PRF # 57801-ND9

Project Title: In Situ Small Angle Scattering Analysis of Ultrasound Excitation of Emulsion Droplets

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Research Objectives and Milestones:

Objective 1: Design of an ultrasound sample environment for SANS and SAXS analysis

A new sample environment has been built, characterized and demonstrated for the analysis of emulsion systems under ultrasound fields. Figure 1 shows a picture of the setup along with a schematic description of the components in the system. The sample environment consists of two face-to-face coaxial high intensity focused ultrasound (HIFU) transducers that produce a 'cigar' shaped beam in the center of the sample environment where the sample being analyzed is sitting. Scattering experiments are simultaneously run with either an x-ray or neutron beam that is orthogonal to the acoustic field. The description and examples of intended uses for the new sample environment have been published in a recent paper in the journal Soft Matter. The citation has also been reported to the ACS PRF system and the program is acknowledged in the funding sources as instructed. Although the system has been developed and this meets the milestones outlined in Objective 1, we continue to make improvements to the system to 1) increase the available acoustic frequencies that can be used, 2) minimize the scattering contributions of sample that is not acoustically insonated and 3) enable the use of time-resolved measurements to track changes in the samples due to acoustic fields.

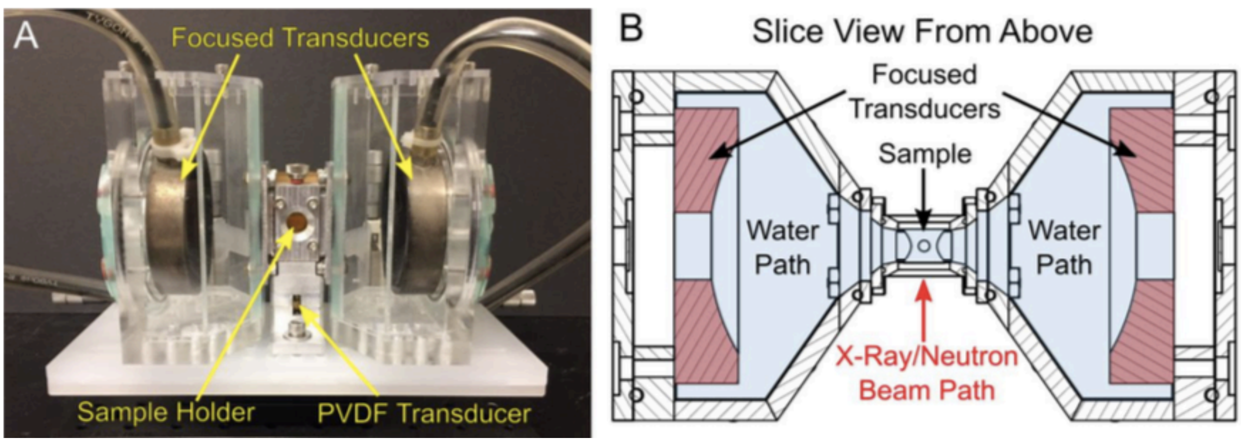

Figure 1: A) Photograph of the sample environment for ultrasound and SAXS/SANS analysis. B) Schematic drawing (top view) of the sample environment showing all critical components.

Objective 2: Probe effects of ultrasound fields on emulsion structure and interactions

This objective outlines the bulk of the ongoing work and also the work that will be our focus for the rest of the project. Here we have pursued three main directions: 1) Analysis of ultrasound field effects on emulsion size distributions, 2) Analysis of effects of ultrasound fields on the interfacial structure of Pickering (particle-stabilized) emulsions and 3) Time resolved analysis of mass transport in emulsion systems with and without ultrasound fields.

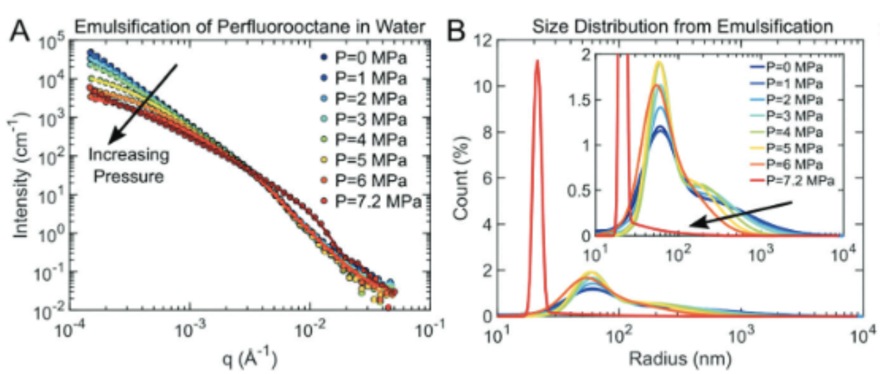

Figure 2: A) USAXS profiles for PFO emulsions under variable acoustic intensities. B) Droplet size distributions obtained from fits to the USAXS profiles. Cavitation only occurred when the pressure was >6.5 MPa.

