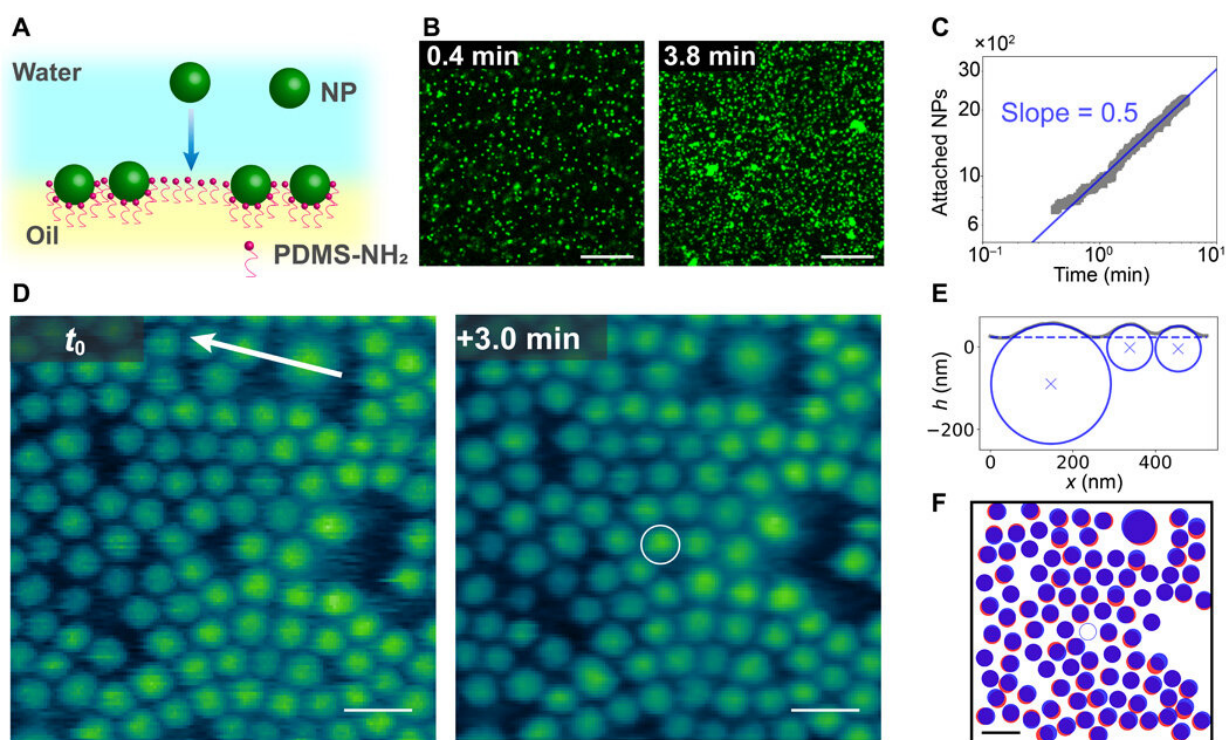


Nanoparticle jamming at the water-oil interface

December 4 2020, by Thamarasee Jeewandara



Attachment of NPs to sparsely populated water-oil interface. (A) Schematic diagram showing the attachment of a NP to the pristine water-oil interface. (B) Confocal microscopy images showing the attachment of 500-nm NPs to the water-oil interface. (C) Number of attached 500-nm NPs as a function of time, where the slope follows at power law of 0.5. (D) In situ AFM image of 100- and 300-nm NPs assembled at the water-oil interface at different times: t_0 and $t_0 + 3.0$ min, with a circle highlighting an attachment event. (E) Section data along arrow in (D) showing fit for NP diameter size and position in the interface. (F) Positions of the assembled NPs at different times: t_0 (red) and $t_0 + 3.0$ min (blue), where the open blue circle represents the newly attached NP. Scale bars,

20 μm (B) and 200 nm (D and F). Credit: Science Advances, doi: 10.1126/sciadv.abb8675

