PRF#: *58038-DNI5*

Project Title: *ACS PRF DNI: Microstructure and Transport of Nanoparticle Laden Foams in Porous Media*

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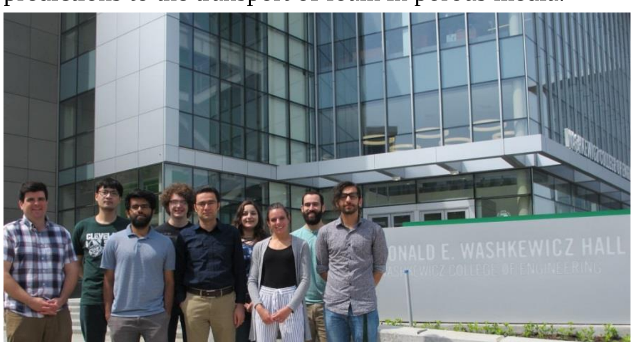
Summary: Multiphase fluids are important to many applications found in the petroleum industry. Two timely examples are the use of foams in the areas of shale fracturing and enhanced oil recovery (EOR). Greater efficacy of foam fracking fluids would substantially reduce the volume of water required for unconventional natural gas drilling, while foams have been used in EOR as effective displacing fluids, as well as sweeping fluids for environmental remediation. Nanoparticle stabilized foams have many of the properties that make them desirable for these two applications, including strong stability in the presence of oil and also favorable rheological and mechanical properties. Yet, there has been very little work on how particle properties and interfacial microstructure influences the transport of nanoparticle stabilized foams in porous media. Funds from the ACS PRF DNI program are helping our group fill this gap in knowledge by predicting particle microstructure and interfacial properties, and subsequently applying these predictions to the transport of foam in porous media.



Wirth Lab – June 2018
Left to Right: Chris Wirth, Jiarui Yan, Selwin Varghese, Ken Gregg, Aidin Rashidi, Marola Issa, Marissa Trivisonno, Naik Yusufi, Mohammed Kalil
Not Pictured: Dan Stralka, Marissa Kostandaras

Impact on participating students and on my career and participating students: Funds provided via the ACS PRF DNI program had a significant positive impact. Four graduate and two undergraduate students have been involved in the project thus far, in either major or minor roles. Two graduate students completed their MS degrees, while another MS and one PhD student are working towards finishing their degrees. Of the graduated students, one entered the PhD program at Cleveland State University working in my lab, while the second is currently interviewing for PhD positions in Europe. I expect the current MS student to finish his degree in the spring or summer of 2019 (and return to work at Sherwin Williams), while the PhD student expects to finish his degree in spring 2020. The undergraduate students involved in the project reported having a positive experience, with both continuing on in my laboratory past their initial commitment. Both 3rd year undergraduate students are considering their career options, expressing interest in either entering the workforce or pursuing PhD studies after graduation in spring 2020. Initial work on this project has also had a positive impact on my career by providing much needed personnel and supplies support to push this and related projects forward. I recently received an NSF CAREER award for a complementary project, focused on measuring interactions of complex particles near interfaces.

Activities during the budget period 2017 – 2018: Our research activities over the past year have focused in three areas: (1) fabrication of anisotropic particles, (2) microstructure measurement of particles at fluid/fluid interfaces, (3) fabricating and testing microfluidic devices to simulate porous media.

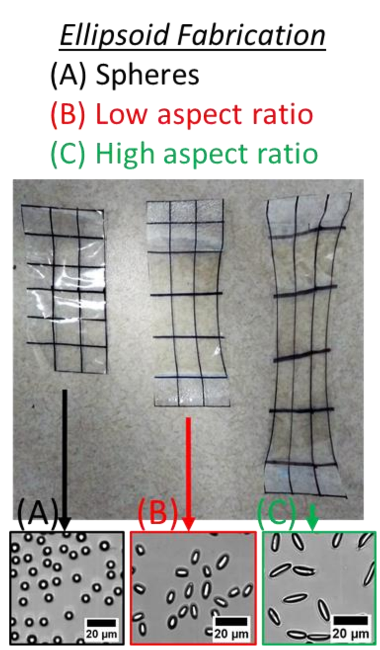


Figure 1: Ellipsoid fabrication via film stretching. Polystyrene spheres are heated and stretched to various aspect ratios in a polyvinyl alcohol film.

(1) Fabrication of anisotropic particles: A key initial component of the project is to implement fabrication methods for the production of nanometer to micrometer scale particles with variations in surface chemistry and shape. For the purposes of fabricating non-spherical particles, we used a film stretching technique (see **Fig. 1**) to produce ellipsoidal polystyrene particles subsequently used in microstructure measurements described later. Briefly, polystyrene spherical particles were dispersed and cast in a polyvinyl alcohol film. Following casting, the film was stretched in an oven at high temperature. The stretching process deformed spheres to some specified aspect ratio (AR). The stretched films were cooled, dissolved, and cleaned to obtain spherical (AR = 1), low-aspect ratio (AR = 1.74), and high aspect ratio (AR = 2.38) particles (see **Fig. 1**). In addition, "Janus" particles were fabricated with glancing angle

Janus particle Fabrication

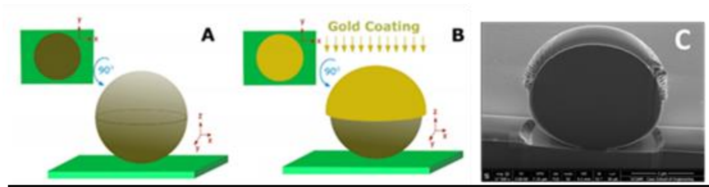


Figure 2: Janus particle (A & B) fabrication via glancing angle deposition and (C) characterization of cap. Adapted with permission from[1]. Copyright (2018) ACS.

deposition (see **Fig. 2**). One key initial result from our work on Janus particles was recently published[1]. We found via direct measurement that the thickness of a Janus particle cap will vary across the contour of the particle, which will affect how Janus particles interact with nearby interfaces.

