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13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.
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14. ABSTRACT
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15. SUBJECT TERMS
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16. SECURITY CLASSIFICATION OF:	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Thomas Russell
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU	19b. TELEPHONE NUMBER 413-658-8380

# RPPR Final Report

## as of 09-Apr-2020

Agency Code:

Proposal Number: 66055MS

Agreement Number: W911NF-17-1-0003

### INVESTIGATOR(S):

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**Report Date:** 14-Mar-2020

Date Received: 09-Apr-2020

**Final Report** for Period Beginning 15-Dec-2016 and Ending 14-Feb-2020

**Title:** Liquid Tubules by the Self-Assembly of Self-Regulating NP Surfactants - Area 9.1 Materials by Design

**Begin Performance Period:** 15-Dec-2016

**End Performance Period:** 14-Feb-2020

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**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

**STEM Degrees:** 1

**STEM Participants:** 2

**Major Goals:** Dendrimer-based nanoparticles, DNPs, will assemble at the interface between two immiscible fluids, forming a disordered monolayer at the interface that will stabilize spherical droplets of one fluid in another and, also, prevent coalescence. Due to the inherent negative charge of the oil/water interface, DNPs dispersed in an aqueous medium, are not interfacially active. However, with polymers, having a complementary functionality dissolved in the oil phase, the interactions between the NPs and the functionalized polymers at the interface result in the formation of DNP-surfactants at the interface between the two fluids, i.e. by appending a well-defined number of polymer ligands that are hydrophobic to the NPs that are hydrophilic, DNP-surfactants are formed increasing the energy holding each NP-surfactant at the interface. When the fluids are deformed, more DNP-surfactants will form at the interface and, when relaxed, the DNP-surfactants jam at the interface, locking in non-spherical shapes. Unlike hard NPs, the DNP are soft, and the nature of the jamming and potential deformation of the DNPs when compressed is unknown and will be investigated. We will take advantage of jamming behavior to generate tubules of one liquid in another by Electrospinning, producing droplets of one fluid in another with a microfluidic device, or by jetting one fluid in a second affording a platform for the fabrication of all-liquid separations media or encapsulants that we will gear towards "soldier-in-the-field" applications. Being all fluid, the devices are resistant to shock and, if disrupted, the DNP-surfactant assemblies will self-heal, enhancing the integrity and longevity of devices.

Alternative strategies will be used, in particular using polyelectrolyte-based materials to effect the all liquids constructs.

**Accomplishments:** Vapor-Induced Motion of Two Pure Liquid Droplets

Inducing and controlling the movement of droplets in a preset manner on a solid substrate has important ramifications for technical applications, ranging from coatings to microfluidics to heat transfer devices, but also can aid in our understanding of phenomena observed in nature where the motion of water droplets, for example, is critical for survival. Usually droplet motion can be achieved by an imbalance in the interfacial tension of the droplet with the substrate and the surface energies of the droplet and the substrate. This can be triggered by gradients in temperature or composition of a liquid surface, which is well-known as the Marangoni effect<sup>4</sup>, for example, the "tears of wine" phenomenon observed in a wine glass. Variations in the surface tension of a solid substrate, e.g. a surface with a gradient in the surface energy or wettability, that give rise to a hysteresis in the contact angle, can also induce such a directed motion. Here, liquid droplets that have a surface energy lower than that of the substrate, will move towards the area with higher surface energy to reduce the free energy of the system. High energy substrates were achieved by cleaning glass microscope slide in a piranha solution (a 30% mixture of H<sub>2</sub>O<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub>). After removal from the acid bath, the substrates were thoroughly washed in de-ionized water and then dried under a nitrogen gas flow. The substrates were used immediately after cleaning or stored in an inert

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atmosphere until use. All experiments were performed in a controlled humidity chamber at room temperature. n-hexane is used as the model droplet in this study, due to its vapor pressure and, importantly, it can form stable, nearly flat droplets on a high energy substrate, with a contact angle of 6.5°. This conforms to the model conditions used in the theoretical model with  $R \gg H$ , where R and H are the radius and heights of the droplet. PG and water are not suitable candidates because they spread completely when deposited on the substrate, where the spreading parameter  $S = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL}) > 0$ , where  $\gamma_{SV}$ ,  $\gamma_{LV}$ , and  $\gamma_{SL}$  are the interfacial tensions between solid/ vapor, liquid/ vapor, and solid/liquid. In this case, no gradient of in the evaporation rate is formed across the droplets and, as a result, no droplet motion is observed.

