Soft Matter
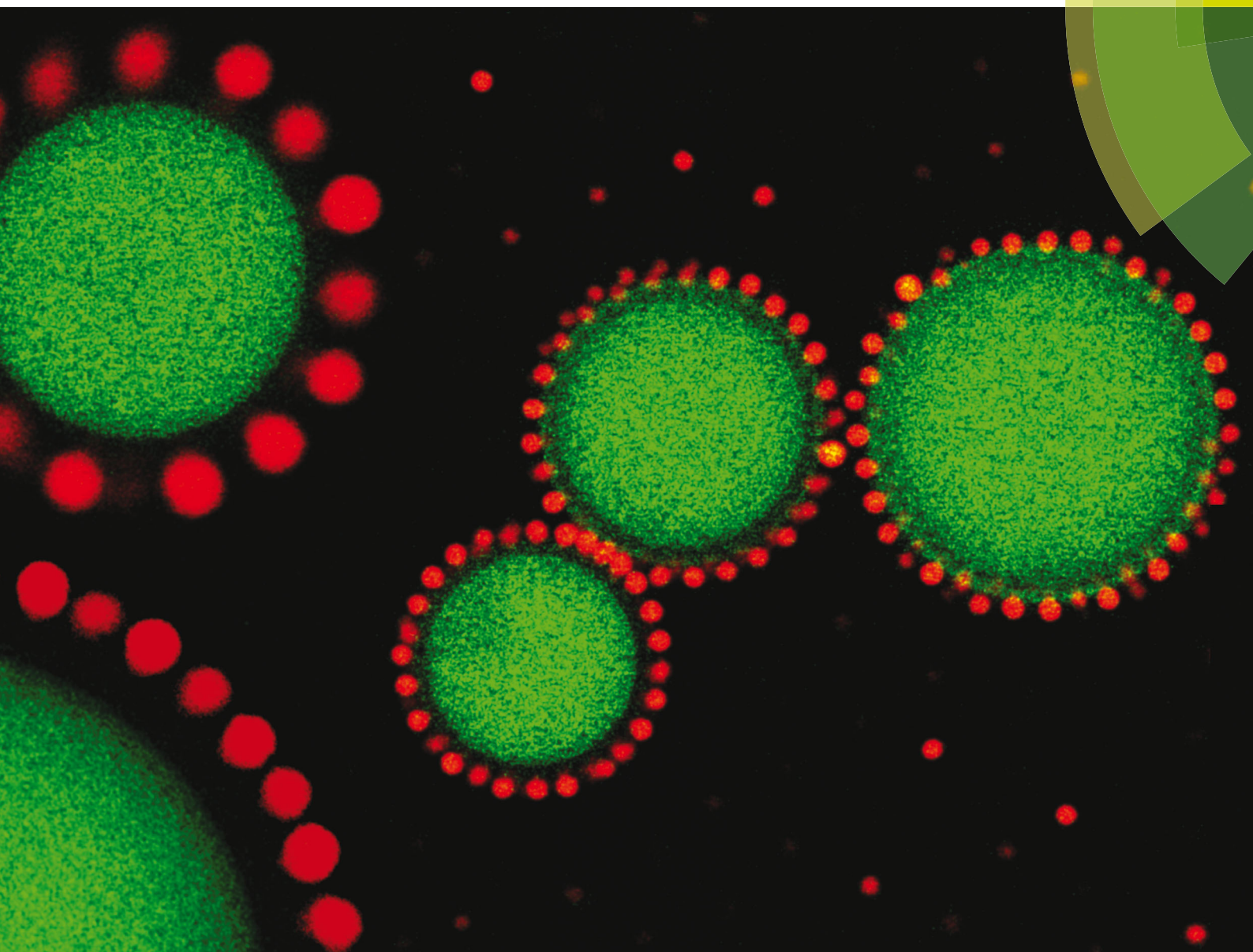
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non-touching colloids

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Soft Matter

Repulsive van der Waals forces enable Pickering emulsions with non-touching colloids†

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Emulsions stabilized by solid particles, called Pickering emulsions, offer promising applications in drug delivery, cosmetics, food science and the manufacturing of porous materials. This potential stems from their high stability against coalescence and 'surfactant-free' nature. Generally, Pickering emulsions require that the solid particles are wetted by both phases and as a result, the adsorption free energy is often large with respect to the thermal energy ($k_{\mathrm{B}}T$). Here we provide the first experimental proof for an alternative scenario: non-touching (effectively non-wetting), charged, particles that are completely immersed in the oil phase through a balance of charge induced attractions and repulsions caused by van der Waals forces. These particles nonetheless stabilize the emulsion. The main advantage of this novel adsorption mechanism is that these particles can easily be detached from the interface simply by adding salt. This not only makes the finding fundamentally of interest, but also enables a triggered de-emulsification and particle recovery, which is useful in fields like enhanced oil recovery, heterogeneous catalysis, and emulsion polymerization.

