 70 °C. At this time, the initiator $K_2S_2O_8$ (60 mg, 2.4 mol%), which was separately dissolved in degassed water (10 mL), was directly injected into the monomer solution. The synthesis was carried out under a nitrogen atmosphere and constant stirring for 5 h.

The reaction mixture was then cooled to room temperature. Microgels were cleaned by several centrifugation and redispersion cycles using Milli-Q water. After five centrifugation/redispersion cycles, the air–supernatant interfacial tension was 69 mN/m, which is very close to the water surface tension, therefore ensuring high-quality purification of the microgels. Then, the microgels were freeze dried. The size and the VPTT of the microgels were determined by dynamic light scattering experiments. The radius of the particles is 350 nm at 20 °C and shrinks down to 150 nm when the temperature reaches 35 °C, which is very close to the LCST of polyNiPAM.

Micron-sized NiPAM microgels were synthesized following a protocol adapted from Meng et al. (2009) using a temperature-programmed ramp during the first step of the microgel synthesis. Unlike in the latter reference, there was no addition of charged acrylic acid comonomers; hence, the polydispersity was higher than what is reported by Meng et al. (2009). The size of the microgels decreases from $1.2 \pm 0.5 \mu\text{m}$ at $T = 25 \text{ }^\circ\text{C}$ to $0.48 \pm 0.10 \mu\text{m}$ at $T = 40 \text{ }^\circ\text{C}$. Supporting information S1 reports DLS measurements of the hydrodynamic radius of the two types of microgel particles.

Microgels solutions were prepared by dissolving the freeze-dried microgels into deionized water (Milli-Q system from Millipore) under magnetic stirring for 24 h at room temperature.

Microscopy measurements

To track the large microgels, we used a standard optical microscope (Olympus BX51WI) equipped with a camera Sony XCD-X710 (15 fps). The solution is poured into a small cell, 1 cm diameter, of low depth (2 mm) covered with a glass slide to avoid convection as much as possible. The optical contrast of the particles in water is sufficient to track the particles without any particular precaution. The diffusion coefficients were determined using image analysis tools of MatLab. To suppress the contribution of the displacement arising from collective displacement of the particles because of macroscopic drifts, we use the relative mean square displacement of two particles i and j , defined in a two-dimensional space as follows:

$$\text{MSD} = \left\langle (\Delta \vec{r}_{ij}(t + \tau) - \Delta \vec{r}_{ij}(t))^2 \right\rangle = 8Dt \quad (1)$$

where D is the diffusion coefficient. Note that this equation is valid for both our bulk and surface measurements. Indeed, even for the particles diffusing in the bulk solution, using our microscope, we can only capture trajectories occurring in the plane of focalization. However, it is easy to make sure that the measurement is done at the interface or in the bulk because the particles in the bulk diffuse out of the field

of view within a few seconds, whereas the adsorbed particles remain in the same plane during the observation time. We have, thus, determined the microgel diffusion coefficients both at the interface with air and in the bulk of the suspension, denoted respectively $D_{\text{interface}}$ and D_{bulk} . Each measurement is an average over six relative displacements. The error on the measurements is of the order of 25 % because of the polydispersity of the particles.

Surface tension and surface compression rheology measurements

The surface tensions and the surface compressional moduli were measured using the pendant drop method (Teclis, Tracker, France). The shape of the drops was fitted to Laplace's equation in order to determine the interfacial tension. Our analysis of the interfacial tension with temperature takes into account the temperature dependence of the density of water. For the dilational rheology measurements, the surface area of the drop is oscillated at a frequency of 0.1 Hz using a strain of 5 %. The analysis and Fourier analysis are performed with the help of the software provided by IT Concept. The surface compression–dilation modulus E is defined as the derivative of the surface tension γ with respect to the surface area A of the drop $E = \frac{\partial \gamma}{\partial \ln A}$. For oscillation experiments, the area of the drop is oscillated, and we record the variation of the surface tension with time. One can define a storage modulus, $E' = E \cos \Phi$ and a loss modulus $E'' = E \sin \Phi$ with Φ the lag between the surface tension and the area oscillations. The interfacial strain is defined as dA/A_0 , where dA is the amplitude of the area variation during an oscillation of the drop, and A_0 is the initial area of the drop. The error on the determination of the moduli is of the order of 2 mN/m.

Thin liquid film drainage

Drainage experiments were performed with a thin-film balance apparatus, which is described in detail elsewhere (Bergeron and Radke 1992). Briefly, an individual foam film is formed in the hole of a horizontal porous plate connected to a vertical capillary tube which is placed in a 200 cm³ hermetically sealed cell. The drainage of the film is caused by the capillary suction in the pores of the plate. Observations of the film and its drainage patterns are made under white-light thin-film interference conditions using an optical microscope in reflexion (angle of incidence is zero). From the color, we obtain the thickness of the film using the color chart found in http://www.kcvs.ca/map/java/applets/thinfilm/thinfilm_unconverted.html, assuming a refractive index equal to 1.33 and a bottom index of 1. In supporting information, S2 is a sheet with a list of the

corresponding thickness colors. In this study, we focus our attention on the type of film drainage that occurs when different adsorption layers are formed at the air–water interface, which are strongly influenced by the surface viscosity. Joye et al. (1992, 1994) have identified two characteristic drainage patterns for individual, horizontal foam films. They classify these patterns as *symmetric* and *asymmetric*. In symmetric drainage, the film develops a so-called dimple in the center of the film, which slowly drains in an axisymmetric fashion into the surrounding Plateau border region. Conversely, asymmetric drainage is the result of a surface-tension-driven instability that causes rapid expulsion of the dimple into the Plateau border. Furthermore, Joye et al. (1992, 1994) have shown that the surface-tension-driven instability is stabilized for shear surface viscosities higher than $2 \cdot 10^{-4}$ Pa/ms. In the case of asymmetric drainage fluctuations in the barrier ring (zone between the dimple and the meniscus), thickness can develop, resulting in the rapid expulsion (less than a second) of the liquid from the film.