Figure 1 shows the motions of two 5  $\mu$ L n-hexane droplets on the substrate. No movement was observed when a single droplet is placed on the substrate. However, in the presence of another droplet of the same liquid in close proximity (<5mm apart), by long-range interactions, the two droplets move toward each other induced by the evaporation of the n-hexane, and then coalescence into one droplet. In these and other experiments we prove that, on a high energy surface that remains uniform, the motion of two pure liquid droplets can be induced by a gradient in the evaporation rate. The droplets always attract each other, moving from the high evaporation side to the low evaporation side, to reduce energy dissipation. By varying the volume of the droplets or the distance between droplets, the motion of the droplets can be effectively controlled.

**Water-in-Water Compartmentalization:** A hallmark of biological systems is the ability to compartmentalize and coordinate system functions, which has been difficult to reproduce even in the most sophisticated synthetic mimics. Here, we demonstrate a strategy to fabricate 3D compartmentalized water-in-water constructs, stabilized by an elastic polyanion–polycation coacervate membrane. Using a 3D printer, the length, shape, and diameter of all-aqueous tubules can be controlled. We found and capitalized on a directional diffusion of ionic species across the membrane dictated by the preferential affinity of the polyelectrolyte in the oppositely charged phase. In conjunction with microfluidic techniques, continuous selective diffusion and compartmentalized reactions were shown in such all-aqueous systems. A layer-by-layer strategy is also used to tune the membrane's mechanical properties and to functionalize them. A new platform is demonstrated for developing and manipulating continuous separations media or compartmentalized reactive systems that function independently, or can be coupled by selective diffusion across the membrane (Figure 2).

These all-aqueous printed structures provide a unique platform for the study and fabrication of more controlled, complex and even compartmentalized all-aqueous systems. We have developed systems where two parallel, orthogonal chemical reactions occur in separate compartments defined by the coacervate membrane where the products of one reaction selectively diffuse across the coacervate membrane to participate in a reaction in the second compartment. We have demonstrated different strategies by which the all-liquid constructs can be realized in addition to the 3D printing.

**Hanging Droplets:** Usually objects sink in the less dense liquids. Water-walking anthropods and biomimetic water-walking robots are some exceptions to this rule but there is still an open question. Does the additional force to support the dense object on the interface have its origins in the buoyant force based on the generalized Archimedean principle or does it arise from the surface tension acting on the body? By hanging a coacervate-encased droplet of a denser aqueous dextran solution from the surface of an aqueous solution of poly(ethylene glycol) (PEG) we find support for the surface tension argument and exclude a modified Archimedean principle. Supported and held by a polyelectrolyte coacervates formed at the interface between two aqueous phases, a droplet containing the denser dextran solution is arrested at the surface of the aqueous PEG solution and hangs on the water/air or water/oil interface where the displaced meniscus, based on the generalized Archimedean principle, is not large enough to balance the gravitational force acting on the droplet. The magnitude of the surface tension acting on the droplet and shapes of the droplets are varied by changing the height from where the droplet is released, the falling height, droplet size, the densities of two aqueous solutions, and the concentrations of polyelectrolytes. We also exploit this phenomenon in complex systems, including horizontal droplet stacking and vertical droplet stacking, to fabricate structured liquids or droplets with heterogenous surface. Such a surface-hanging heterogenous droplet is straightforward to generate by droplet printing, so we expect that the outlined principles for hanging droplets will be of interest both for fundamental exploration in water-floating and for applications in functional micro-reactors, micro-motors and biomimetic micro-robots.