The online cover of *Science Advances* this week features the assembly of nanoparticle surfactants at a solid-liquid interface using advanced microscopy techniques such as laser scanning confocal microscopy and atomic force microscopy. Materials scientists had explored the assembly of solids at a liquid interface for decades to understand ore (a complex and stable chemical compound) purification, emulsion and encapsulation processes. In a new report, Yu Chai and a research team at the Lawrence Berkeley National Laboratory, University of California Berkeley, the Hong Kong Polytechnic University and the Tohoku University, in the U.S., China and Japan, showed how electrostatic interactions between nanoparticles and ligands formed nanoparticle surfactants at water-oil interfaces. The resulting 'jammed' structures produced a solid-like layer. When the area density of the nanoparticle surfactants increased at the interface, further attachment required cooperative displacement of previously assembled nanoparticle surfactants. The high space-time resolution of their observations revealed the complex mechanism of attachment and the nature of nanoparticle assembly.

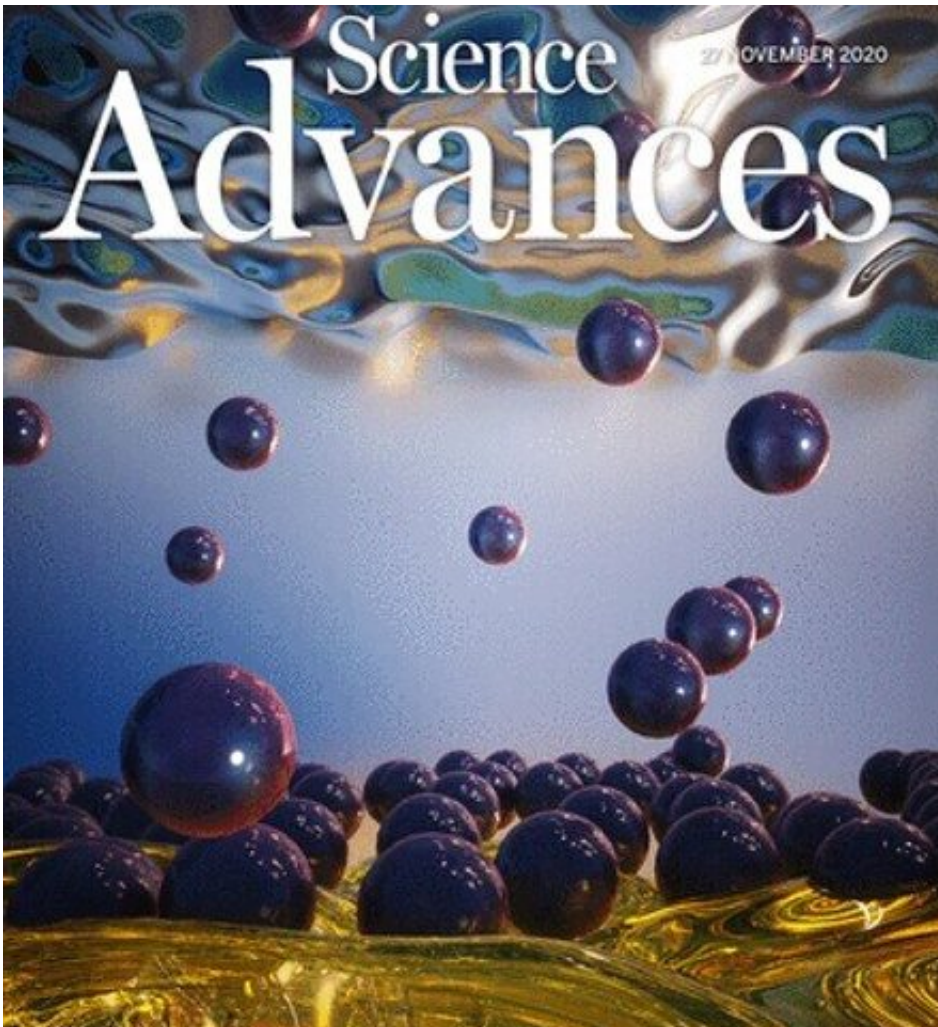
Observing solids at liquid interfaces

In this work, Chai et al. used [atomic force microscopy](#) (AFM) coupled with [laser scanning confocal microscopy](#) (LSCM) to obtain remarkable details of solids at liquid interfaces to provide insight into the nanoparticle jamming phenomena. Materials researchers in applied engineering are interested on the assembly of