Results

Brownian diffusion of the microgels at the interface and compression surface rheology

To determine the interfacial dynamics of the particles at the interface, we tracked the Brownian motion of micron-sized microgel particles using an optical microscope in the bulk solution and at the interface for concentrations ranging from 10^{-3} to 0.1 wt%. Using Eq. 1, we relate the mean square relative displacement of particles to the bulk and surface diffusion coefficients, respectively, D_{bulk} and $D_{\text{interface}}$. For a concentration of 10^{-3} wt%, we find $D_{\text{bulk}} = 0.25 \pm 0.05 \mu\text{m}^2/\text{s}$. Using the Stokes–Einstein relation, which is valid in such a dilute suspension,

$$D_{\text{bulk}} = \frac{kT}{6\pi\eta R}, \quad (2)$$

we find that the radius of the particles is $R = 1.3 \pm 0.25 \mu\text{m}$, which is consistent with the size determined by light scattering. In Fig. 1, we show the evolution of $D_{\text{interface}}$ as a function of the weight fraction of microgels in the solutions. For concentrations of 10^{-3} wt%, individual particles can be seen at the interface, which diffusion coefficient is roughly equal to the bulk one, $D_{\text{interface}} = 0.20 \pm 0.05 \mu\text{m}^2/\text{s}$. From Brenner and Leal (1978), we know that for a hard sphere floating at the air–liquid interface, the 2D diffusion coefficient writes as $D_{\text{interface}} = \frac{kT}{f\pi\eta R}$, where f is a nonlinear and complex function of the three-phase contact angle at the particle surface. For a contact angle equal to 90° , i.e., when the sphere is half immersed in the liquid, f equals to 3 (Danov et al. 1995), meaning that the surface diffusion

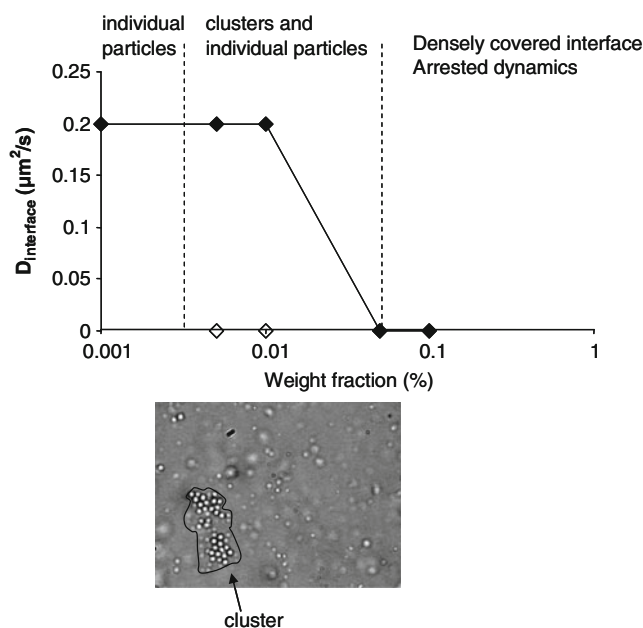


Fig. 1 Diffusion coefficient of microgel particles at the air–water interface as a function of particles weight fraction. Below 10^{-3} wt%, the particles diffuse freely at the interface with $D_{\text{interface}} = D_{\text{bulk}}$. Between $5 \cdot 10^{-3}$ and 10^{-2} %, the interface is covered with mixtures of isolated particles with $D_{\text{interface}} = D_{\text{bulk}}$ and clusters of particles where diffusion is arrested. Above 0.01 wt%, the interface is covered with particles which relative displacement is arrested. The micrograph represents the surface of a solution of $5 \cdot 10^{-3}$ wt% microgels. One cluster can be seen at the interface. Note that some particles appear darker than others, probably because their spreading and anchoring at the interface is different

coefficient is twice larger than the bulk one. In our study, the measured hydrodynamic friction is equal to the bulk one, within experimental error, which is consistent with the picture of a particle almost completely immersed in water in line with recent results from Geisel et al. (2012). However, we never observed any desorption event of the particles during the measurements, showing that the particles adsorb irreversibly at the interface; hence, the interface is probably not in equilibrium with the bulk solution.

For $5 \cdot 10^{-3}$ and 10^{-2} wt%, isolated particles as well as clusters of particles can be observed at the interface (see Fig. 1). Individual particles diffuse freely at the interface with the same diffusion coefficient $D_{\text{interface}} = 0.2 \mu\text{m}^2/\text{s}$ as for 10^{-3} wt%. For particles situated inside the clusters, the relative motion of the particles is arrested. As a conclusion, for these concentrations, $D_{\text{interface}}$ is either $0.2 \mu\text{m}^2/\text{s}$ (filled diamonds) or zero (open diamonds), depending on which particles are considered for the measurement.

