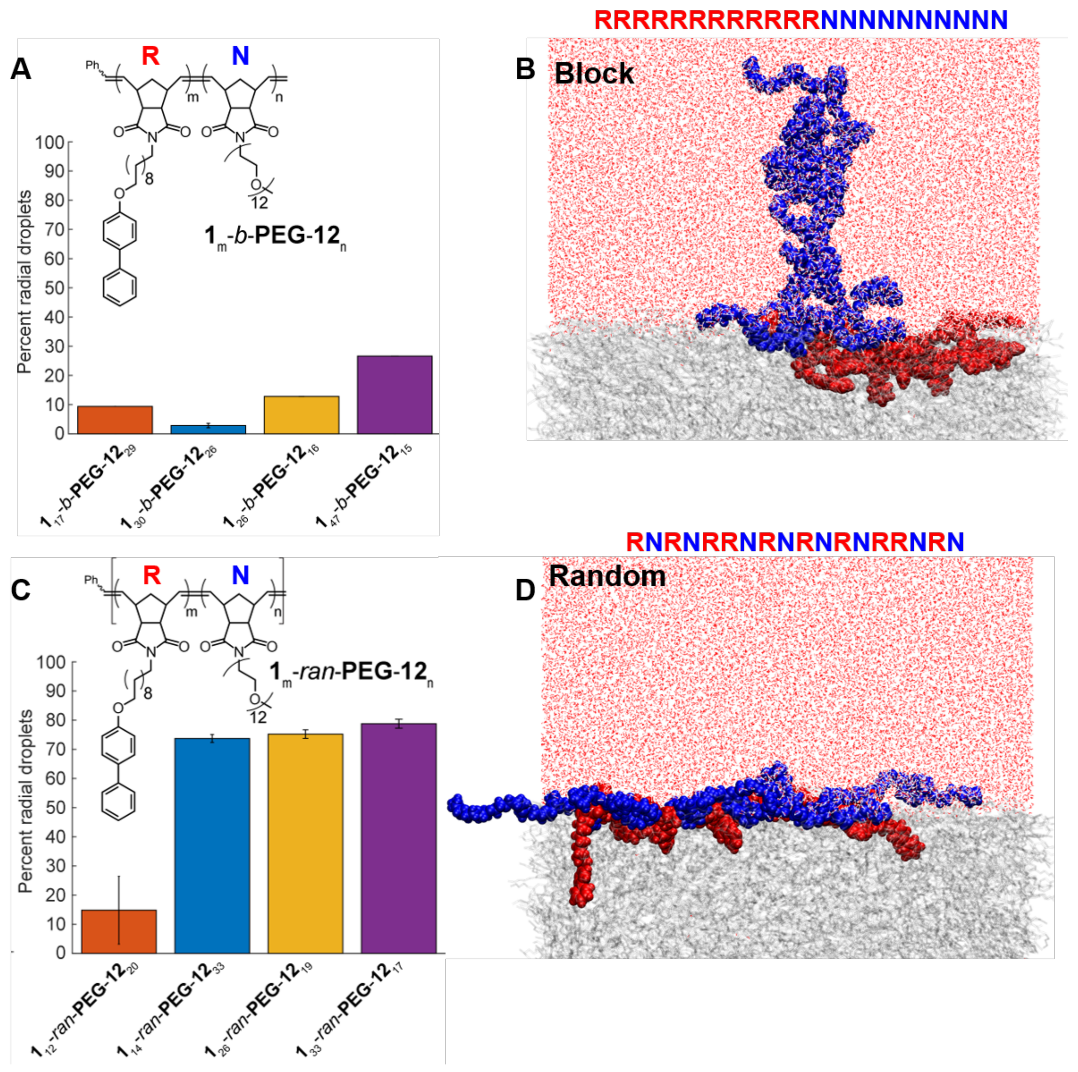
Multi-Scale Studies of Structures and Dynamics of Triggerable Assemblies