1 Introduction

Solid particles at liquid interfaces provide important opportunities for self-assembly on liquid interfaces, studies of 2D phase behavior, the formation of porous colloidosomes and stabilization of liquid–liquid interfaces.[1,2] The latter results in so-called Pickering emulsions, and has many applications in industry.[3,4] The 'surfactant-free' nature of these Pickering emulsions prevents adverse effects (irritancy, hemolytic behavior, contamination of environment) associated with conventional emulsions stabilized by surfactants[3,4] which, in addition, are difficult to remove once used. Moreover, the high resistance to coalescence results in an improved shelf life[4,5] and even allows for the formation of stable double emulsions and millimeter-sized droplets.[3]

It is generally accepted that interfacial adsorption requires wetting particles which penetrate the interface, becoming simultaneously wetted by both oil and water.[1,6,7] Such adsorption results in an interfacial free energy gain (V)

$$V = 2\pi R^2 (\gamma_{\mathrm{pw}} - \gamma_{\mathrm{po}})(1 + \cos\theta) - \pi R^2 \gamma_{\mathrm{wo}}(1 - \cos^2\theta) \quad (1)$$

which depends on the size of the particle (radius R), the wetting behavior (contact angle θ) and the surface tensions of the particle–water (γ_{pw}), particle–oil (γ_{po}) and water–oil interface (γ_{wo}).[8,9]

For micron-sized colloids, this adsorption energy is much larger than the thermal energy,[9,10] e.g. approximately $3 \times 10^7 \, k_{\mathrm{B}}T$ for silica colloids ($R = 1 \, \mu\mathrm{m}$, $\theta = 90°$) at a toluene–water interface ($\gamma_{\mathrm{wo}} = 36 \, \mathrm{mN \, m^{-1}}$[9]). As a result, interfacial entrapment is effectively irreversible for these particle sizes,[5,7,10] causing interfaces to crumble upon compression[11] and limiting the collapse of the system to lateral directions when adding salt, as particles do not detach.[11] Particles which are either too hydrophilic or too hydrophobic will recede into the bulk liquids and will not adsorb at the interface, resulting in unstable emulsions.[9] As far as we know, particles adsorbed at oil–water interfaces that do not penetrate the interface have not been conclusively determined experimentally.

Our group recently showed that, surprisingly, charged poly-(methyl-methacrylate) (PMMA) particles dispersed in the oil cyclohexyl bromide (CHB) can be bound to an interface via image charge attraction alone.[12,13] Although not driven by surface tension contributions, this purely attractive force would in principle still result in a wetting state in which particles are immersed in both oil and water. As we show in this paper, an oil soluble salt (tetrabutylammonium bromide, TBAB) can be used to dislodge the particles from the interface. As we will argue, this salt-induced dislodgement cannot be interpreted in terms of the conventional adsorption mechanism in which particles are wetted by both water and oil, because any (partial) wetting of
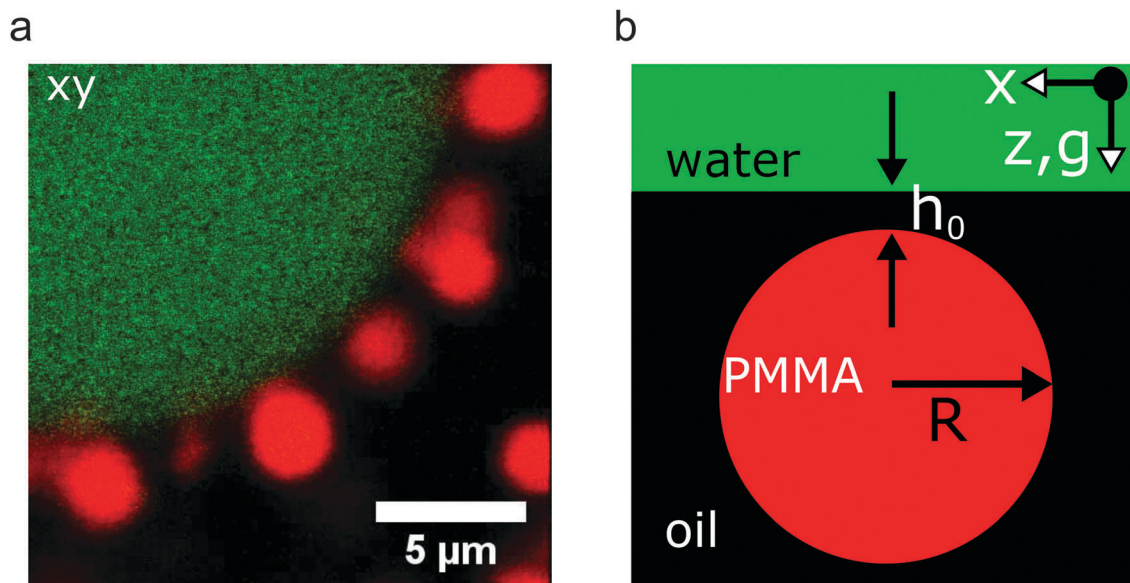
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Fig. 1 Non-touching colloidal particles, fully immersed in the oil phase, but attached to an oil–water interface, as a result of a force balance. (a) PMMA particles (1.4 μm in radius, RITC labeled, red) are completely immersed in the oil phase (CHB–decalin, 32 wt%) while being permanently bound to an aqueous phase (Alexa-488 dyed, green). (b) Schematic illustration of a non-touching particle, immersed in the oil phase and kept at a finite distance ($h_0 \leq 50$ nm) away from the interface as a result of a force balance between image charge attractions and van der Waals repulsions.