solids at liquid interfaces for applications such as [ore purification](#), [emulsion](#) and [encapsulation](#) based on [interfacial segregation](#). When the particle size decreases, the binding energy of the particle at the [interface](#) can decrease, resulting in

the adsorption and desorption of [nanoparticles](#). If nanoparticles that are soluble in one liquid interacts with end-functionalized ligands in a second immiscible liquid, researchers can increase the binding energy of nanoparticles to the interface to form [nanoparticle surfactants](#). The very high binding energy of adsorption can drive the system to a non-equilibrium state.

Regulating the interfacial tension

The team characterized the interface between two immiscible liquids by calculating the [interfacial tension](#) (γ). When negatively charged nanoparticles were dispersed in the aqueous phase, the interfacial tension was not affected because the nanoparticles did not assemble at the interface due to the inherently negative charge at the water-oil interface. However, polymeric surfactants such as [amine-terminated polydimethylsiloxane](#) (PDMS-NH₂), dissolved in silicone oil and assembled into a monolayer at the interface to reduce the interfacial tension. The magnitude of reduced interfacial tension depended on the concentration of PDMS-NH₂ and [molecular weight of the PDMS chain](#).



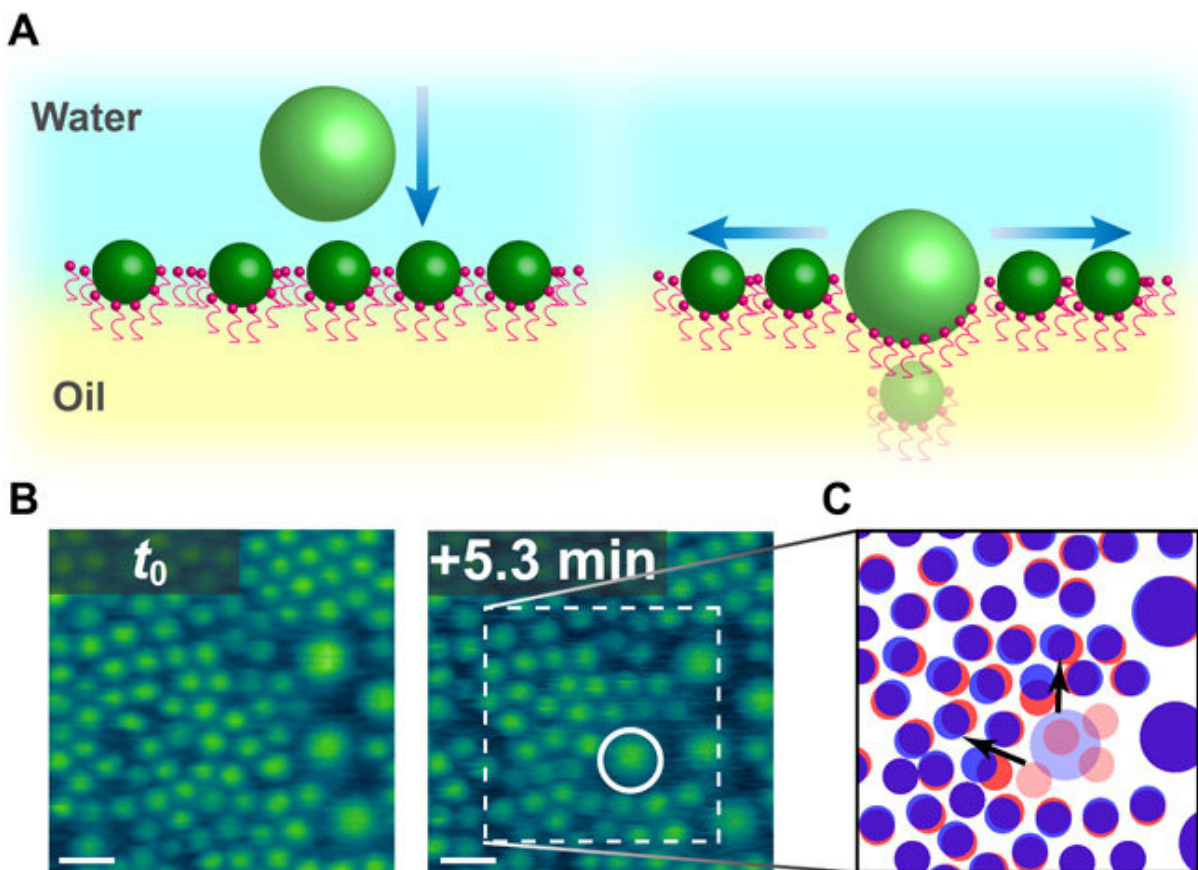
Online cover – nanoparticle (NP) jamming. Nanoparticle surfactants attach to oil-water interfaces. Credit: Science Advances, doi: 10.1126/sciadv.abb8675