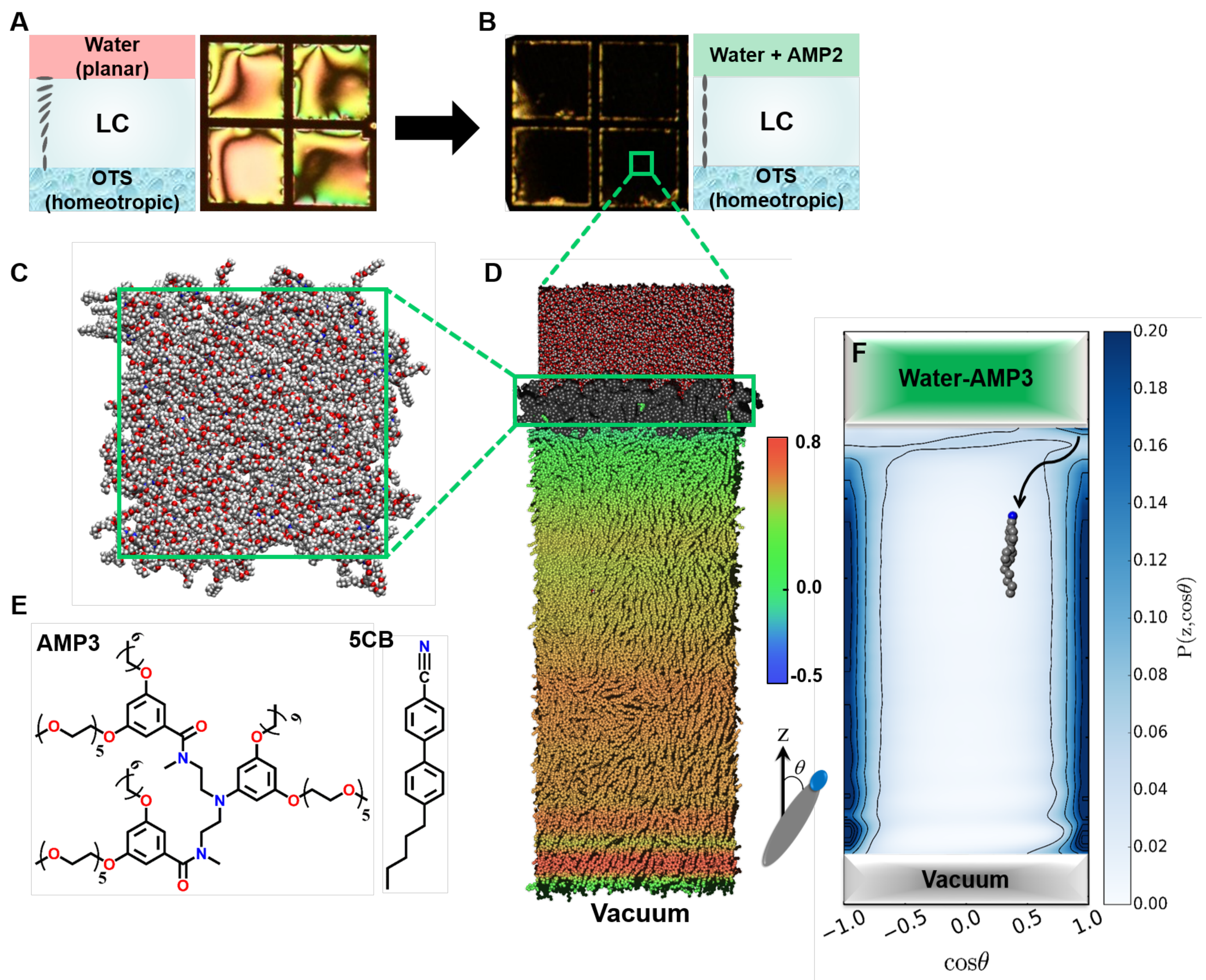
Lucas Antony[1], Hadi Ramezani-Dakhel[1], Abelardo Ramirez-Hernandez[1], Rui Zhang[1], Mohammad Rahimi[1], Poornima Rangadurai[2], Lucas R. Parent[3], Joel Pendery[4], Youngki Kim[4], Benoît Roux, Nathan C. Gianneschi[3], S. Thayumanavan[2], Nicholas L. Abbott[4], and Juan J. de Pablo [1]