the 2.8 μm sized colloids would result in irreversibly trapped colloids. Moreover, we will show explicitly using cryo-focused ion beam-scanning electron microscopy (cryo-FIB-SEM) that these particles do not wet the water phase. We explain this behavior using an alternate and novel adsorption mechanism, namely a force balance between image charge attractions and van der Waals repulsions that keeps the non-touching particles fully immersed in the oil, at a finite distance ($h_0 < 50$ nm) from the interface. While repulsive van der Waals effects have been reported in experimental systems,[14] their repulsive effect on interfacial adsorption was only postulated theoretically for particles at an oil–water interface.[15] As far as we know, no experimental evidence has been described for such a novel adsorption mechanism based on repulsive van der Waals forces; nor was the implication raised that it enables a reversible particle adsorption. Here we provide the first experimental proof for the existence of this novel force balance and show that it enables reversible particle adsorption, and even emulsion breakage of water-in-oil emulsions.

2 Results and discussion

2.1 Salt-induced particle dislodgement

To explore the non-wetting properties of the interfacial colloids, we examined a system similar to the one in ref. 12 and 13. Specifically, we dispersed 2.8 μm PMMA colloids, which contained a charged and a steric stabilizer, in CHB. This dispersion was exposed to water later on, leading to the desired oil–water mixture. Note that CHB is a low-polar medium[16] (dielectric constant $\varepsilon_m = 7.92$[17]) which has several important features. First, the particles can acquire charges spontaneously, in

contrast to more commonly used apolar oils like octane ($\varepsilon_m \sim 2$) that require charge stabilizing surfactants.[18] Second, the ion concentration, and hence the inter-particle interaction, can be varied in CHB (without surfactants): from soft spheres (by deionizing the oil) to almost hard spheres (by addition of an oil soluble salt like tetrabutylammonium bromide, TBAB).[19,20] Meanwhile, the desirable properties of apolar solvents are maintained (immiscibility with water, low conductivities, micrometer-sized double layers).[21] Finally, when necessary, the PMMA particles can be density matched to the oil phase by replacing the pure CHB by a mixture of CHB and *cis*-decalin (27.2 wt%).

In Fig. 1a we show a typical confocal micrograph of an emulsion consisting of fluorescent water droplets, covered with a layer of PMMA particles, in a mixture of deionized CHB and *cis*-decalin. In agreement with ref. 12 and 13, there is no indication of any significant wetting of the particles by the water phase. Moreover, during these experimental studies we did not observe the particles leaving the interface, indicating that they were permanently bound to the interface.

In order to examine the properties of the interfacial colloids in more detail, we designed a setup (Fig. S1A, ESI†) that enabled us to image both the in-plane and out-of-plane interfacial structures. Note that in this quasi 2D system the colloids are confined to a planar monolayer. In Fig. 2a and c we show the in-plane and out-of-plane structures, respectively. From Fig. 2a we can deduce that the particles interact via a long-range repulsive potential resulting in in-plane ordering and, as shown in Fig. 2c, the particles are clearly confined to the oil–water interface. Subsequently, we explored what the effect of salt is on this interfacial geometry. While the addition of 50 mM of salt (NaCl) to the aqueous phase did not change the interfacial
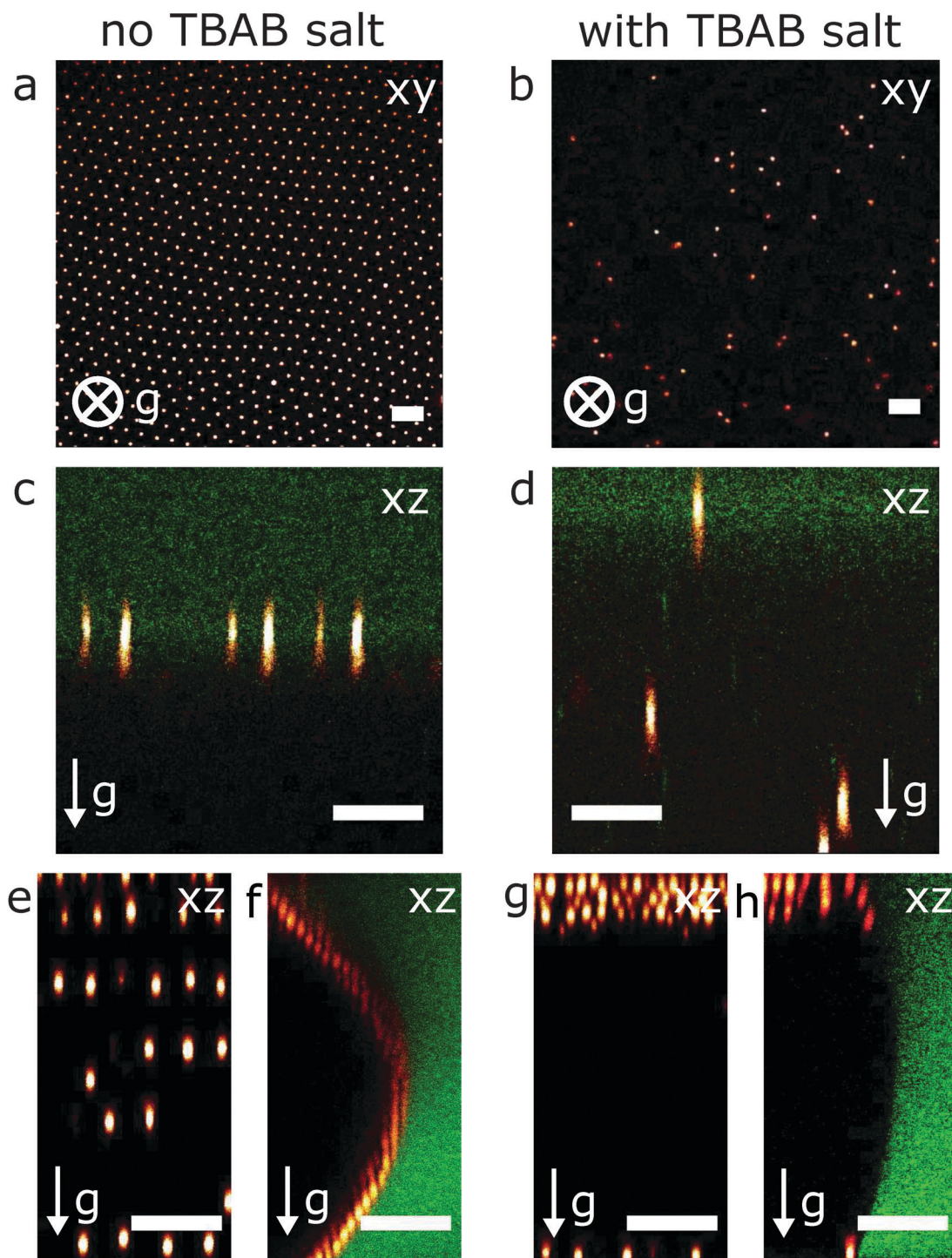
no TBAB salt   with TBAB salt