Supported and held by polyelectrolyte coacervates formed at the contacting interface of two aqueous phases, falling droplets will stop sinking into the less dense bulk solution and hang on the water/air interface or water/oil interface where the displaced meniscus based on the generalized Archimedes' principle is not large enough to balance gravitational forces acting on the droplet and thus the surface tension is supposed to be the only additional source to support it (Figure 3). We demonstrate that the magnitude of the surface tension on the droplet and corresponding morphologies are controllable by varying the falling height, droplet size, densities of two aqueous solutions and concentrations of polyelectrolytes. We also exploit this phenomenon in complex systems, including horizontal droplet stacking and vertical droplet stacking, to fabricate structured liquids or droplets with

## RPPR Final Report as of 09-Apr-2020

heterogenous surface. Such a surface-hanging heterogenous droplet is straightforward to generate by droplet printing, so we expect that the outlined principles for hanging droplets will be of interest both for fundamental exploration in water-floating and for applications in functional micro-reactors

**Training Opportunities:** During the course of the proposed studies, students and post-doctoral fellows were engaged in the research during which they learned of the interfacial behavior of materials and the use of materials, like Janus copolymers and polyelectrolytes, to structure liquids. In addition, we engaged researchers at the University of Hong Kong and the University of Muenster in the research, providing the researcher supported by the award the opportunity to expand international contacts.

**Results Dissemination:** The results froths research were published in the open literature, as delineated in the report. The results were also presented at the AmericanPhysical Society the American Chemical Society and Materials Research Society meetings over the period of the award.

**Honors and Awards:** Russell was elected into the national Academy of Inventors in 2018 and was awarded the Shull Prize of the Neutron Scattering Society if America in 2020.

### Protocol Activity Status:

**Technology Transfer:** Nothing to Report

### PARTICIPANTS:

**Participant Type:** Postdoctoral (scholar, fellow or other postdoctoral position)

**Participant:** Ganhua Xie

**Person Months Worked:** 12.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Yufeng Jiang

**Person Months Worked:** 9.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Zhan Chen

**Person Months Worked:** 8.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

### ARTICLES:

## RPPR Final Report as of 09-Apr-2020

**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published  
**Journal:** ACS Applied Materials & Interfaces  
Publication Identifier Type: DOI      Publication Identifier: 10.1021/acsami.7b10981  
Volume: 9      Issue: 38      First Page #: 33327  
Date Submitted: 7/18/18 12:00AM      Date Published: 9/1/17 7:00AM  
Publication Location:

**Article Title:** Interfacial Assembly and Jamming Behavior of Polymeric Janus Particles at Liquid Interfaces

**Authors:** Yufeng Jiang, Tina I. Löbbling, Caili Huang, Zhiwei Sun, Axel H. E. Müller, Thomas P. Russell

**Keywords:** Janus nanoparticles, interfacial tension, interfacial assembly, jamming, wrinkling

**Abstract:** The self-assembly and interfacial jamming of spherical Janus nanoparticles (JNPs) at the water/oil interface were investigated. Polymeric JNPs, made by cross-linking polystyrene block - polybutadiene-block -poly (methyl methacrylate) (PS-PBPMMA), with a high interfacial activity assemble at the water/oil interface. During the self-assembly at the interface, the interfacial energy was reduced and a dynamic interlayer was observed that is responsive to the pH of the aqueous phase. Unlike hard particles, the JNPs are composed of polymer chains that can spread at the liquid/liquid interface to maximize coverage at relatively low areal densities. In a pendant drop geometry, the interfacial area of a water droplet in oil was significantly decreased and the JNPs were forced to pack more closely. Entangling of the polymer chains causes the JNPs to form a solid-like interfacial assembly, resulting in the formation of wrinkles when the interfacial area is decreased.