[1]de Pablo Research Group, The University of Chicago [2]Thayumanavan Research Group, University of Massachusetts Amherst [3]Gianneschi Research Group, Northwestern University [4]Abbott Research Group, University of Wisconsin-Madison

Molecular Design of Triggerable Amphiphiles

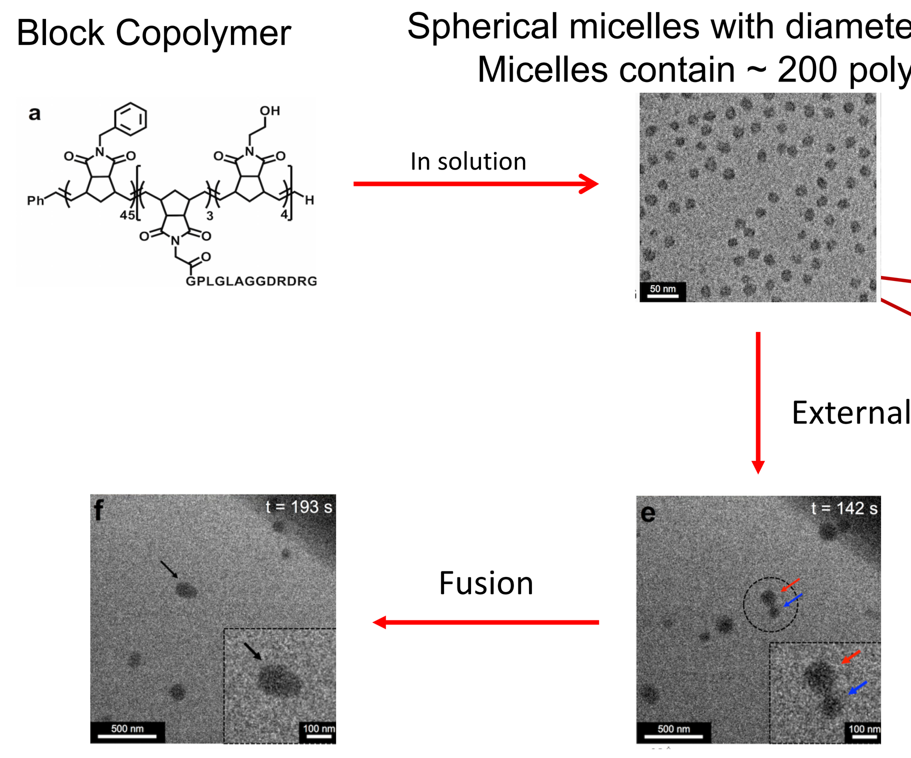


The architectures of copolymers composed of a hydrophilic segment and a mesogenic hydrophobic segment can be engineered to trigger an anchoring transition in LC droplets.