Above 10^{-2} wt%, the Brownian motion of the adsorbed particles is arrested, and the interface is fully covered with particles. As can be seen in Fig. 2, for the 0.03 % solution, the bulk of the solution is very dilute, but the microgel particles form a dense interface only a few minutes after the

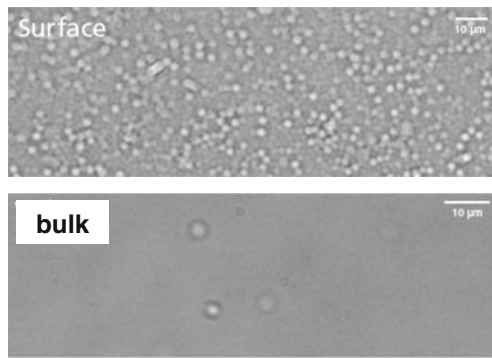


Fig. 2 Optical microscopy of the air–water interface (*top*) and the bulk solution (*bottom*) of a solution of microgels of weight fraction 0.03 wt% at ambient temperature. At this concentration, the Brownian motion of the particles at the interface is arrested. In the supporting information, we provide a video showing an example of such arrested Brownian motion at the interface

interface is created. Again, this is due to the irreversible adsorption of the particles at the interface.

Particles at the interface are seen to move collectively because of a macroscopic drift, but their individual Brownian motion is totally stopped, whereas the particles diffuse freely in the bulk. Interestingly, NiPAM microgels adsorb spontaneously at the air–water interface, whereas hard colloids usually need to be forced to adsorb to interface by injecting mechanical energy into the system (Tcholakova et al. 2008), either by shaking or using flow-focusing techniques in microfluidic devices (Subramaniam 2006a, b). We have also investigated the effect of temperature on the interface: from ambient to 40 °C, the apparent size of the adsorbed particles shrinks, but the interface remains very dense, and the relative displacement of the particles remains arrested.

In Fig. 3, we present values of the elastic compressional moduli, both the real part E' and the imaginary part E'' of microgel solutions (weight fraction 0.1 %) as a function of temperature. For our microgel solutions, the values of the elastic moduli range between 5 and 8 mN/m for all temperatures, which is almost not significantly higher than the residual measurement obtained for a pure air–water interface of the order of 1 to 3 mN/m. These results are of the same order as Brugger’s data for microgels at the oil–water interface (Brugger et al. 2010). These values are two orders of magnitude lower than those obtained by Cicuta et al. (2003) for hard latex particles adsorbed at the oil–water interface ($E' \sim 100$ mN/m) and one order of magnitude below what is obtained for linear PNiPAM chains around the LCST (Guillermic and Saint-Jalmes 2013). Moreover, the compressional elastic moduli are weakly influenced by the temperature, consistently with the fact that the structure of the layers and the Brownian diffusivity are not strongly influenced by temperature.

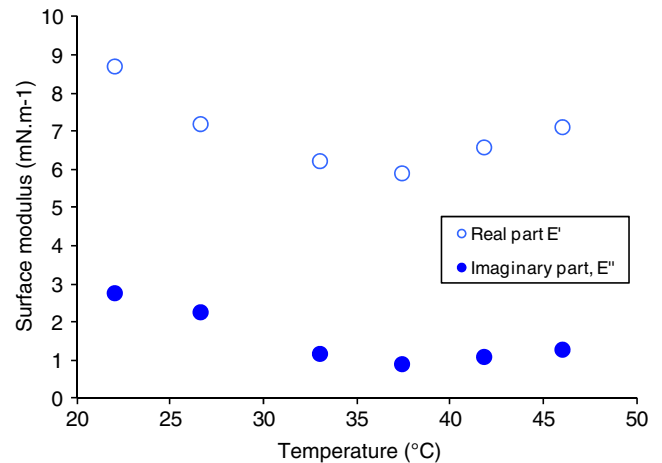


Fig. 3 Compression-dilatation surface moduli as a function of temperature for a microgel weight fraction equal to 0.1 %. E' (open circles), E'' (full circles)

Drainage of thin liquid films

We formed a horizontal free-standing soap film of the microgel solution and observed its drainage under white light. A series of photos of the film is shown in Fig. 6a for times, $t = 1, 10, 20, 42,$ and 56 s, after the formation of the film. At $t = 1$ s, the symmetric rings show that a dimple is formed in the film (see Section “Thin liquid film drainage”). At least 6-N fringes can be seen, so the thickness at the top of the dimple is at least of the order of $1.8 \mu\text{m}$ thick. The dimple profile is evolving axisymmetrically in contrast to a standard surfactant (Joye et al. 1992, 1994), which usually drain to a flat film in a few seconds. This slow drainage is consistent with a high surface viscosity. At $t = 10$ s, a zone of lower thickness is nucleated on the left of the film. The corresponding Newton color is yellow. This zone grows and becomes thinner over time; the Newton color becomes blue for $t = 42$ s. It can be noted that the contour of this zone is very irregular, indicating that a strong surface viscosity prevents the relaxation to a more circular shape, which is expected for a simple fluid minimizing its surface energy.