Fig. 2 Salt-induced particle dislodgement of non-touching particles from an oil–water interface. (a−d) Confocal micrographs recorded in a 2D-setup, before (a and c) and directly after ($t \sim 5$ min) (b and d) adding 150 μM TBAB salt to the oil (CHB) phase. The water phase (depicted in green) was fluorescently labeled with FITC. The interfacial structure of the PMMA colloids (depicted in glow) was imaged in the xy-direction (a and b), and the particle dislodgement from the interface was imaged in the xz-direction (c and d). (e−h) Confocal images of capillaries half filled with the particle−oil dispersion (CHB) and half filled with water (FITC dyed, green), recorded in the xz-direction. Without TBAB salt, PMMA particles (shown in glow) formed extended crystals in bulk oil (e) and were located at the interface (f). In the presence of 300 μM TBAB in the oil phase, the long-range order in the bulk oil collapsed (g) and no particles were located at the interface (h). Images (e−h) were taken ∼1 hour after sample preparation. Scale bars in all images denote 25 μm.

structure (Fig. S2A, B and G, ESI†), the addition of 150 μM of TBAB to the oil phase caused a collapse of the in-plane ordering resulting in a 2D colloidal fluid (Fig. S2C, D and G, ESI†). This is

consistent with the previous observation[12,13] that the inter-particle repulsion was dominated by charges in the oil phase. However, a very surprising observation was made soon after

adding TBAB to the oil ($t < 15$ min): particles dislodged from the interface, resulting in a decrease in surface coverage as the particles moved into the bulk oil phase (Fig. 2b and d). To exclude drift, we also performed control experiments in capillaries (Fig. 2e–h and Fig. S1B, ESI†) and under density matching conditions (Fig. S3A–D, ESI†). Also in these control experiments, particles dislodged from the interface minutes after adding TBAB salt.

While this salt induced particle dislodgement cannot be described in terms of the conventional picture of wetting particles, our findings can be explained by a novel adsorption mechanism, postulated by Oettel[15] where the particles do not wet the water phase. This 'non-touching' adsorption mechanism occurs due to a force balance between an image charge attraction[12,13] and a van der Waals repulsion[15] that keeps the PMMA particles completely immersed in the oil, a finite distance (h_0) away from the interface (Fig. 1b). For this force balance to occur, a number of conditions must be met. Specifically, the image charge attraction occurs when the colloidal particles (with charge Z) are dispersed in an oil medium with a dielectric constant ε_m, and are exposed to a higher dielectric constant (water) phase[12,13] (ESI†). Additionally, the repulsive van der Waals interaction that prevents wetting exists when the dielectric constant of the intervening oil medium (ε_m) is between that of water (ε_w) and PMMA (ε_p) over a wide frequency range

($\varepsilon_w > \varepsilon_m > \varepsilon_p$).[14,22–24] Assuming that these requirements are met, the force balance leads to:[15]

$$h_0 \approx \frac{R}{Z}\sqrt{\frac{2A_{wmp}R}{3k_BT\lambda_B}}. \tag{2}$$

where h_0 is the distance between the particle and the interface, R is the particle radius, A_{wmp} is the Hamaker constant, λ_B is the Bjerrum length, and k_BT is the thermal energy. Due to the use of a low-polar oil medium in our specific case, the static dielectric constants of our system fulfill the above trend ($\varepsilon_w = 80$,[24] $\varepsilon_m = 7.92$,[17] $\varepsilon_p = 2.6$[25]). This, combined with refractive index matching in the visible region, is predicted to result in a negative Hamaker constant of about $-0.3\ k_BT$ (ESI†). Specifically, it follows that $h_0 \sim 10$ nm from the Hamaker constant ($A_{wmp} = -0.3\ k_BT$), the Bjerrum length in CHB ($\lambda_B = 7.1$ nm[21]) and the colloidal charge ($Z = +930e$, see below). Note that screening effects are not included in eqn (2); nor are any Coulomb repulsions between a particle and a like charged interface. However, including these factors in the theory would be required to improve the accuracy.