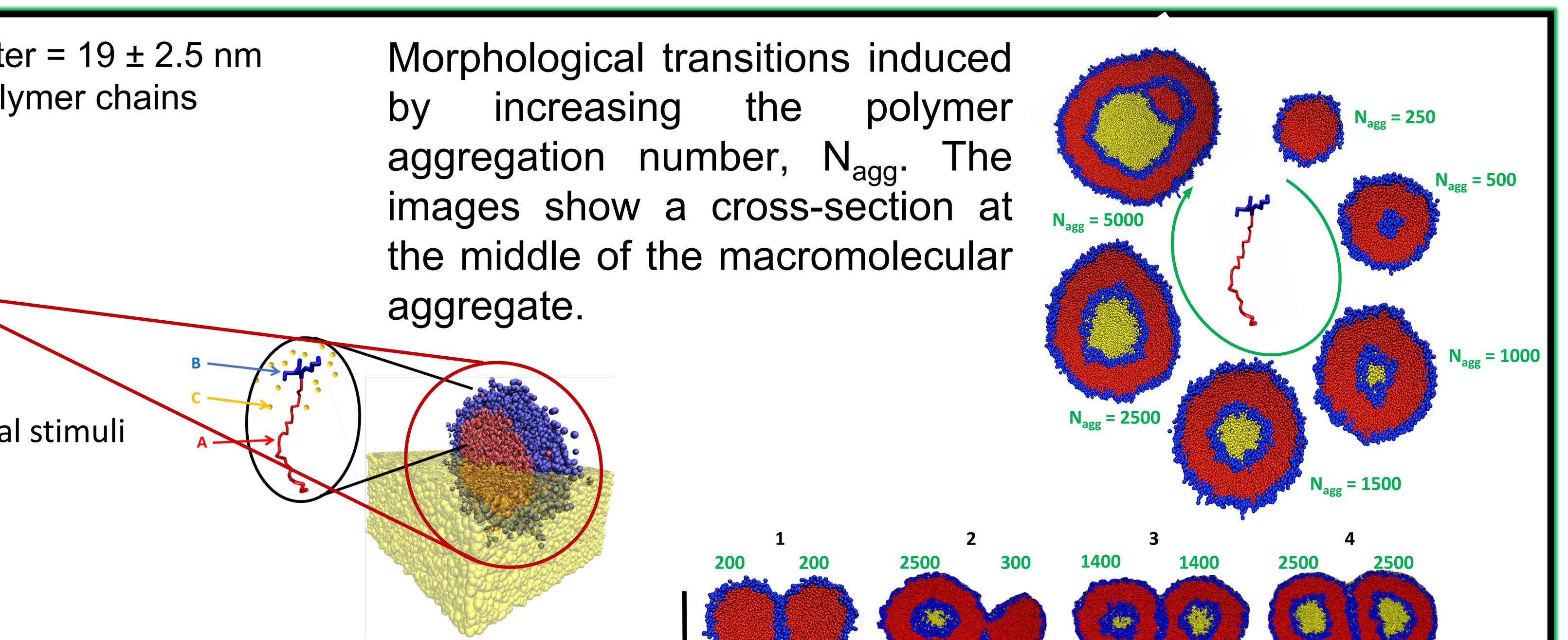


A monolayer decoration of surfactants at aqueous interfaces of LCs disturbs antiparallel orientations of LC molecules to cause a nematic-to-isotropic phase transition within a ~2 nm layer at the interface.

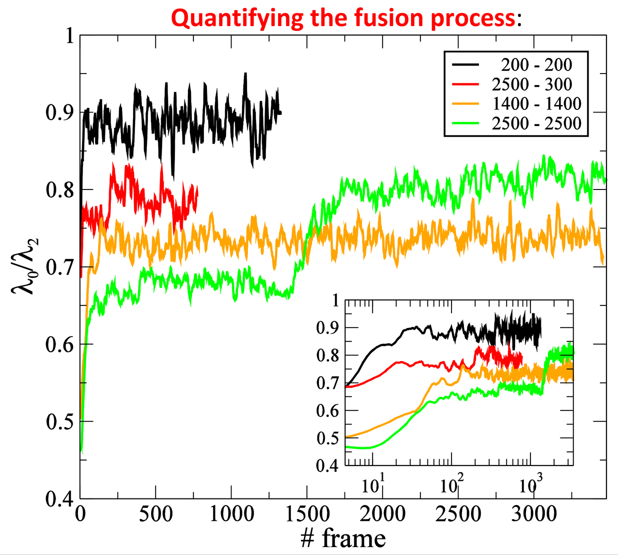
Coarse Grained Modeling of Micelle-Micelle Fusion

