

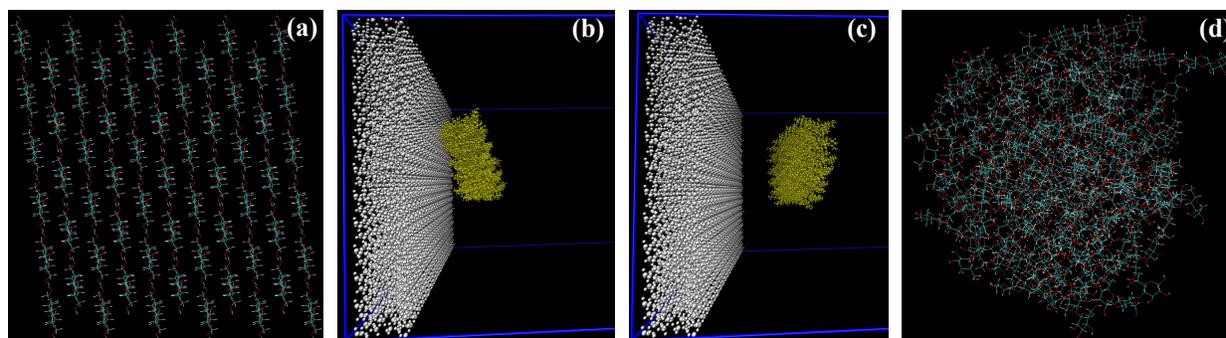
**PRF Grant Number:** 58630

**Project Title:** Understanding Novel Shale Hydration Inhibitors for Water-Based Drilling Fluids Using Molecular Simulation

**PI, Affiliation:** Francisco R. Hung, Department of Chemical Engineering, Northeastern University (no co-PI)

In this project our team is performing classical molecular dynamics simulations, with the objective of fundamentally understanding the mechanisms by which cellulose nanomaterials can inhibit hydration of clays. Such a fundamental understanding is relevant to the possible use of cellulose nanomaterials as biodegradable and environmentally friendly additives for water-based drilling fluids, in order to prevent excessive water uptake by shales in reservoirs during oil and gas drilling operations. Shale hydration issues can lead to reservoir instability problems and wellbore damage, causing important economic losses (>\$500M/year) during drilling operations.

In our initial studies, we have focused on accurately computing the interactions between the surfaces of smectite clays and cellulose nanocrystals (CNCs). These crystalline nanomaterials were found in experimental studies<sup>1</sup> to prevent clay hydration, with strong interactions between the surfaces of the CNCs and the clays postulated to be the driving force behind these observations. Using all-atom models for the smectite clays, the CNCs and the other species present in the system (i.e., water, ions), we are computing the potential of mean force (PMF, or free energy) between the surfaces of the clays and the CNCs, as a function of the distance between these surfaces. These free energies are mediated by ions and water molecules, which are ubiquitous in these systems. After preliminary simulations to test our molecular models, we are currently computing the free energies between the basal plane of the clays and several relevant facets of the CNC. Simulation snapshots of representative systems are presented in Figure 1. We are also computing the interfacial adhesion forces between the montmorillonites and a model cellulose microfibril (CNF, Figure 1), in which the cellulose chains form amorphous regions, as experimental studies<sup>1</sup> have found that CNFs have inferior clay hydration inhibition properties as compared to CNCs.

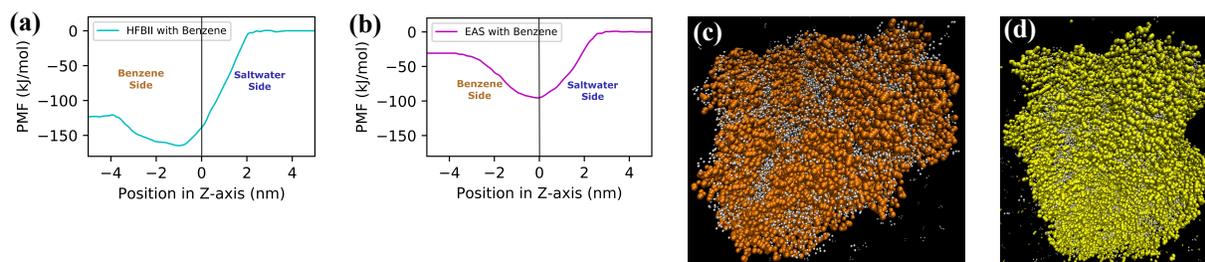


**Figure 1.** (a) Top view of a cellulose nanocrystal; (b, c) simulation snapshots from potential of mean force calculations of a cellulose nanocrystal (yellow) at varying distances from a montmorillonite clay (silver); (d) top view of a model cellulose microfibril. Water molecules and ions not depicted in any of the figures for clarity.

---

<sup>1</sup> Li, M.-C.; Wu, Q.; Song, K.; Qing, Y.; Wu, Y. Cellulose Nanoparticles as Modifiers for Rheology and Fluid Loss in Bentonite Water-based Fluids. *ACS Applied Materials & Interfaces* **2015**, *7*, 5006-5016.

In another set of studies, we performed classical molecular dynamics simulations of hydrophobins near interfaces involving oil and water having dissolved salts. Hydrophobins are fungal proteins that have low molecular weight (~10 kDa), are natural surfactants and have very surface-active properties, and thus could be used in synergy with cellulose nanomaterials to inhibit shale hydration in reservoirs. As a starting point to explore these possible synergies, we examined systems of two widely studied hydrophobins, EAS and HFBII, near oil-saltwater interfaces. Using coarse-grained models in our simulations, we first determined potentials of mean force when the hydrophobins are dragged from the saltwater phase into the benzene phase, across the benzene-saltwater interface (Figure 2). These results show that these small proteins prefer to lie near the interface (approximately located at  $z = 0$  in the plots below), as indicated by the deep free energy minima observed near  $z = 0$ . Furthermore, these results indicate that both hydrophobins have smaller free energies when they are deep into the benzene phase, compared to when they are in the saltwater. Finally, as experimental studies<sup>2</sup> reported that hydrophobins can encapsulate oil and gas into elongated structures when in water solution, we examined the stability of sub-micron structures formed by the encapsulation of benzene by the hydrophobins (Figure 2). In follow-up studies we intend to consider systems of hydrophobins and CNCs near montmorillonite clays.



**Figure 2.** (a, b) Potentials of mean force associated with moving the hydrophobins HFBII (a) and EAS (b) from a seawater phase into a benzene phase, across a benzene/seawater interface located at  $z = 0$  in the plots. (c, d) Representative simulation snapshots of non-spherical nanodroplets formed by benzene (silver) encapsulated by the hydrophobins HFBII (orange, c) and EAS (yellow, d). Water and ions not depicted for clarity. Both of these nanodroplets have characteristic sizes on the order of 10 nm.

Support from this grant have been key in helping the PI gets established in a new research direction and obtain preliminary results critical for launching new investigations in this field. In addition, monies from this grant has been used to support a PhD student, Andrés Vodopivec, who was responsible for the work described here and is scheduled to have his thesis proposal defense in Fall 2019. He has also presented his work in two contributed oral talks at the ACS Fall 2018 National Meeting & Exposition (Boston), and at the 2018 AIChE Annual Meeting (Pittsburgh), and will have another oral presentation at the 2019 AIChE Annual Meeting (Orlando).

<sup>2</sup> Zhang, X.; Blalock, B.; Huberty, W.; Chen, Y.; Hung, F.; Russo, P. S. Microbubbles and Oil Droplets Stabilized by a Class II Hydrophobin in Marinelike Environments. *Langmuir* **2019**, *35*, 4380-4386