It clearly follows from eqn (2) that the distance h_0 depends on the charge Z of the colloid. This in turn explains the salt-induced particle dislodgement. First, adding salt reduces the effective charge of the particles via screening (Fig. S4, ESI†). Second, TBAB is known to alter the intrinsic charge Z of the colloid. Specifically,
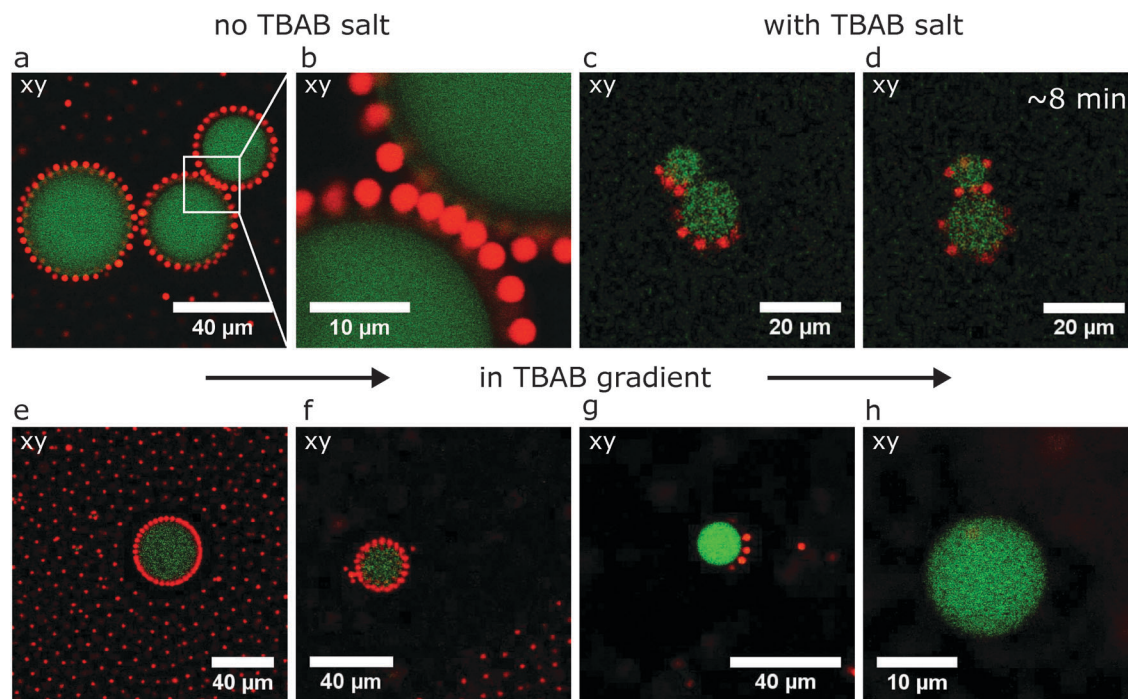

Fig. 3 Water-in-oil emulsions, initially stabilized by non-touching PMMA colloids, became uncoated in the presence of TBAB salt. (a and b) Water droplets (Alexa-488 dyed, green) bridged and stabilized by non-touching PMMA colloids (radius of 1.4 μm, RITC labeled, red). The oil phase was composed of a mixture of CHB and *cis*-decalin (32 wt%). (c and d) Water droplets, only partially coated by PMMA particles due to the presence of TBAB salt, still stabilized by the bridging PMMA colloids. (e–h) Confocal images of the water-in-oil emulsion within a TBAB gradient (maximum TBAB concentration ~220 μM), imaged after about 30 min of equilibration. (e) Far away from the TBAB salt, excess PMMA colloids still showed long-range behavior and water droplets were fully coated by PMMA. Upon increasing TBAB concentrations, first the long-range behavior of the excess particles collapsed (f) after which salt-induced PMMA dislodgement resulted in partially (g) and fully uncoated (h) water droplets. All images were recorded in the *xy*-direction.