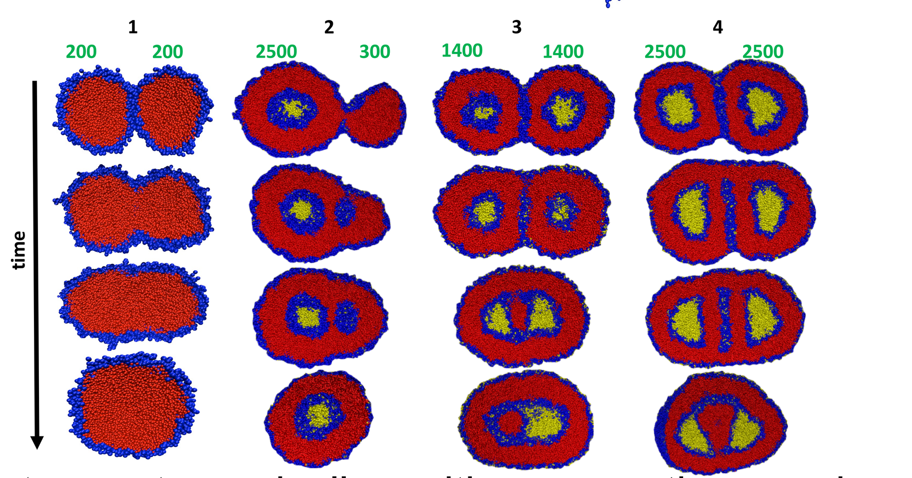


Morphological transitions induced by increasing the polymer aggregation number, N_{agg}. The images show a cross-section at the middle of the macromolecular aggregate.



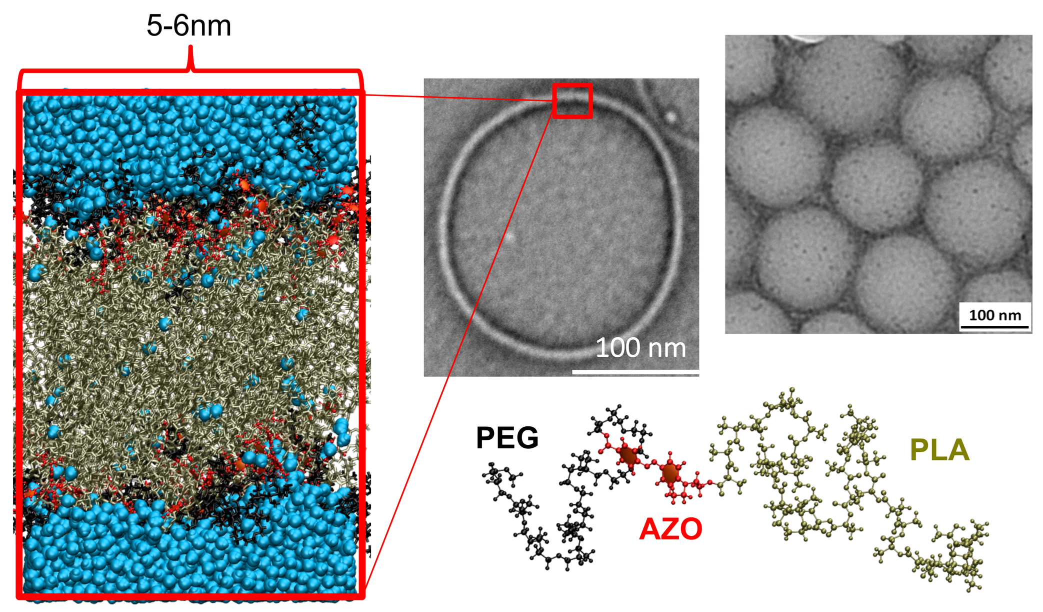
Time evolution of the eccentricity for fusion events between two aggregates with aggregation numbers as indicated. The eccentricity is defined as the square root of the ratio between the smallest and largest eigenvalues of the gyration tensor, **G**.