**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors

Acknowledged Federal Support: Y

**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published  
**Journal:** Macromolecules  
Publication Identifier Type: DOI      Publication Identifier: 10.1021/acs.macromol.7b02601  
Volume: 51      Issue: 3      First Page #: 1181  
Date Submitted: 7/18/18 12:00AM      Date Published: 1/1/18 4:00PM  
Publication Location:

**Article Title:** Morphological Behavior of A2B Block Copolymers in Thin Films

**Authors:** Hyeyoung Kim, Beom-Goo Kang, Jaewon Choi, Zhiwei Sun, Duk Man Yu, Jimmy Mays, Thomas P. Russell

**Keywords:** Mikto arm terpolymers, morphology, thin films

**Abstract:** (P2VP)<sub>2</sub> PS in the bulk showed a hexagonally packed cylindrical microdomain morphology with PS forming the cylindrical microdomains in a P2VP matrix. In thin films, after solvent annealing in the vapors of a chloroform/ethanol mixture, the cylindrical microdomain morphology was retained and the microdomains were oriented parallel to the substrate surface. With the addition of ethanol into the annealing solvent, the morphology of (P2VP)<sub>2</sub> PS was transformed from a bicontinuous morphology to one with cylindrical microdomains of PS oriented parallel to the substrate. The lamellar microdomain of the PS-*b*-P2VP copolymer changed to a morphology composed of PS cylindrical microdomains oriented normal to the substrate. The different orientations of the morphologies arise from the preferential interaction of P2VP with the substrate and the mediation of these interactions by the solvent. The morphological evolution of (P2VP)<sub>2</sub> -PS thin films was also investigated

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**Publication Type:** Journal Article

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**Publication Status:** 1-Published

**Journal:** Langmuir

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Publication Identifier: 10.1021/acs.langmuir.7b02009

Volume: 33

Issue: 36

First Page #: 8961

Date Submitted: 7/18/18 12:00AM

Date Published: 8/1/17 12:00AM

Publication Location:

**Article Title:** Coassembly Kinetics of Graphene Oxide and Block Copolymers at the Water/Oil Interface

**Authors:** Dayong Chen, Zhiwei Sun, Thomas P. Russell, Lihua Jin

**Keywords:** mikto arm terpolymers, thin films morphology

**Abstract:** The coassembly kinetics of graphene oxide (GO) nanosheets and diblock copolymers at the water/toluene interface is probed by tracking the dynamic interfacial tension using pendant drop tensiometry. The diblock copolymer significantly enhances the surfactancy of the GO nanosheets at the interface. It is found that diblock copolymers rapidly adsorb to the water/toluene interface and enhance the adsorption affinity of GO nanosheets to the interface. The continuous adsorption of GO at the interface leads to a random loose packing state, at which the adsorbed GO and diblock copolymers start to form an elastic film. After this transition, GO continues to adsorb to the interface, however, at a much slower speed, yielding a more solid-like elastic film in the long time equilibrium limit.