A recent study from Destribats et al. (2012) reports the influence of microgels deformability on the structure of emulsion films. Their “rigid” microgels—3.5 % BIS and diameter = 800 nm at ambient temperature—are very similar to ours and form a monolayer bridging the droplet interfaces of thickness from 250 to 500 nm as estimated from Cryo-TEM experiments. More compressible microgels form a bilayer separated by a thin film of water, the total thickness of the film being equal to 500 to 700 nm. It seems reasonable to assume that in our case, the blue zone nucleating outside the dimple and the borders corresponds to a bridged zone (see drawing in Fig. 6b), consistent with Destribats’ results. Then, the blue Newton color may correspond either to the first fringe, 250 nm assuming that the index of

refraction equals 1.33, or to the second Newton fringe, 445 nm (see supplementary information S1). At $t = 0$, the film is probably stabilized by a bilayer of microgels separated by a water film. After a few seconds, the bridged zone composed of a monolayer of microgels nucleates and invades the thin film as shown in Fig. 6b.

Surprisingly, despite the symmetric drainage of the dimple, the film breaks only after 56 s, which is quite fast compared to other systems forming gels in thin liquid films, which can be stable for hours (Monteux et al. 2004). We repeated this experiment several times, and each time on the last image recorded, a thinner zone (yellow zone pointed by an arrow for $t = 56$ s) appears, corresponding either to $e = 130$ nm or $e = 340$ nm for the first or second fringes, respectively. In either case, the microgel monolayer is probably highly compressed. We did not observe any gray or black film, 1 to 10 nm, before coalescence unlike standard surfactants.

Discussion

Our observations have shown that the NiPAM particles spontaneously adsorb at the air–water interface in a dense layer, which is very compressible. Moreover, an attractive force between the particles leads to the formation of particles clusters which eventually cover the whole interface. Below, we discuss the origin of these observations.

Origin of the surface activity of the microgel particles

We measured the surface tension of pure NiPAM microgel solutions as a function of temperature (Fig. 4) for weight fractions ranging from 0.004 to 0.1 %. For all the concentrations investigated in this study, the surface tensions exhibit the same trend, i.e., a decrease of the surface tension between 44 and 38.5 mN/m, when increasing the temperature from 20 to 35 °C. Low surface tensions were also observed by Zhang and Pelton (1999a, b) for pure NiPAM microgel particles. Interestingly, these low values of the surface tension are almost identical to the ones measured by Jean (2000) and Lee et al. (1999) for solutions of linear NiPAM polymer chains as a function of temperature (dotted line in Fig. 4). Their neutron-scattering experiments showed that the surface tension does not depend on the polymer concentration because the proximal zone of the water surface, i.e., the zone comprised within the first few angstroms below the surface, is rapidly saturated with NiPAM repeat units even at very low polymer concentration. Combining surface tension and neutron experiments, the authors found that the adsorption energy for one NiPAM repeat unit at the interface is 0.15 kT; hence, NiPAM repeat units are intrin-

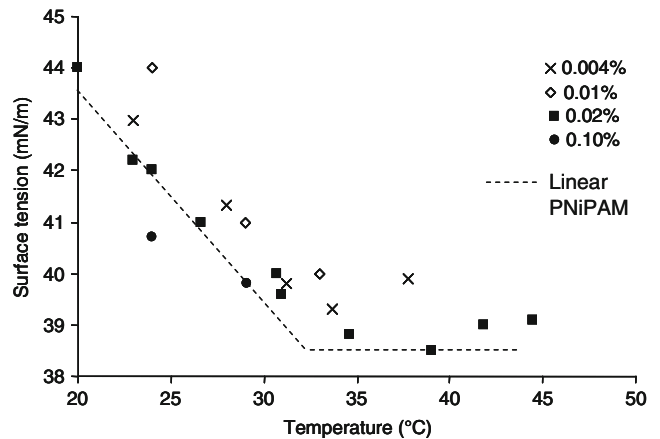


Fig. 4 Surface tension of pure NiPAM microgel solutions as a function of temperature for various weight fractions: 0.004 % (crosses), 0.01 % (open diamonds), 0.02 % (full squares), and 0.1 % (full circles). The dotted line represents results obtained for solutions of linear PNiPAM from Jean (2000) and Lee et al. (1999)

sically surface active, and their adsorption is spontaneous. The similar values of surface tensions for NiPAM microgels and linear PNiPAM chains can be explained by the fact that the proximal zone of the interface is filled with NiPAM repeat units for both systems. Using Cryo-MEB, Destribats et al. (2011a, b) and Brugger et al. (2009) have shown that uncross-linked NiPAM dangling arms at the periphery of the particles spread at interfaces. Destribats et al. (2011a, b) showed that these dangling arms lead to the irreversible adsorption of the particles. Therefore, we suggest that the proximal zone of the interface is filled with these flexible NiPAM arms leading to the same surface tension as linear PNiPAM solutions.

Origin of the low compression moduli

For fluid interfaces, the surface compression modulus E depends on how the surface tension γ varies when the interfacial layer is compressed during oscillations of the surface area, A , $E = d\gamma/d\ln A$ (Ermi 2011). E is, therefore, a measure of resistance against surface tension gradients and is sensitive to the diffusion of molecules between the bulk solution and the interface (Lucassen and Vandente 1972). For interfaces covered with irreversibly adsorbed species such as polymers, the compression modulus also depends on the intrinsic mechanical properties of the adsorbed material (Carvajal et al. 2011), $E \approx E_{\text{Young}}h$, where E_{Young} is the Young's modulus of the 3D material, and h is the thickness of the adsorbed layer.

Our data show that the surface tension does not depend strongly on the temperature or the microgel concentration. Furthermore, Brugger et al. (2010) have measured the surface pressure isotherms of microgel laden oil–water

interfaces and recorded a variation of only 2.5 mN/m for surface compressions up to 70 %. These observations are consistent with low values of $d\gamma/d\ln A$.