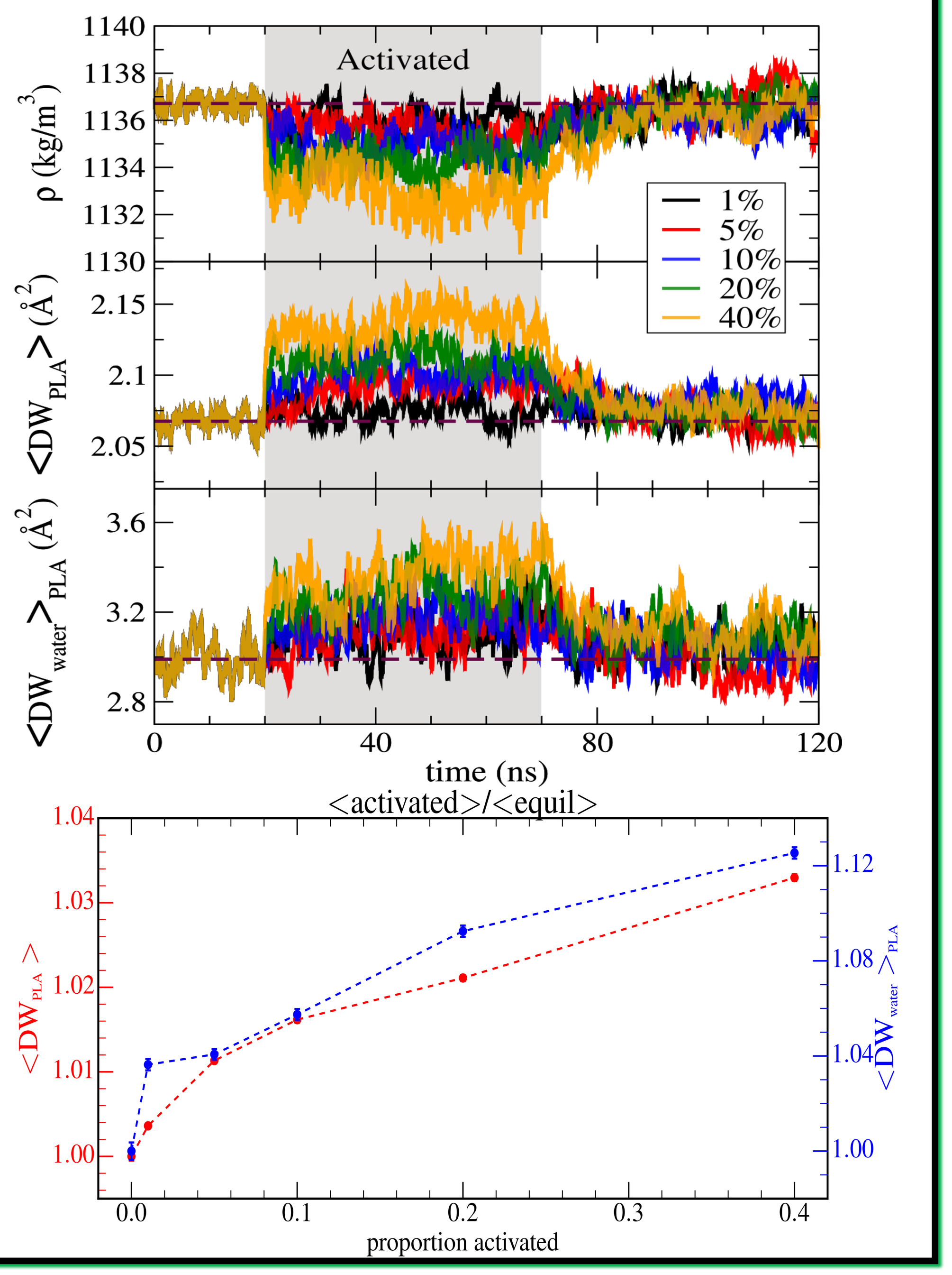
Fusion events between two micelles with aggregation number as indicated on the top of each aggregate (not at same time and length scale). (Column 1) The fusion of two small micelles proceeds by the creation of bridge between the A blocks (red) on the contact interface. Column 2 and 3 display the fusion of larger aggregates where at least one of them contains a pocket of solvent.

Photo-induced Release in Nano-encapsulation



Connecting a hydrophilic PEG polymer block to a hydrophobic PLA block via an azobenzene derivative forms vesicles capable of nano-encapsulation. Upon light irradiation the azobenzene groups undergo isomerization, changing configuration from *trans* to *cis* and thermally relaxing back to *trans*.