while PMMA particles are initially positively charged due to the preferred adsorption of H$^+$ ions,[21] adding TBAB has been found to induce charge reversal.[13,19] This is thought to be due to a larger specific adsorption of bromide ions as compared to specific adsorption of the cation.[13,19] To explore the charge Z of the colloids as a function of the TBAB concentration, we performed electrophoresis experiments in bulk oil, both in pure CHB and in CHB–decalin (27.2 wt%) (Fig. S5, ESI†). The particle charge, without TBAB, was found to be $Z = +930e$ in CHB and $Z = +221e$ in CHB–decalin. For high TBAB concentrations (10–150 μM) negative mobilities were measured, whereas hardly any mobility, indicating a point-of-zero charge, was measured for 1–5 μM TBAB both in CHB and CHB–decalin. The similar value in the different compositions is most likely fortuitous and could originate from the initial lower particle charge and a lower degree of TBAB dissociation in CHB–decalin, compared to pure CHB, caused by the reduction in ε$_m$.[21] Close to the point-of-zero charge, the image charge attractions can become small enough compared to the thermal energy. Consequently, the repulsive forces start to dominate the behavior and thereby induce particle dislodgement from the interface. Note that dislodgement was not observed for positively charged PMMA at a TBAB concentration below the concentration required for charge inversion (*i.e.* at 0.5 μM) (Fig. S3G, ESI†). This suggests that charge inversion plays a key role in particle dislodgement. This is further evidenced by the observation that no significant dislodgement was seen for negatively charged PMMA particles (Fig. S3H–K, ESI†) ($Z = −280e$ in CHB–decalin, 20 wt%[21]), for which TBAB can only screen, but not invert, the particle charge.

2.2 Pickering emulsions with non-touching colloids

Importantly, we found that the salt-induced particle dislodgement occurred not only for macroscopic interfaces in a 2D-setup or in a capillary, but also for microscopic emulsion droplets. Specifically, we examined water-in-oil emulsion droplets, as shown in Fig. 3, and studied the effect of TBAB salt on the PMMA surface coverage. In the absence of TBAB salt, stable emulsions were formed in which PMMA particles stabilized and bridged the interfaces (Fig. 3a and b). Bridging requires contact angles significantly larger than 90° in the case of wetting particles.[26,27] However, in our case of non-contacting adsorption, bridging is completely decoupled from the surface tension of the particles.

Note that the PMMA particles were always present in excess. The particles were initially spaced with distances significantly larger than the particle size because of the long-range repulsions (Fig. 3a and e). As expected, for large TBAB concentrations (up to ~220 μM) such a long-range order collapsed (Fig. 3f), followed by salt-induced PMMA-particle dislodgement, resulting in partially (Fig. 3g) and even fully (Fig. 3h) uncoated water droplets. We found that particle release from smaller droplets, formed upon sonication, was not fully complete. It is possible that the larger interfacial area resulted in a faster leakage of TBAB to the water phase,[13] limiting the salt effect. Note that most droplets

contained a few remaining particles that could still stabilize the droplets by bridging (Fig. 3c and d).

The salt-induced particle dislodgement also enabled a macroscopic de-emulsification when concentrating the dispersed phase in a gravitational field. To concentrate the water droplets and to separate them from any dislodged and excess particles, the density of the oil was tuned (CHB–decalin, 32 wt%) to be between that of water (droplets cream up) and PMMA (excess and dislodged particles sediment). Without TBAB, the compressed emulsion phase was stable, and we observed no strong indications for
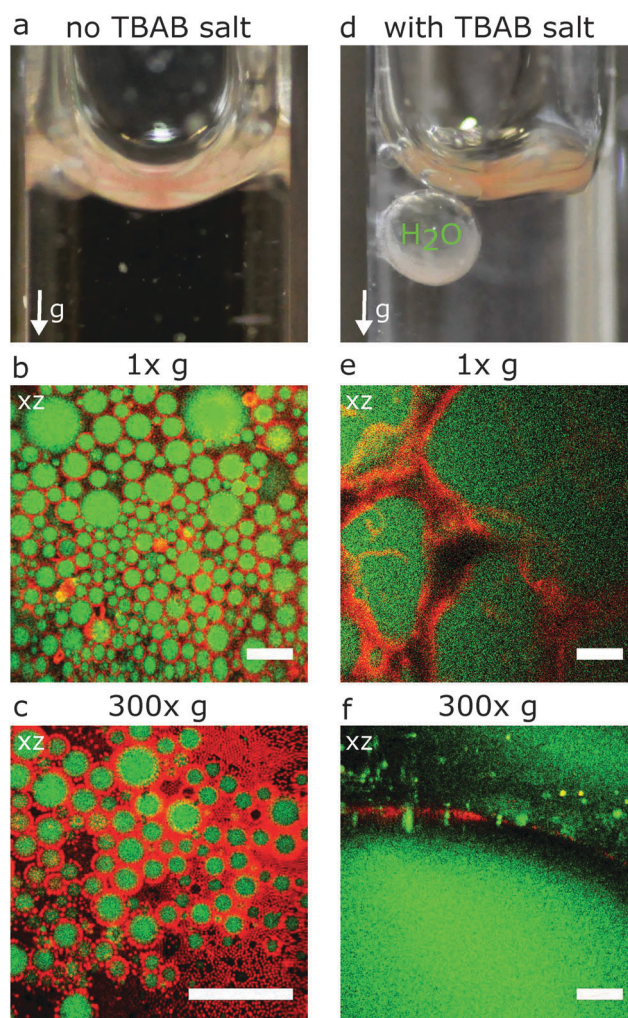