**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors

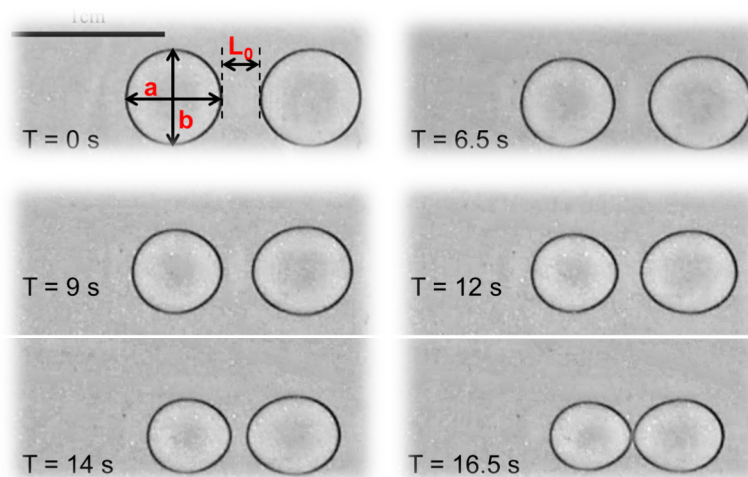
Acknowledged Federal Support: Y

## Vapor-Induced Motion of Two Pure Liquid Droplets

Inducing and controlling the movement of droplets in a preset manner on a solid substrate has important ramifications for technical applications, ranging from coatings to microfluidics to heat transfer devices, but also can aid in our understanding of phenomena observed in nature where the motion of water droplets, for example, is critical for survival. Usually droplet motion can be achieved by an imbalance in the interfacial tension of the droplet with the substrate and the surface energies of the droplet and the substrate. This can be triggered by gradients in temperature or composition of a liquid surface, which is well-known as the Marangoni effect<sup>4</sup>, for example, the “tears of wine” phenomenon observed in a wine glass. Variations in the surface tension of a solid substrate, e.g. a surface with a gradient in the surface energy or wettability, that give rise to a hysteresis in the contact angle, can also induce such a directed motion. Here, liquid droplets that have a surface energy lower than that of the substrate, will move towards the area with higher surface energy to reduce the free energy of the system.

High energy substrates were achieved by cleaning glass microscope slide in a piranha solution (a 30% mixture of H<sub>2</sub>O<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub>). After removal from the acid bath, the substrates were thoroughly washed in de-ionized water and then dried under a nitrogen gas flow. The substrates were used immediately after cleaning or stored in an inert atmosphere until use. All experiments were performed in a controlled humidity chamber at room temperature. *n*-hexane is used as the model droplet in this study, due to its vapor pressure and, importantly, it can form stable, nearly flat droplets on a high energy substrate, with a contact angle of 6.5°.

This conforms to the model conditions used in the theoretical model with  $R \gg H$ , where  $R$  and  $H$  are the radius and heights of the droplet. PG and water are not suitable candidates because they spread completely when deposited on the substrate, where the spreading parameter  $S = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL}) > 0$ , where  $\gamma_{SV}$ ,  $\gamma_{LV}$ , and  $\gamma_{SL}$  are the interfacial tensions between solid/ vapor, liquid/ vapor, and solid/liquid. In this



**Figure 1.** The motion behavior of two 5  $\mu$ L *n*-hexane droplets on a high energy substrate. These two droplets are deposited from left to right in a short time, with a shortest edge-to-edge distance of  $\sim 2.7$  mm.

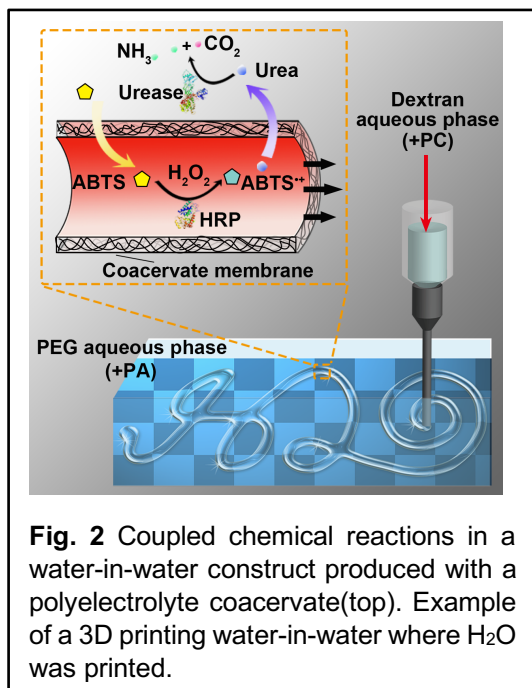
Figure 1. The motion behavior of two 5  $\mu$ L *n*-hexane droplets on a high energy substrate. These two droplets are deposited from left to right in a short time, with a shortest edge-to-edge distance of  $\sim 2.7$  mm.

case, no gradient of in the evaporation rate is formed across the droplets and, as a result, no droplet motion is observed.