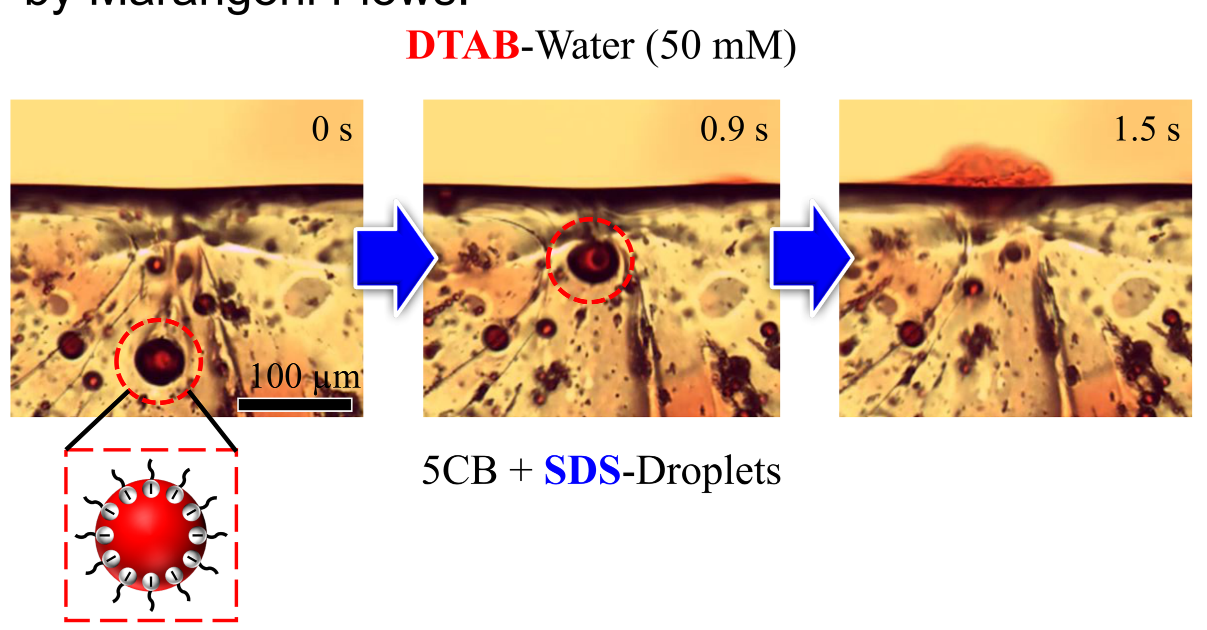
All-atom simulations used to model the bilayer led to a better understanding of the mechanism of release. The Debye-Waller factor, a mean-squared displacement for a set time-interval, was used as a measure of mobility for different components of the bilayer. The mechanical response caused by isomerization athermally breaks up the glassy PLA matrix ($T_g \approx 330K$).



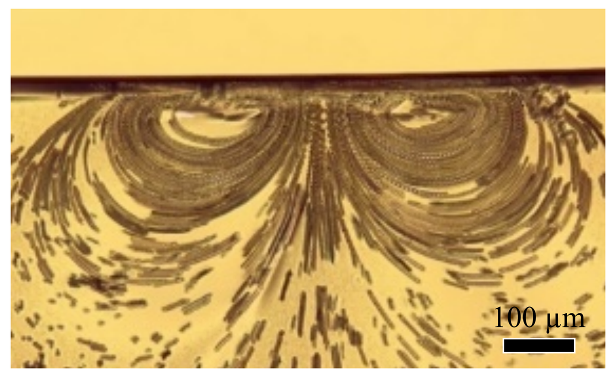
LC-Based Triggerable Interfaces

LC-based triggerable interfaces:
LC interface is responsive to addition of surfactants, which triggers a cascade of events.

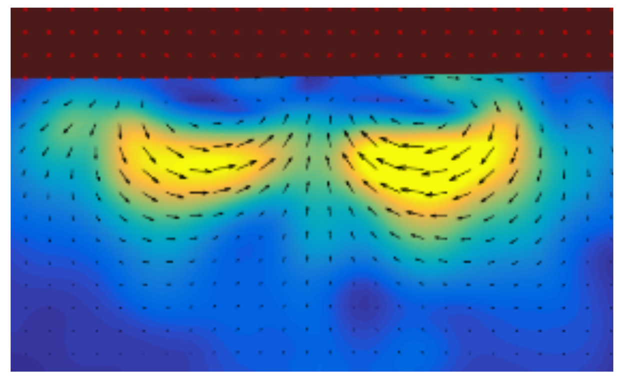
Experiments: Transport and Ejection of Microdroplets by Marangoni Flows.