(2) Microstructure measurement of particles at fluid/fluid interfaces: Experiments were conducted to measure the microstructural evolution of particles at a fluid/fluid interface (see **Fig. 3**). The primary motivation for these measurements is to elucidate the influence of electrostatics on the flocculation of non-spherical particles at a fluid/fluid interface. These systems (particles near water/oil interfaces) are regularly found in the oil and gas industry. Of particular interest to us is determining at what aspect ratio capillary attraction dominates electrostatic repulsion. Our data from the past year suggests that capillary attraction is still dominant at an aspect ratio ~1.74. We are currently running experiments to determine the critical aspect ratio for when capillary attraction balances electrostatic repulsion at AR < 1.74.

Microstructure measurement

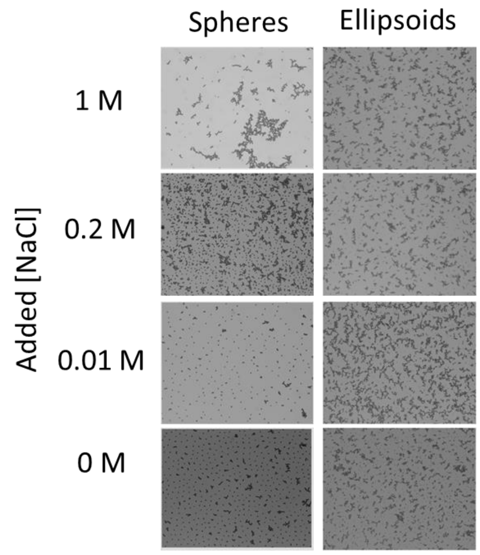


Figure 3: Microstructure of polystyrene spheres and ellipsoids at a water/oil interface with varying salinity. The spheres remain stable <0.2 M NaCl, but the ellipsoids start to flocculate in the absence of added salt. These experimental data are being completed with simulated data to determine the impact of electrostatic interactions for non-spherical colloids at a water/oil interface.

(3) Fabricating and testing microfluidic devices to simulation porous media: We also designed and fabricated the microfluidic device for micromodel experiments of foams in porous media (see **Fig. 4**). The polydimethylsiloxane (PDMS) microfluidic device consists of a flow focusing "foam generator" (see **Fig. 4(A)**) and also a porous media micromodel (see **Fig. 4(B)**). The molds were initially designed with SolidWorks and then fabricated at the University of Louisville Micro/Nano Technology Center. Once fabricated, we began to make PDMS devices and to benchmark our device fabrication process.

Microfluidic device fabrication

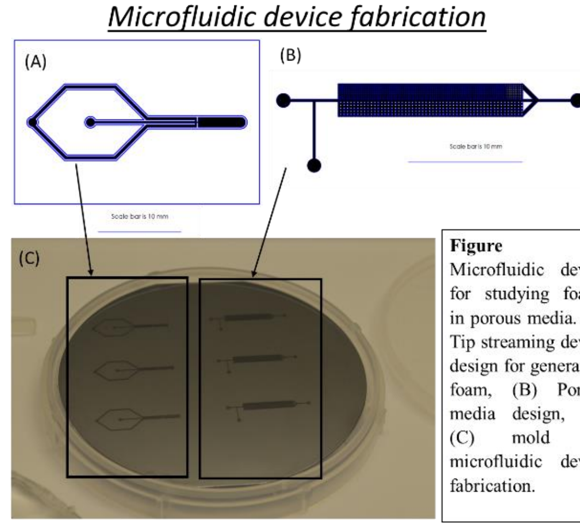


Figure 4: Microfluidic device for studying foams in porous media. (A) Tip streaming device design for generating foam, (B) Porous media design, and (C) mold for microfluidic device fabrication.

Nest steps: The key accomplishments from 2017-2018 consisted primarily of developing and benchmarking our fabrication techniques, experimental protocols as related to the microstructure measurements, and also microfluidic device fabrication. Next steps are focused on two main intellectual contributions: (1) What influence does electrostatics play in the microstructure of non-spherical particles at a water/oil interface and what is the "critical" aspect ratio? (2) How does a particle laden foam structure in porous media and what role particle shape and surface chemistry plays in foam structure in porous media?

References:

(1) Rashidi, A.; Issa, M. W.; Martin, I. T.; Avishai, A.; Razavi, S.; Wirth, C. L. Local Measurement of Janus Particle Cap Thickness. *ACS Appl. Mater. Interfaces* **2018**, acsami.8b11011.