Figure 1 shows the motions of two 5  $\mu\text{L}$  *n*-hexane droplets on the substrate. No movement was observed when a single droplet is placed on the substrate. However, in the presence of another droplet of the same liquid in close proximity (<5mm apart), by long-range interactions, the two droplets move toward each other induced by the evaporation of the *n*-hexane, and then coalesce into one droplet. In these and other experiments we prove that, on a high energy surface that remains uniform, the motion of two pure liquid droplets can be induced by a gradient in the evaporation rate. The droplets always attract each other, moving from the high evaporation side to the low evaporation side, to reduce energy dissipation. By varying the volume of the droplets or the distance between droplets, the motion of the droplets can be effectively controlled.

**Water-in-Water Compartmentalization:** A hallmark of biological systems is the ability to compartmentalize and coordinate system functions, which has been difficult to reproduce

even in the most sophisticated synthetic mimics. Here, we demonstrate a strategy to fabricate 3D compartmentalized water-in-water constructs, stabilized by an elastic polyanion–polycation coacervate membrane. Using a 3D printer, the length, shape, and diameter of all-aqueous tubules can be controlled. We found and capitalized on a directional diffusion of ionic species across the membrane dictated by the preferential affinity of the polyelectrolyte in the oppositely charged phase. In conjunction with microfluidic techniques, continuous selective diffusion and compartmentalized reactions were shown in such all-aqueous systems. A layer-by-layer strategy is also used to tune the membrane’s mechanical properties and to functionalize them. A new platform is demonstrated for developing and manipulating continuous separations media or compartmentalized reactive systems that function independently, or can be coupled by selective diffusion across the membrane (**Figure 2**).



**Fig. 2** Coupled chemical reactions in a water-in-water construct produced with a polyelectrolyte coacervate(top). Example of a 3D printing water-in-water where H<sub>2</sub>O was printed.

These all-aqueous printed structures provide a unique platform for the study and fabrication of more controlled, complex and even compartmentalized all-aqueous systems. We have developed systems where two parallel, orthogonal chemical reactions occur in separate compartments defined by the coacervate membrane where the products of one reaction selectively diffuse across the coacervate membrane to

participate in a reaction in the second compartment. We have demonstrated different strategies by which the all-liquid constructs can be realized in addition to the 3D printing.

**Hanging Droplets:** Usually objects sink in the less dense liquids. Water-walking

arthropods and biomimetic water-walking robots are some exceptions to this rule but

there is still an open question. Does the additional force to support the dense object

on the interface have its origins in the buoyant force based on the generalized Archimedean principle or does it arise from

the surface tension acting on the body? By hanging a coacervate-encased droplet of

a denser aqueous dextran solution from the surface of an aqueous solution of poly(ethylene glycol) (PEG) we find support

for the surface tension argument and exclude a modified Archimedean principle.

Supported and held by a polyelectrolyte coacervates formed at the interface between two aqueous phases, a droplet

containing the denser dextran solution is arrested at the surface of the aqueous PEG solution and hangs on the water/air or

water/oil interface where the displaced meniscus, based on the generalized Archimedean principle, is not large enough

to balance the gravitational force acting on the droplet. The magnitude of the surface tension acting on the droplet and shapes of

the droplets are varied by changing the height from where the droplet is released, the falling height, droplet size, the densities of

two aqueous solutions, and the concentrations of polyelectrolytes. We also exploit this phenomenon in complex systems, including horizontal droplet stacking and vertical

droplet stacking, to fabricate structured liquids or droplets with heterogeneous surface. Such a surface-hanging heterogeneous droplet is straightforward to generate by droplet