In a recent study, Hashmi and Dufresnes measured Young's moduli of individual microgel particles adsorbed on a solid surface using an AFM (Hashmi and Dufresne 2009) and compared their results with the Flory–Rhener model, taking into account the bulk and the shear modulus as a function of temperature. According to the Flory–Rhener model, the shear modulus increases monotonically with temperature for systems exhibiting a VPTT like the NiPAM microgels because the polymer volume fraction inside the gel particle increases as the volume of the particles decreases. However, the bulk modulus, which is the inverse of the osmotic compressibility, exhibits a non-monotonic evolution with temperature; it decreases with temperature below the VPTT and increases above the VPTT. Experimentally, below the LCST, the authors found that the elastic modulus of individual particles decreases from 10 to 1 kPa, and it is dominated by the increasing osmotic compressibility because PNiPAM undergoes a good to theta solvent transition. Above the VPTT, the particles elastic modulus increases from 1 to 100 kPa because of the increase of the density of the particles. We estimate the corresponding 2D elastic modulus of the layer, using the scaling $E \sim E_{\text{Young}} D$, where D is the diameter of the particles, and E_{Young} is Young's modulus of the particles. We use the values of the particles diameters obtained by dynamic light scattering and the values of E_{Young} obtained by Hashmi and Dufresnes for each temperature. Interestingly, we find that the compression modulus E is of the order of 0–10 mN/m, which is the same order of magnitude of our measurements. Above the VPTT, this approach leads to values of E' of the order of 30 mN/m, which are much larger than our results. However, this scaling approach does not take into account lateral interactions between the particles, as well as rearrangements upon compression. In fact, above the VPTT, it is known that the attraction between bulk particles increases (Romeo et al. 2010).

Origin of clusters formation and fragility of the thin liquid films

Interestingly, the particles form clusters at the interface but do not form aggregates in the bulk solution. In Fig. 5, we report a sequence of images showing an aggregation event between a particle and a cluster of three particles even at ambient temperature. It can be seen that there is no relative displacement of the particles inside the cluster. Moreover, after the particle sticks to the cluster, its motion stops, and no unsticking event was observed. This shows that the aggregation of the particles in the clusters is irreversible and, thus, that the depth of the well of the interaction potential between particles is much larger than the thermal energy, in kiloton. Since the attraction between the microgels adsorbed at the interface is sufficient to prevent Brownian diffusion of the adsorbed particles, even at rather low concentrations, it is likely that the interaction is a large range one. It should be emphasized that in the bulk, there is no aggregation of the particles, and they diffuse freely. In line with the picture given by Brugger et al. (2009) and Destribats et al. (2011a, b), who recently reported Cryo-MEB images of overlapping coronas of dangling chains of NiPAM around the adsorbed microgels, we suggest interactions between the dangling NiPAM arms leading to the network formation. These authors showed that only 3 % of the PNiPAM repeat units are adsorbed at the interface, corresponding to an anchoring energy of 10^4 kT per microgel. The number of repeat units involved between two adsorbed microgels inside a cluster is probably of the same order of magnitude. Hence, the binding energy between two particles is also probably very large compared to kiloton and thus provokes the formation of clusters and stops the Brownian motion of the particles at the interface.

Hard colloidal particles adsorbed at interfaces are known to interact strongly through attractive capillary interactions when the interface is deformed around the particles (Kralchevsky and Denkov 2001). In the case of small particles, where gravity is negligible, capillary interaction

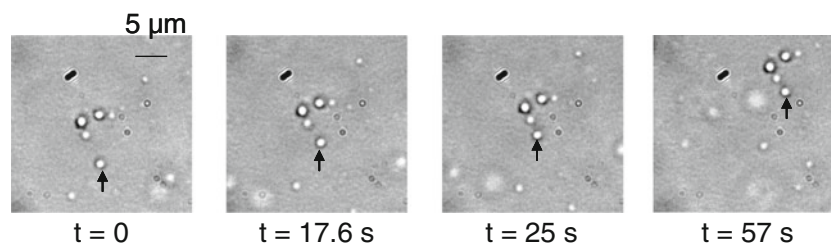


Fig. 5 Sequence of images showing the sticking between a particle and a cluster at the surface of a solution of $5 \cdot 10^{-3}$ wt% microgels. The particle marked with an *arrow* diffuses toward the clusters containing three particles. At $t = 25$ s, the particles stick to the cluster. For $t >$

25 s, the relative distance between the particle and the cluster remains constant. Although the particle fluctuates slightly around its position because of thermal energy, it stays bound to the cluster

