PRF # 57523-DNI9
Project Title: **Mesoscale Modeling of Nanoemulsion in Porous Media**
PI: **Ming Tang**, Department of Materials Science and NanoEngineering, Rice University

The goal of this project is to obtain a mechanistic understanding of the formation and stability of nanoemulsion structure in porous media with relevance to enhanced oil recovery (EOR). Nanoemulsion provides a potentially cost-effective alternative to microemulsion EOR, but much of the fundamental knowledge required to assess its feasibility remains absent. Herein, we aim to use mesoscale modeling to provide insights on several important questions, including the efficiency of nanoemulsion production through in-situ methods and the stability of nanoemulsion flowing in confined porous channels. Support from this project has enabled the PI's group to develop a mesoscale model and computer code "EmuPFM" for emulsion evolution simulations and obtain valuable preliminary results, which helps build the foundation for a competitive proposal on the subject. The project also provided valuable trainings to two graduate students in the topical area along with numerical algorithm development and high-performance computing.

In the current project period, we developed a phase-field model for simulating the emulsion evolution process in surfactant-containing fluids. The model captures the self-assembly tendency of surfactants in solutions and the effect of bending curvature energy of surfactant layers on emulsion morphology. It can also account the effect of hydrodynamic flow on emulsion evolution. An MPI-based parallel computer code "EmuPFM" was developed in-house to numerically implement the model using the pseudo-spectral method. The code is found to exhibit excellent scaling performance on supercomputers such as Stampede2 at the Texas Advanced Computing Center, see Figure 1, which makes large-scale emulsion simulations possible. To investigate the feasibility of producing nanoemulsion droplets through in-situ phase inversion

Figure 1 Scaling performance of the parallel simulation code on Stampede2 cluster.

during chemical flooding, the code was applied to simulate emulsification in the interfacial region between surfactant-rich displacing and surfactant-lean displaced fluids.
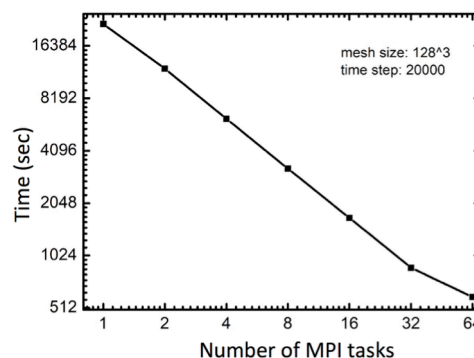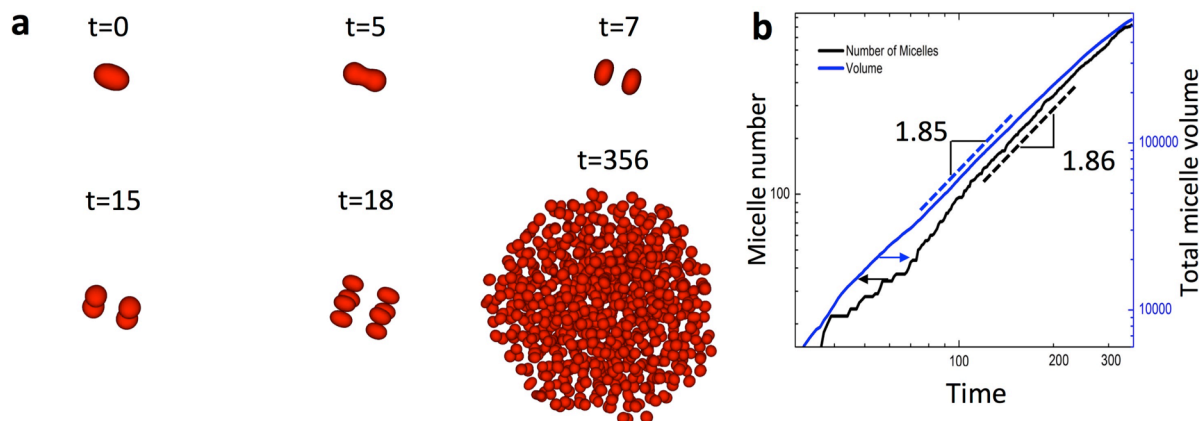

Figure 2 a) Phase-field simulation of the autocatalytic emulsion droplet generation mechanism by repeated micelle splitting. Times are in dimensionless unit. b) The growth of total droplet volume and droplet number exhibits parabolic time dependence due to the mixed control of micelle splitting rate and long-range surfactant transport. Dashed lines are linear least square fittings to the growth curves.