The team noted an attachment process, where carboxylic acid-functionalized nanoparticles diffused to the interface and interacted with cationic polymeric surfactants (PDMS-NH₃⁺) to form nanoparticle surfactants. By labeling the nanoparticles with fluorescent markers, Chai et al. examined the adsorption process under low resolution using laser scanning [confocal microscopy](#). The adsorption kinetics complied with [Fick's Law](#); i.e., going from a high-concentration area to a low-concentration area proportional to the concentration gradient, with

notable Fickian diffusion control of attachment. The results, therefore, supported diffusion-controlled adsorption to the interface, where the energy barrier to attachment was lower than the thermal energy of the system. The nanoparticles then remained at the interface after contacting the interface.

Using atomic force microscopy to distinguish nanoparticles

When more nanoparticles assembled at the water-oil interface, the laser scanning confocal [microscopy](#) technique could not effectively distinguish them individually—since the minimal separation distance exceeded the resolution of the instrument. The team therefore used atomic force microscopy, to directly visualize the attachment of nanoparticles on the water-oil interface in space-time. They then determined the diameters and position of nanoparticles relative to the interface and showed the binding energy of nanoparticles to the interface as a function of particle size and surface tension, at the oil-water interface. Based on the behavior of nanoparticles at the water-oil interface, Chai et al noted how the increasing charge density more strongly influenced the attachment of the surfactant to the nanoparticle, increasing its [surface energy](#) and driving the particles further into the oil phase. The movement dynamics of nanoparticles slowed down at the interface due to the more densely packed arrangement.