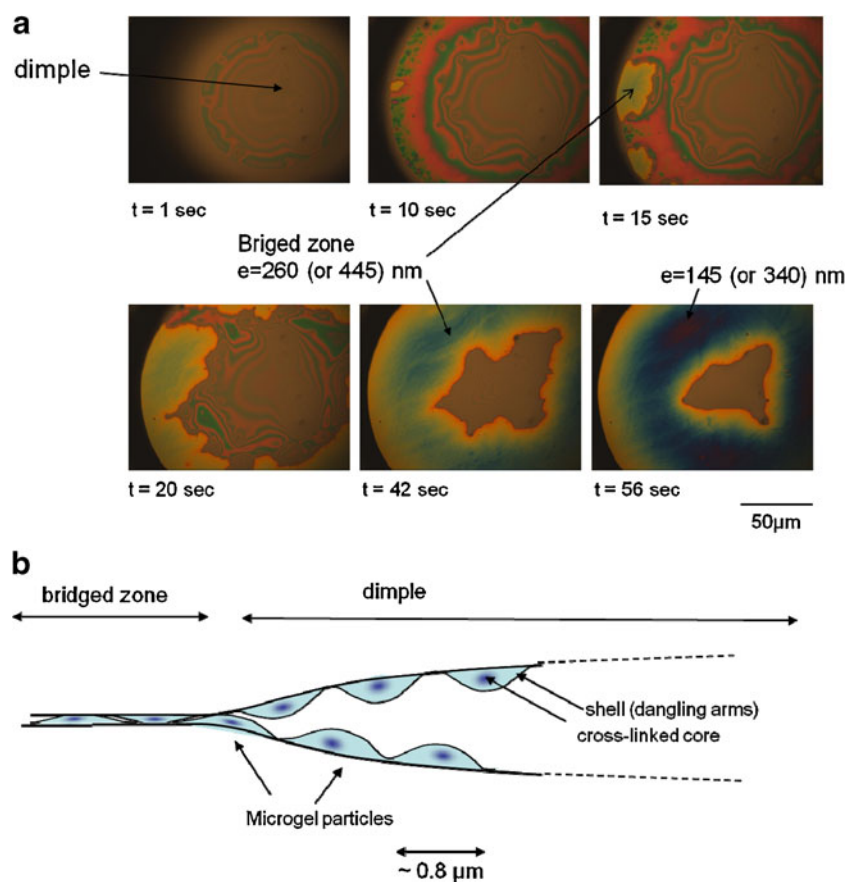
can arise from undulation of the contact line around the particles because of surface roughness or chemical heterogeneity at the nanometer scale. In the case of soft particles, it has been shown that capillary forces can be stronger than for hard particles because the wetting radius is larger when the particles are deformable (Butt et al. 2010). Capillary interactions strongly depend on the surface tension and can be suppressed when the surface tension is lowered by surfactants (Subramaniam et al. 2006a, b). To test the possible influence of capillary interactions, we have lowered the surface tension of the microgel suspensions by either adding a neutral surfactant ($C_{12}E_5$) or mixing ethanol to water. We observed cluster formation at the interface in all the investigated conditions; however, we cannot rule out capillary attractions between microgel particles as the driving force for cluster formation. The interface of the microgel particles is probably very fuzzy because of the gradient in the density of cross-linkers inside the particles. The resulting surface heterogeneity could induce capillary attraction between the particles, therefore bringing the particles closer to each other at the interface leading to an overlap of the dangling PNIPAM arms which can also interact through short-range forces.

We performed macroscopic surface rheology using the magnetic needle surface rheometer (Verwijlen et al. 2011)

(not shown) and found surface viscosities of the order of $2 \cdot 10^{-5}$ Pa/ms. Considering several theoretical studies (Fischer 2004; Fischer et al. 2006; Stone and Ajdari 1998; Danov et al. 1995), such a surface viscosity is sufficiently high to stop the Brownian motion of the particles consistently with our results.

Surprisingly, we found that the lifetime of the thin liquid films made with the microgel particles is short in comparison to other systems which undergo similar symmetric drainage (Monteux et al. 2004). In the last image of sequence shown in Fig. 6a, a thin zone (thickness either 145 or 340 nm) appears outside the dimple. The initial diameter of the microgel being 800 nm, the microgel monolayer is probably highly compressed and stretched in this zone explaining the fragility of the films. Indeed, for hard particles, it is known (Tcholakova et al. 2008) that particles forming monolayers are less efficient to stabilize thin liquid films than bilayers, because in monolayers, zones of deprived particles are more likely to appear because of fluctuations. Such spots are weak points, which provide no protection against coalescence. In fact, in the case of microgels, a correlation between bridging mechanisms and coalescence for emulsion films containing microgel particles was observed in the literature (Destribats et al. 2012; Liu et al. 2012).

Fig. 6 **a** Series of photos showing the drainage of a thin liquid film formed from a microgel solution of concentration 0.1 %. The diameter of the microgel particles is 700 nm at ambient temperature. The concentric rings observed at $t = 1$ s show that a dimple is formed. The dimple drains symmetrically ($t = 10$ to 20 s). At $t = 10$ s, a zone of thickness 250 nm nucleates on the left border of the film, with irregular shape. The dimple drains further, and the zone outside the dimple thins down to 145 nm (arrows) on the top of the image corresponding to $t = 56$ s. **b** Drawing representing the dimple and the bridged zone where microgels are compressed. The microgels are represented flattened, containing a cross-linked core and a shell composed of dangling arms, consistently with the pictures from Destribats et al. (2012) and Geisel et al. (2012)



Conclusion

In our study, we report for the first time the interfacial dynamics of thermosensitive soft microgel particles adsorbed at the air–water interface. We study the effect of temperature on the adsorption, interfacial dynamics, and surface rheology of pure NiPAM microgel particles at the air–water interface. We found that the surface tensions of the solutions are the same as those of PNiPAM solution; hence, their adsorption properties are dominated by the surface activity of the NiPAM repeat units of the particles. The interfacial Brownian diffusivity was found to be arrested even at very low microgel concentrations, above 10^{-2} wt%, although the particles diffuse freely in the bulk. Capillary interaction due to the rough surface of the particles as well as attractions between the dangling arms may be responsible for the formation of these clusters. A precise measurement of the interaction potential between the particles may help in understanding the origin of the clusters at the interface. Compressional elastic moduli are one or two orders of magnitude below those obtained for hard particles and NiPAM chains, and their value is probably dominated by the intrinsic compressibility of the particles and the fact that the interface is saturated with NiPAM repeat units. The thin liquid films made from microgels exhibit a symmetric drainage, consistent with a high surface viscosity, but their lifetime is surprisingly short, illustrating the fragility of the films. We observed the formation of a monolayer of microgels bridging the two interfaces of the film outside the dimple. This zone grows and thins over time to a point where the microgels are highly compressed and stretched, resulting in the rupture of the film. In the future, we believe that combining these techniques would help in designing soft particles with interesting chemistries to produce stable foams.