We discovered an autocatalytic mechanism of emulsion droplet generation via droplet splitting process, which potentially provides an efficient and facile pathway to nanoemulsion production. As shown in Figure 2a, an emulsified droplet under suitable conditions can rapidly proliferate into a cluster of micelles through repeated splitting and re-growth. However, analysis shows that the droplet number N_{tot} and total emulsion volume V_{tot} increase at a rate less than exponential growth, which is expected when all droplets undergo splitting simultaneously. Instead, a parabolic time dependence, $N_{tot}, V_{tot} \propto t^2$, is observed, as shown in Figure 2b. A closer examination of the simulation results reveals that such behavior arises because only droplets within the outer shell of the micelle cluster actively split and few splitting events occur in the inner core. As shown in Figure 3, the "active

Figure 3 Distribution of the distances of splitting events (black squares) to the center of micelle cluster as a function of time. Red curve represents the radius of the outmost micelle in the cluster.

splitting zone" maintains a relatively constant shell thickness and moves with the outer sphere of the cluster. This suggests that the droplet splitting process is kinetically limited by the local supersaturation and long-range transport of surfactants.
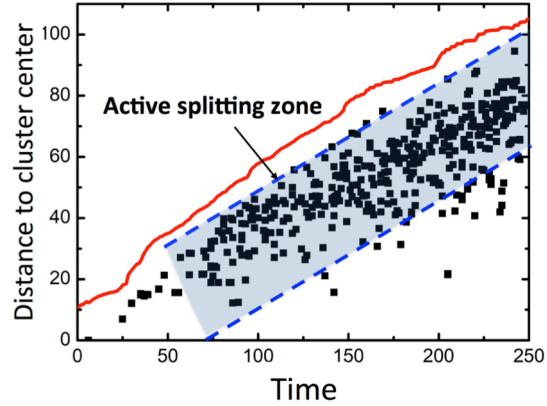
A population dynamics model was developed to explain the salient features of the autocatalytic droplet reproduction mechanism observed from simulations. The model asserts that the growth speed of the micelle cluster is jointly controlled by the individual micelle splitting rate, which is a function of local surfactant supersaturation, and the diffusion of surfactants from surrounding towards the cluster surface required by the formation of emulsion droplets. Individually, the two kinetic steps give rises to cubic and linear time dependence of total micelle volume ($V_{tot} \propto t^3$ and t), respectively. A splitting process under their mixed control will produce a scaling relation $V_{tot} \propto t^\alpha$ with the exponent $1 < \alpha < 3$ as observed in simulations. We also investigated the effect of fluid flow on the micelle droplet splitting kinetics. Simulation (Fig. 4) shows that

Figure 4 Comparison of the autocatalytic micelle growth kinetics with vs without the presence of lamellar flow.

droplet splitting in a lamellar flow confined in a porous channel is significantly accelerated while retaining the same $V_{tot} \propto t^2$ growth behavior.
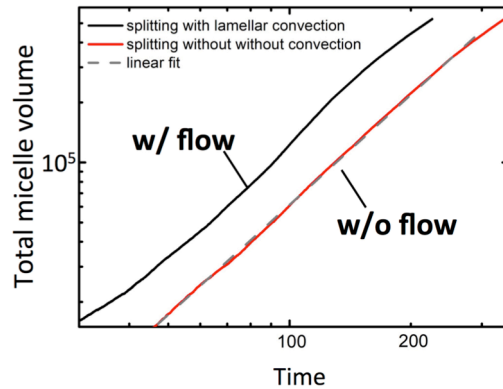
The results obtained from the project so far suggest that the splitting-based autocatalytic micelle growth mechanism can be potentially exploited to improve the effectiveness and efficiency of in-situ nanoemulsion production. Nevertheless, phase-field simulations also reveal that the operation of this mechanism has sensitive dependence on the fluid conditions (e.g. surfactant supersaturation) and intrinsic surfactant properties such as the spontaneous curvature value, which highlight the need for careful design and selection of chemical EOR agents and flooding conditions to control the displacing/displaced fluid interface configuration. In the next phase, we will combine numerical simulations and analytic model development to shed light on the scientific basis of such design criteria. The phase-field model will also be extended to account for the interaction between emulsion structure and pore wall surface for studying nanoemulsion formation and stability in porous structure.