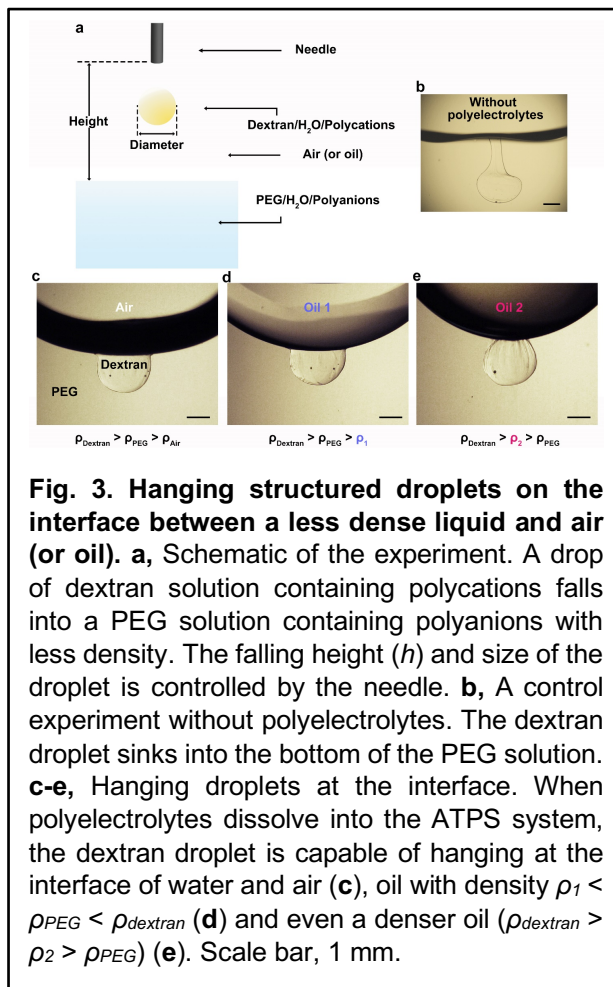
printing, so we expect that the outlined principles for hanging droplets will be of interest both for fundamental exploration in water-floating and for applications in functional micro-

reactors, micro-motors and biomimetic micro-robots.

Supported and held by polyelectrolyte coacervates formed at the contacting interface of two aqueous phases, falling droplets will stop sinking into the less dense bulk solution

and hang on the water/air interface or water/oil interface where the displaced meniscus based on the generalized Archimedes' principle is not large enough to balance

gravitational forces acting on the droplet and thus the surface tension is supposed to be

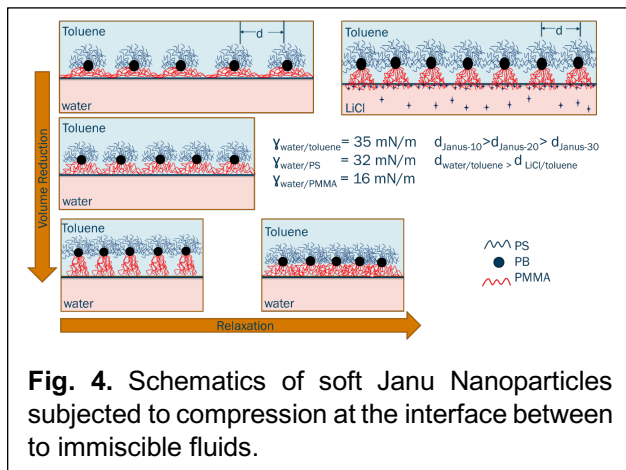


**Fig. 3. Hanging structured droplets on the interface between a less dense liquid and air (or oil).**

**a**, Schematic of the experiment. A drop of dextran solution containing polycations falls into a PEG solution containing polyanions with less density. The falling height ( $h$ ) and size of the droplet is controlled by the needle. **b**, A control experiment without polyelectrolytes. The dextran droplet sinks into the bottom of the PEG solution. **c-e**, Hanging droplets at the interface. When polyelectrolytes dissolve into the ATPS system, the dextran droplet is capable of hanging at the interface of water and air (**c**), oil with density  $\rho_1 < \rho_{PEG} < \rho_{dextran}$  (**d**) and even a denser oil ( $\rho_{dextran} > \rho_2 > \rho_{PEG}$ ) (**e**). Scale bar, 1 mm.