Fig. 4 Emulsion breakage, triggered by the addition of TBAB salt. (a–c) Images of the water-in-oil emulsion without TBAB salt. A compressed emulsion phase (a), stabilized by the non-touching PMMA colloids, was observed in the absence of salt, after centrifugation. Confocal micrographs of this compressed phase before centrifugation (b) and after centrifugation (c) reveal that no (significant) coalescence occurred under these conditions. The water phase (green) was dyed with Alexa-488, and the colloids (red) with RITC. (d–f) Images of the water-in-oil emulsion, with approximately 90 μM TBAB salt in the oil phase. After centrifugation, emulsion breakage was achieved (d) due to the salt-induced particle dislodgement. Already before centrifugation (e) the increase in the droplet size and the irregular droplet shape indicated droplet coalescence. This was enhanced by centrifugation (f), resulting in macroscopic phase separation. Scale bars in all images denote 100 μm.

coalescence before (Fig. 4b) and after centrifugation at 300g (Fig. 4a and c). This is in strong contrast to the system containing 90 μM of TBAB, in which we observed larger, irregularly shaped droplets before centrifugation (Fig. 4e) and macroscopic phase separation after centrifugation at 300g (Fig. 4d and f). In some

attempts, the system became quenched into a state similar to Fig. 4e, even after centrifugation. We speculate that TBAB leakage into the water-rich phase (now concentrated) limited the effect of salt. Moreover, coalescence between partially uncoated droplets will make the coalescence process self-limiting. However, the
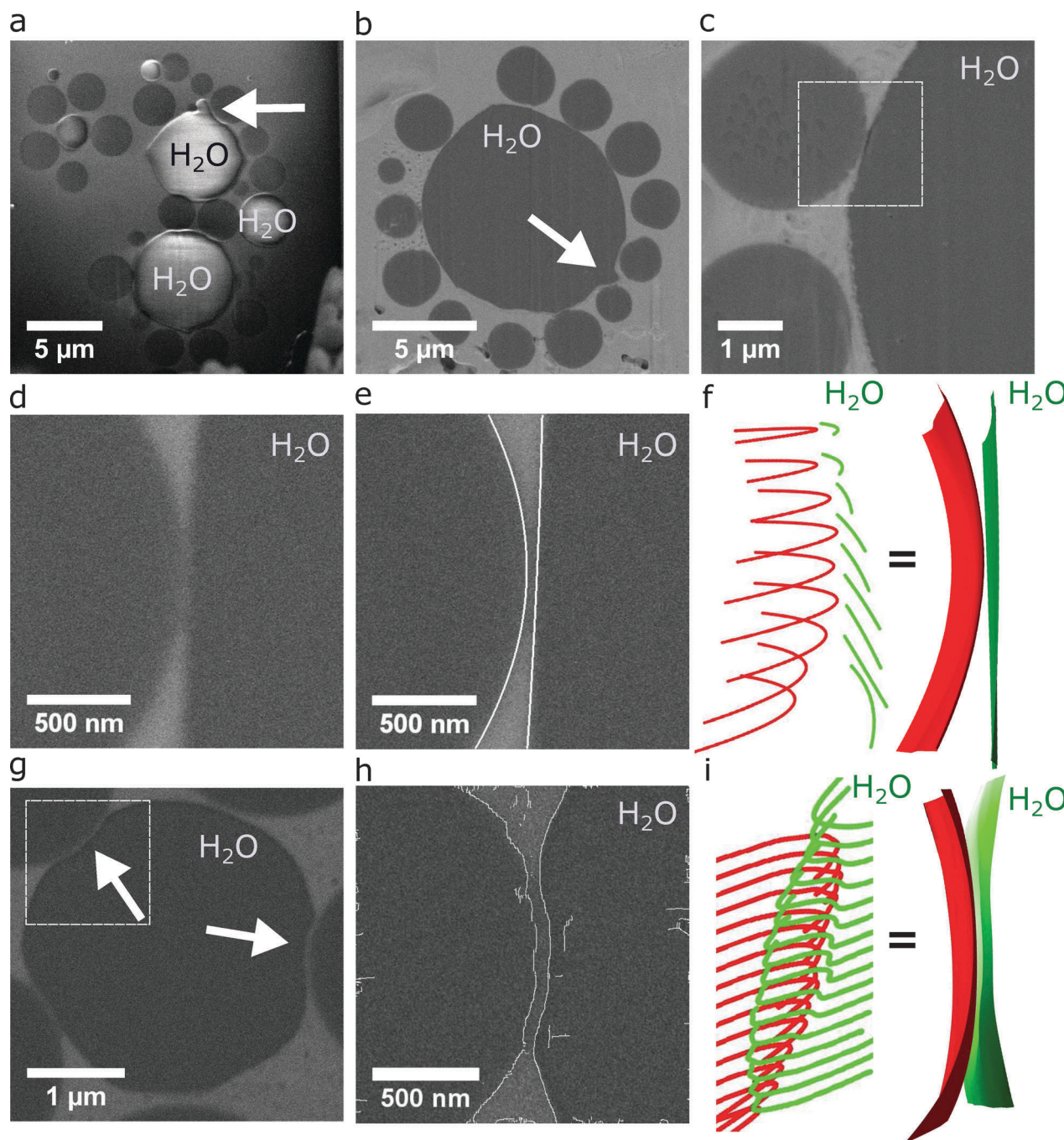