Optical image:



PIV:

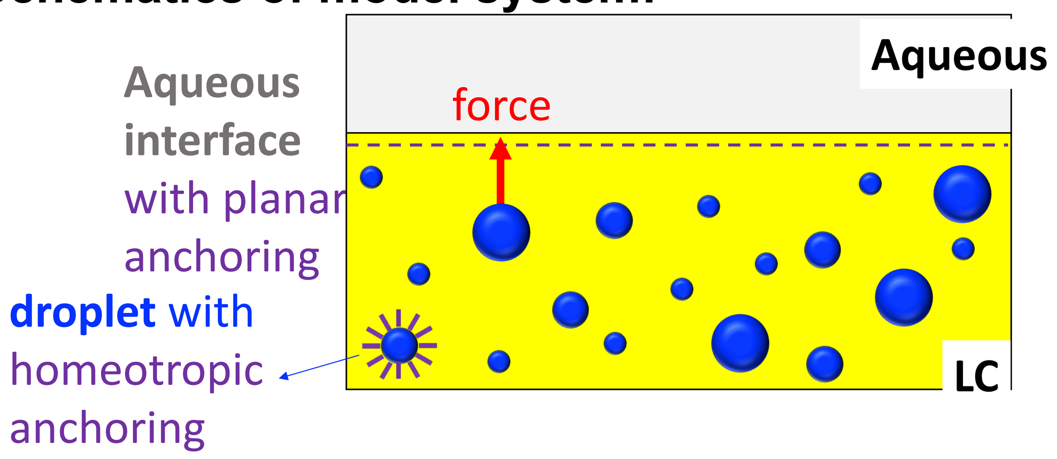


Modeling: Unique Features in the continuum model:
1. Multiphase and Inhomogeneity.
2. Coupling between concentration and structure.
3. Coupling between structure and hydrodynamics.

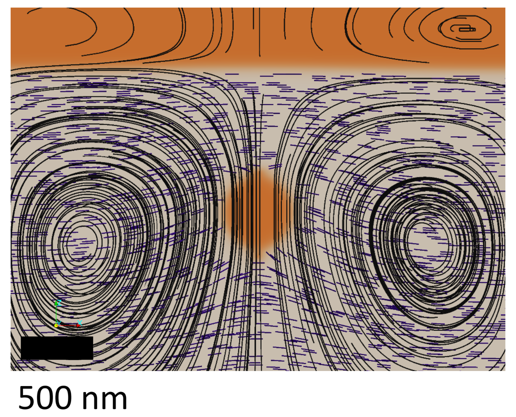
Free energy:

$$f = A\left\{(\alpha-\beta\phi)Q_{ij}Q_{ij} - \gamma Q_{ij}Q_{jk}Q_{ki} + \frac{9}{16}\left(Q_{ij}Q_{ij}\right)^2\right\} + \frac{1}{2}L\partial_i Q_{jk}\partial_i Q_{jk} + A_\phi\left\{\frac{1}{4}\phi^2 - \frac{1}{2}\phi^3 + \frac{1}{4}\phi^4\right\} + \frac{1}{2}\kappa\partial_i\phi\partial_i + W\partial_i\phi Q_{ij}\partial_j\phi$$

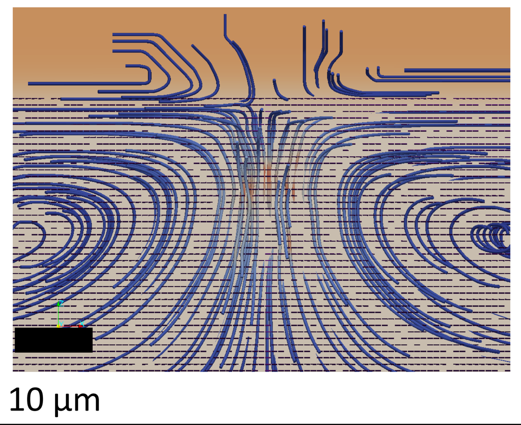
Schematics of model system:



Simulating droplets



Treat droplets as point particles:



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