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References

- Alsayed AM, Islam MF, Zhang J, Collings PJ, Yodh AG (2005) Premelting at defects within bulk colloidal crystals. *Science* 309:1207–1210
- Bergeron V, Radke CJ (1992) Equilibrium measurements of oscillatory disjoining pressures in aqueous foam films. *Langmuir* 8:3020–3026
- Binks BP, Horozov TS (2005) Aqueous foams stabilized solely by silica nanoparticles. *Angew Chem Int Ed* 44:3722–3725
- Brenner H, Leal LG (1978) Micromechanical derivation of Fick's law for interfacial diffusion of surfactant molecules. *J Coll Int Sci* 65:191–209
- Brugger B, Richtering W (2008) Emulsions stabilized by stimuli-sensitive poly(N-isopropylacrylamide)-co-methacrylic acid polymers: microgels versus low molecular weight polymers. *Langmuir* 24:7769–7777
- Brugger B, Rosen BA, Richtering W (2008) Microgels as stimuli-responsive stabilizers for emulsions. *Langmuir* 24:12202–12208
- Brugger B, Rütten S, Phan KH, Möller M, Richtering W (2009) The colloidal suprastructure of smart microgels at oil–water interfaces. *Angew Chem Int Ed* 121:4038–4041
- Brugger B, Vermant J, Richtering W (2010) Interfacial layers of stimuli-responsive poly-(N-isopropylacrylamide-co-methacrylic acid) (PNIPAM-co-MAA) microgels characterized by interfacial rheology and compression isotherms. *Phys Chem Chem Phys* 12:14573–14578
- Butt HJ, Barnes WJP, Del Campo A, Kappl M, Schönfeld F (2010) Capillary forces between soft, elastic spheres. *Soft Matter* 6:5930–5936
- Carvajal D, Laprade EJ, Henderson KJ, Shull KR (2011) Mechanics of pendant drops and axisymmetric membranes. *Soft Matter* 7:10508–10519
- Cervantes-Martinez A, Rio E, Delon G, Saint-Jalmes A, Langevin D, Binks BP (2008) On the origin of the remarkable stability of aqueous foams stabilised by nanoparticles: link with microscopic surface properties. *Soft Matter* 4:1531–1535
- Cicuta P, Stancik EJ, Fuller GG (2003) Shearing or compressing a soft glass in 2D: time-concentration superposition. *Phys Rev Lett* 90:236101
- Cloitre M, Borrega R, Leibler L (2000) Rheological aging and rejuvenation in microgel pastes. *Phys Rev Lett* 85:4819–4822
- Danov K, Aust R, Durst F, Lange U (1995) Influence of the surface viscosity on the hydrodynamic resistance and surface diffusivity of a large Brownian particle. *J Coll Int Sci* 175:36–45
- Debord JD, Lyon LA (2000) Thermoresponsive photonic crystals. *J Phys Chem B* 104:6327–6331
- Destribats M, Lapeyre V, Wolfs M, Sellier E, Leal-Calderon F, Ravaine V, Schmitt V (2011a) Soft microgels as Pickering emulsion stabilisers: role of particle deformability. *Soft Matter* 7:7689–7698
- Destribats M, Lapeyre V, Sellier E, Leal-Calderon F, Schmitt V, Ravaine V (2011b) Water-in-oil emulsions stabilized by water-dispersible poly(N-isopropylacrylamide) microgels: understanding anti-Finkle behavior. *Langmuir* 27:14096–14107
- Destribats M, Lapeyre V, Sellier E, Leal-Calderon F, Ravaine V, Schmitt V (2012) Origin and control of adhesion between emulsion drops stabilized by thermally sensitive soft colloidal particles. *Langmuir* 28:3744–3755
- Erni P (2011) Deformation modes of complex fluid interfaces. *Soft Matter* 7:7586–7600
- Fernandez-Nieves A, Wyss H, Mattson J, Weitz DA (2011) Microgels suspensions: fundamentals and applications. Wiley, Weinheim
- Fischer TM (2004) Comment on “shear viscosity of Langmuir monolayers in the low-density limit”. *Phys Rev Lett* 139603:92
- Fischer TM, Dhar P, Heinig P (2006) The viscous drag of spheres and filaments moving in membranes or monolayers. *J Fluid Mech* 558:451–475
- Geisel K, Isa L, Richtering W (2012) Unraveling the 3D localization and deformation of responsive microgels at oil/water interfaces: a step forward in understanding soft emulsion stabilizers. *Langmuir* 28:15770–15776
- Guillermic RM, Saint-Jalmes A (2013) Dynamics of poly-nipam chains in competition with surfactants at liquid interfaces: from thermoresponsive interfacial rheology to foams. *Soft Matter* 9:1344–1353
- Hashmi SM, Dufresne ER (2009) Mechanical properties of individual microgel particles through the deswelling transition. *Soft Matter* 5:3682–3688