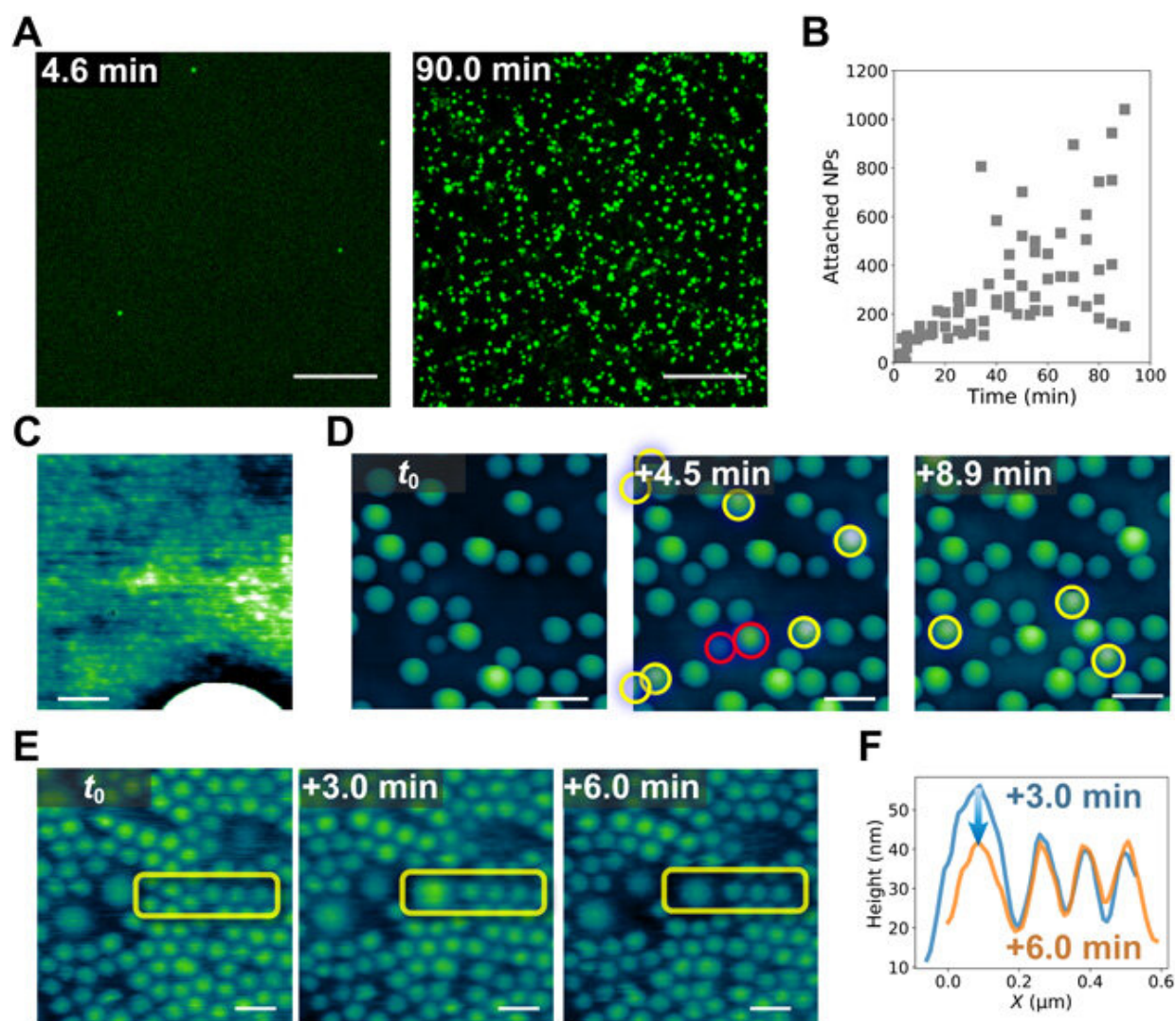


Attachment of 300-nm NPs to thoroughly populated water-oil interface. (A) Schematic diagram of the attachment of a 300-nm NP where previous NPs are displaced laterally and vertically. (B) Time-dependent in situ AFM showing the attachment of 300-nm NP to the water-oil interface, where the white circle indicates the newly adsorbed NP. (C) NPS positions at t_0 (red) and $t_0 + 5.3$ min (blue), where the faded blue dot represents the newly attached NP and the faded red dots represent NPs that cannot be located by AFM after attachment of the newly attached NP. Scale bars, 200 nm. Credit: Science Advances, doi: 10.1126/sciadv.abb8675