Fig. 5 Cryo-focused ion beam-scanning electron microscopy (cryo-FIB-SEM) images and 3D reconstructions of the non-touching PMMA colloids at a CHB–water interface. (a) A FIB milled cross-section through water droplets covered with non-touching PMMA colloids. Water droplets charged up in secondary electron imaging mode, allowing direct discrimination between the droplets and the PMMA particles. (b and c) No breaching of the oil–water interface by the PMMA particles was observed, images recorded in back scattering mode. (d–i) FIB-SEM tomography series were used to image the intervening oil layer between the PMMA particles and the interface. Images (d–f) and (h and i) are close-ups of the regions indicated with the white squares in (c) and (g), respectively. Surfaces were located using either a fit with a polynomial function (e) or an edge detection method (h), and resulted in the 3D reconstructions shown in (f) and (i), respectively.

ability of the non-touching Pickering emulsion to respond to an external trigger is an important requirement for potential applications, enabling liquid-phase extraction and particle recovery in fields like enhanced oil recovery (EOR),[3] heterogeneous catalysis, and emulsion polymerization.[4] Hence, non-touching Pickering emulsions can form an interesting alternative to the stimuli-responsive Pickering emulsions which have, in recent years, received a considerable amount of attention.[4]

2.3 Imaging the non-touching behavior

Finally, to further confirm that the PMMA colloids do not touch the water phase (Fig. 1b), we imaged the system using tomography. Given the theoretical $h_0 \sim$ 10–30 nm distance, methods like X-ray microscopy (spatial resolution 43 nm[28]) and confocal microscopy (spatial resolution 30 nm[28]) are excluded based on their resolution. Another state-of-the-art technique is based on freeze-fracture cryo-scanning electron microscopy (cryo-SEM), but requires particles that are partially immersed in both phases.[29] We therefore adapted this novel *in situ* method, adding Focussed-Ion-Beam (cryo-FIB-SEM) milling,[30] resulting in a FIB-SEM tomography series through an emulsion droplet. Although images were recorded with a pixel size of 2.5 nm, the actual resolving power is lower because of the interaction volume of the electrons.[30] Typical SEM images are shown in Fig. 5a–c, which show no particles breaching the oil–water interface. From the SEM images, we made two 3D reconstructions of the particle surfaces, which were initially identified in 2D. One method for the 2D surface identification was based on polynomial fits (Fig. 5d–f) and another one on an edge detection algorithm based on intensity gradients (Fig. 5g–i) (ESI†, and Fig. S6 and S7). The processed FIB-SEM tomography data showed that the particles were non-touching with a distance h_0 of less than 60 nm, in accordance with the theoretical prediction (eqn (2)).[15] The interfacial deformations (white arrows in Fig. 5a, b and g) indicate the existence of both attractive forces (leading to protrusions) and repulsive forces (leading to indentations). Such deformations have also been predicted by theory,[15] however for much smaller length scales (<1 Å). The deformations are possibly related to manufacturing artifacts, including, for example, shear. Note that a non-zero h_0 is not in contradiction with the previously reported wetting angle of PMMA at a water–decalin interface in ref. 28, as this system does not meet the requirements, *i.e.* for pure decalin ε_m = 2.176.[25]

3 Conclusions

In conclusion, we have shown that 2.8 μm sized PMMA particles, which were initially permanently trapped at the oil–water interface, dislodge spontaneously after adding TBAB, an oil soluble salt. Our experimental observations could not be interpreted in terms of wetting particles, providing evidence for the existence of a force balance between image charge attractions[12,13] and van der Waals repulsions[15] that keeps the particles at a finite distance ($h_0 \leq$ 50 nm) from the interface. Dislodgement of the non-touching particles is driven by salt-induced particle charge inversion.

Specifically, particles are dislodged by their thermal energy and the repulsive forces when their charge, and hence the image charge attraction, becomes sufficiently small. Additional evidence for the non-touching behavior was obtained from high-resolution, 3D reconstructions of the particle surfaces using cryo-FIB-SEM tomography. Finally, we demonstrated that non-touching Pickering emulsions can be formed, enabling salt-induced de-emulsification for liquid-phase extraction, which is an important requirement for applications.[4] Overall, our study implies that the classical argument that wetting particles are required to form stable emulsions[9] is not always valid.

It should be noted that while we have only examined a specific realization of the non-touching adsorption mechanism proposed by Oettel, many other systems should be able to fulfill the requirements. Specifically, the only requirements include: (1) the system contains two immiscible liquids, A and B, with $\varepsilon_A > \varepsilon_B$, (2) particles are dispersed in phase B which is not too apolar ($\varepsilon_B > 4$), and (3) the overall trend in dielectric constants meets the requirement: $\varepsilon_A > \varepsilon_B > \varepsilon_{particle}$. Potential candidates include colloidal particles that are stabilized by polymer layers such as the PMMA used in this study or dense alkane layers. For these materials, the dielectric constants are often lower than a range of slightly polar solvents like 1,2-dichloroethane or pentanol that do not mix with water. Moreover, in these systems particle dislodgement can be induced by adsorption of an ionic species of opposite charge to the particles. In conclusion, we expect this to be an important new avenue for stabilizing reversible emulsions.

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