Sub-Objective 1 - Size distribution: Changes in emulsion size-distribution were analyzed with ultra-small angle x-ray scattering (USAXS) which is an excellent probe for systems with sizes in the range of 1-10,000 nm. Figure 2 shows an example of USAXS data for perfluorooctane (PFO) emulsions under ultrasound field intensities below and above the cavitation threshold of ~6.5 MPa. These results appear in the recent Soft Matter publication mentioned above.

Sub-Objective 2 – Interfacial structure of emulsions under ultrasound fields: USAXS experiments were also performed for emulsions in the presence of amphiphilic gold nanoparticles to produce Pickering emulsions (particle-stabilized emulsions). Here, we prepared emulsions and amphiphilic particles that were then mixed and exposed to different acoustic conditions. When ultrasound fields were not used, the particles would not adsorb to the oil-water interface because of electrostatic and/or steric repulsion forces. In contrast, when acoustic fields were present and large enough to induce cavitation, we observed that the particles would be pushed to the oil-water interface and produce stable Pickering emulsions. The process was tracked under variable conditions (time, acoustic pressure) and also variable oil types. It was determined that cavitation of the solvent was essential to the production of Pickering emulsions. Moreover, careful analysis of USAXS data allowed us to demonstrate that size-distributions would change at pressures below cavitation, that a significant fraction of 'excess' particles would always remain un-adsorbed and that significant losses of volatile oils (up to ~80 v%) would occur during the ultrasound insonation process. Figure 3 shows an example of the data and fits corresponding to these measurements. This data is now being prepared for publication.

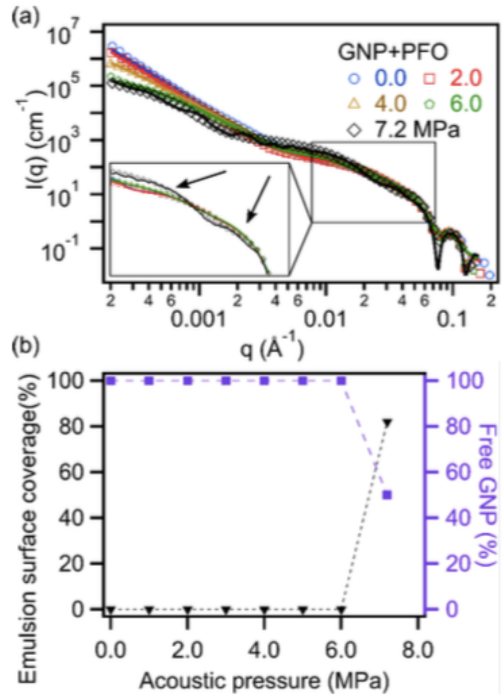

Figure 3: A) USAXS data and fits for PFO emulsions with gold nanoparticles (GNP) sonicated at variable pressures. B) Percent coverage of oil-water interface for emulsions and the percent of GNPs that remain 'free' in dispersion.

Sub-Objective 3 - Time-resolved scattering analysis of mass transport in emulsion systems under ultrasound: Here, we have used small angle neutron scattering with contrast variation to analyze the exchange of oil between emulsion droplets dispersed at rest and during variable acoustic fields. We aim to understand the effect of the acoustic field, oil solubility and interfacial stabilization method (i.e. surfactant, particles or polymers) on the exchange rates of oil. This is without a doubt on of the best demonstrations of the power of scattering analysis of emulsions since this type of data would be incredibly difficult to obtain with other methods. In this work, we prepared identical emulsions of deuterated and hydrogenated oils dispersed in a solvent mixture of water and heavy water. The experiment is designed in such a way that, when all of the oil in the emulsions is perfectly mixed, the scattering signal from the emulsions would vanish to near zero. However, in the un-mixed state, the isotopes of the oil would both have significant scattering signal. Therefore, one can measure the oil exchange rates for these systems and model the data to obtain relevant information on mass transport. So far, we have demonstrated that ultrasound significantly accelerates emulsion mixing processes. Without ultrasound, exchange rates of large oil molecules (e.g. hexadecane) would take several hours to be measureable. In contrast, under acoustic cavitation, oil exchange rates occur in a matter of just a few minutes. We have also demonstrated that the interfacial stabilization mechanism also plays a very important role. When no-surfactant is used, emulsion mixing is incredibly fast (minutes). When surfactants are used to stabilize the droplets, the oil exchange rate decreases appreciably. We are now in the process of evaluating other interfacial stabilizers to more thoroughly explore these effects.

Impacts on education and career development: The project is being primarily run by a graduate student that is pursuing his PhD in Chemical Engineering. He is being mentored by the PI and also by other researchers in the group. As part of this work, the student has learned about acoustic physics, colloidal systems and scattering analysis. We are also going to recruit BS and MS students that may be interested in participating in this project as researchers.

In addition to this, the grant has enabled me (the PI) to explore new research directions in the field of acoustics. I am now able to apply our existing expertise in colloid and scattering sciences to important applications involving ultrasound. I expect that this project will catalyze other research directions related to the acoustic manipulation of materials.