the only additional source to support it (**Figure 3**). We demonstrate that the magnitude of the surface tension on the droplet and corresponding morphologies are controllable by varying the falling height, droplet size, densities of two aqueous solutions and concentrations of polyelectrolytes. We also exploit this phenomenon in complex systems, including horizontal droplet stacking and vertical droplet stacking, to fabricate structured liquids or droplets with heterogenous surface. Such a surface-hanging heterogenous droplet is straightforward to generate by droplet printing, so we expect that the outlined principles for hanging droplets will be of interest both for fundamental exploration in water-floating and for applications in functional micro-reactors, micro-motors and biomimetic micro-robots. ( )

**Soft Janus-Nanoparticle Assemblies:** Soft JNPs, that are made from an ABC triblock copolymers of Poly(styrene-b-butadiene-b- methyl methacrylate) (PS-PB-PMMA) with central PB block crosslinked to form a core, with PS and PMMA chains emanating from the core, are interfacially active and show unusual jamming behavior. Soft JNPs can assemble at a liquid/liquid interface to reduce interface energy, even though the corona chains are not soluble in one of the two liquids. The corona chains are seen to spread at the interface to reduce the interfacial tension balanced again an elastic recovery force. The shorter the corona chains, the less the chains can stretch, and, therefore, the more dense the coverage. Upon compression, the soft JNPs can undergo a reconfiguration, relaxing the imposed stress. The extent decreases with decreasing molecular weight of the corona chains (**Figure 4**).



**Fig. 4.** Schematics of soft Janu Nanoparticles subjected to compression at the interface between to immiscible fluids.

Complexation with salt ions, in the case of PMMA against water, can promote the solubilization of the PMMA in the aqueous phase, eliminating the need to stretch the chains to cover the interface. With complexation, the area density of soft JNPs at the interface increases with the corresponding changes in the response of the assemblies to compression. This provides a convenient means of controlling the density of JNPs at the interface and tailoring the interfacial properties.

Complexation with salt ions, in the case of PMMA against water, can promote the solubilization of the PMMA in the aqueous phase, eliminating the need to stretch the chains to cover the interface. With complexation, the area density of soft JNPs at the interface increases with the corresponding changes in the response of the assemblies to compression. This provides a convenient means of controlling the density of JNPs at the interface and tailoring the interfacial properties.

**Rapid Multi-level Compartmentalization of Stable All-Aqueous Blastosomes by Interfacial Aqueous Phase Separation:** Producing artificial multicellular structures to process multistep cascade reactions and mimicking the fundamental aspects of living systems is an outstanding challenge. Highly biocompatible, artificial, systems consisting of all-aqueous, compartmentalized multicellular systems have yet to be realized. Here, a rapid multi-level compartmentalization of an all-aqueous system where a 3D sheet of sub-colloidosomes encloses a mother colloidosome by interfacial phase separation is

demonstrated. These spatially organized multicellular structures are termed as “blastosomes”, since they appear similar to blastula. The barrier to nanoparticle assembly at the water-water interface is overcome using oppositely charged polyelectrolytes that form a coacervate-nanoparticle-composite network. The conditions required to trigger interfacial phase separation and form blastosomes are quantified in a mapped state diagram. We show a versatile bottom-up model for constructing artificial multicellular spheroids in all-aqueous systems. The rapid interfacial assembly of charged particles and polyelectrolytes can lock in non-equilibrium shapes of water, which also opens opportunities for top-down technologies, such as 3D printing and microfluidics, to program flexible compartmentalized structures.

1. *The Interfacial Assembly of Polyoxometalate Nanoparticle Surfactants*

Caili Huang, Yu Chai, Yufeng Jiang, Joe Forth, Paul D. Ashby, Matthias M. L. Arras, Kunlun Hong, Gregory S. Smith, Panchao Yin, and Thomas P. Russell

*Nano Letters* **2018** 18 (4), 2525-2529

DOI: 10.1021/acs.nanolett.8b00208

**2. Carboxylated Fullerene at the Oil/Water Interface**

Rongqiang Li, Yu Chai, Yufeng Jiang, Paul D. Ashby, Anju Toor, and Thomas P. Russell

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