Observing nanoparticle rearrangement

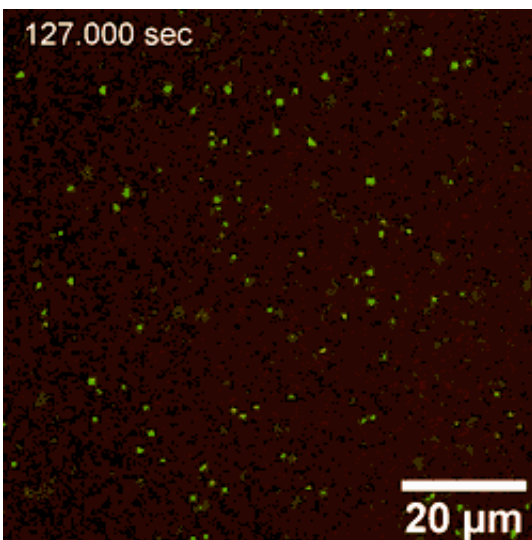
When the local area density of nanoparticles at the interface increased,

there was insufficient space to accommodate the entry of new nanoparticles; therefore, the assembly rearranged on its own. Chai et al. noted this rearrangement using atomic force microscopy, although they did not quantify the observed fluctuations. They observed cooperative structural changes of assembled nanoparticles at the interface to accommodate the attachment of additional particles. Interestingly, several nanoparticles were not detectable, potentially trapped beneath larger nanoparticles added to the system; however, the team could not observe this phenomenon using atomic force microscopy alone. Chai et al. therefore reintegrated laser scanning confocal microscopy (LSCM) to the setup to provide insight to the addition of excess nanoparticles to the already dense assemblies.



Attachment of NPs to the water-oil interface with assembled NPs. (A) LSCM images showing the attachment of 500-nm NPs to the water-oil interface with assembled 70-nm NPs. (B) Number of 500-nm NPs in the field of view as a function of time. (C) In situ AFM images show the coassembly of 30- and 300-nm NPs at the water-oil interface. (D) In situ AFM images showing the attachment of 300-nm NPs to the water-oil interface with assembled 30- and 300-nm NPs. (E) Time-dependent in situ AFM images showing the attachment of a 300-nm NP to the water-oil interface covered by 100- and 300-nm NPs, where the yellow rectangles indicate the affected areas. (F) Line profiles of the region shown in (E) indicate the relaxation of the newly attached 300-nm NP. Scale bars, 20 μm (A), 100 nm (C), 500 nm (D), and 200 nm (E). Credit: Science Advances, doi: 10.1126/sciadv.abb8675

The scientists further incorporated LSCM (laser scanning confocal microscopy) experiments to investigate the mixed dispersion of nanoparticles of varying size to probe their dynamic co-assembly. While large and small particles co-assembled at the interface, only the large nanoparticles could be clearly resolved. Interestingly, the team noted many dark areas in the form of cracks, likely from the contact between water and oil phases in the setup. The crack formation further exposed new interfacial areas, which eventually self-healed [as an important trademark of structured liquids](#) to maintain their integrity in general.



The LSCM video shows the coassembly of 70-nm (red) and 500 nm (green) nanoparticles (NPs) and the self-healing process. Credit: Science Advances, doi: 10.1126/sciadv.abb8675

Outlook on nanoparticle jamming

In this way, Yu Chai and colleagues investigated the assembly of

nanoparticles at the water-oil interface and examined the factors controlling the process of adsorption. By interchangeably using AFM ([atomic force microscopy](#)) and LSCM (laser scanning confocal microscopy), they noted structural changes occurring at the early stage of nanoparticle attachment to the interface, including diffusion-controlled processes. The attachment process was reaction-controlled, where the existing assembly posed an electrostatic barrier to additional nanoparticles approaching the interface; thereby coordinating their rearrangement to accommodate the attachment of new nanoparticles. Using advanced microscopy techniques, the team detailed the attachment process under diverse conditions at high resolution to provide insight to adsorption and jamming in order to aid the design and fabrication of responsive assemblies.

More information: Chai Y. et al. Direct observation of nanoparticle-surfactant assembly and jamming at the water-oil interface, *Science Advances*, 10.1126/sciadv.abb8675

Crossley S. et al. Solid nanoparticles that catalyze biofuel upgrade reactions at the water/oil interface, *Science*, 10.1126/science.1180769

Kaz D. et al. Physical aging of the contact line on colloidal particles at liquid interfaces. *Nature Materials*, doi.org/10.1038/nmat3190

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