- Jean B (2000) Thermosensitive polymer at air–water interface: interaction with surfactants and thin film stabilization. Universite Pierre et Marie Curie, Dissertation
- Joye JL, Miller CA, Hirasaki GJ (1992) Dimple formation and behaviour during axisymmetrical foam film drainage. *Langmuir* 8:3083–3092
- Joye JL, Miller CA, Hirasaki GJ (1994) Asymmetric drainage in foam films. *Langmuir* 10:3174–3179
- Kralchevsky PA, Denkov ND (2001) Capillary forces and structuring in layers of colloid particles. *Curr Opin Colloid Interface Sci* 6:383–401
- Leal-Calderon F, Schmitt V, Bibette J (2007) Emulsion science. Basic principles. Springer, New York
- Lee LT, Jean B, Menelle A (1999) Effect of temperature on the adsorption of poly(N-isopropylacrylamide) at the air–solution interface. *Langmuir* 15:3267–3272
- Lee MH, Reich DH, Stebe KJ, Leheny RL (2010) Combined passive and active microrheology study of protein-layer formation at an air–water interface. *Langmuir* 26:2650–2658
- Li Z, Ngai T (2010) Stimuli-responsive gel emulsions stabilized by microgel particles. *Colloid Polym Sci* 289:489–496
- Liu T, Seiffert S, Thiele J, Abate AR, Weitz DA, Richtering W (2012) Non-coalescence of oppositely charged droplets in pH-sensitive emulsions. *Proc Nat Acad Sci* 109:384–389
- Lucassen J, Vandente M (1972) Dynamic measurements of dilational properties of a liquid interface. *Chem Eng Sci* 27:1283–1291
- Maestro A, Bonales LJ, Ritacco H, Fischer TM, Rubio RG, Ortega F (2011) Surface rheology: macro- and microrheology of poly(tert-butyl acrylate) monolayers. *Soft Matter* 7:7761–7771
- Mattsson J, Wyss HM, Fernandez-Nieves A, Miyazaki K, Hu Z, Reichman DR, Weitz DA (2009) Soft colloids make strong glasses. *Nature* 462:83–86
- Meng Z, Smith MH, Lyon AL (2009) Temperature-programmed synthesis of micron-sized multi-responsive microgels. *Coll Polym Sci* 287:277–285
- Monteux C, Williams CE, Meunier J, Bergeron V (2004) Adsorption of oppositely charged polyelectrolyte/surfactant complexes at the air/water interface: formation of interfacial gels. *Langmuir* 20: 57–63
- Monteux C, Marliere C, Paris P, Pantoustier N, Sanson N, Perrin P (2010) Poly(N-isopropylacrylamide) microgels at the oil–water interface: interfacial properties as a function of temperature. *Langmuir* 26:13839–13846
- Ortega F, Ritacco H, Rubio R (2010) Interfacial microrheology: particle tracking and related techniques. *Curr Opin Colloid Interface Sci* 15:237–245
- Pickering SU (1907) Emulsions. *J Chem Soc Trans* 91:2001–2021
- Ramsden W (1903) Separation of solids in the surface-layers of solutions and ‘suspensions’ (observations on surface-membranes, bubbles, emulsions, and mechanical coagulation). Preliminary. *Account Proc R Soc* 72:156–164
- Romeo G, Fernandez-Nieves A, Wyss HW, Acierno D, Weitz D (2010) Temperature-controlled transitions between glass, liquid, and gel states in dense p-NIPA suspensions. *Adv Mat* 22:3441–3445
- Sanson N, Rieger J (2010) Synthesis of nanogels/microgels by conventional and controlled radical crosslinking copolymerization. *Polym Chem* 1:965–977
- Saunders BR, Vincent B (1999) Microgel particles as model colloids: theory, properties and applications. *Adv Colloid Interface Sci* 80:1–25
- Senff H, Richtering WB (1999) Temperature sensitive microgel suspensions: colloidal phase behavior and rheology of soft spheres. *J Chem Phys* 111:1705–1711
- Stone HA, Ajdari A (1998) Hydrodynamics of particles embedded in a flat surfactant layer overlying a subphase of finite depth. *J Fluid Mech* 369:151–173
- Subramaniam AB, Mejean C, Abkarian M, Stone HA (2006a) Microstructure, morphology, and lifetime of armored bubbles exposed to surfactants. *Langmuir* 22:5986–5990
- Subramaniam AB, Abkarian M, Mahadevan L, Stone HA (2006b) Mechanics of interfacial composite materials. *Langmuir* 22: 10204–10208
- Tcholakova S, Denkov ND, Lips A (2008) Comparison of solid particles, globular proteins and surfactants as emulsifiers. *Phys Chem Chem Phys* 10:1608–1627
- Tsuji S, Kawaguchi H (2008) Thermosensitive Pickering emulsion stabilized by poly(N-isopropylacrylamide)-carrying particles. *Langmuir* 24:3300–3305
- Verwijlen T, Moldenaers P, Stone HA, Vermant J (2011) Study of the flow field in the magnetic rod interfacial stress rheometer. *Langmuir* 27:9345–9358
- Zhang J, Pelton R (1999a) The dynamic behavior of poly(N-isopropylacrylamide) at the air/water interface. *Colloids Surf A Physicochem Eng Asp* 156:111–122
- Zhang J, Pelton R (1999b) Poly(N-isopropylacrylamide) microgels at the air–water interface. *Langmuir* 15:8032–8036