

PRF# 56632-ND7

Project Title: Multi-Scale Modeling of Dynamics of Polymer Gels in Oil-Water Mixtures

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Polymer gels, in particular polyacrylamide (PAM) preformed particles gels, are widely used in enhanced oil recovery (EOR) applications.¹ We model the gel dynamics on multiple length scales. Using the Dissipative Particles Dynamics (DPD)², we focus on the interactions of the PAM gel particle with the oil-water interface at the nanoscale; using a continuum three dimensional gel Lattice Spring Model (gLSM)³, we focus on the dynamics of the mm-scale thermoresponsive gels in temperature gradients.

DPD simulations of PAM gels spreading at oil-water interfaces. We developed a DPD framework to simulate PAM gel network interacting with the oil-water interface. We designed the gel matrix as a diamond-like lattice,⁴ where the lattice points are occupied by the tetrafunctional crosslinks (MBAM) connected by the acrylamide polymer chains. The details of the model are given in the Ref.⁵ and are based on the model of PAM polymer chains proposed in Ref.⁶. We performed DPD simulations using LAMMPS simulation package.

The dynamics of the gel adsorption onto the oil/water interface is shown in Fig. 1. Initially, we equilibrate the gel sample in water and place it within the water phase away from the interface. The gel and oil beads are shown in red and green, correspondingly, and for clarity water beads are not shown. Periodic boundary conditions are applied in all directions. The size of the sample is chosen to be 3x3x3 diamond-like cells (as defined in Ref. ⁵) with $N_x=30$ polymer beads between the crosslinks.

Gel first docks onto the oil interface from the water keeping its original shape close to spherical and then begins spreading over the interface minimizing the number of the unfavorable contacts between the water and oil (Fig. 1a-c). The side (Fig. 1c) and the top (Fig. 1d) view of the gel show that it adopts a ‘pancake’-like shape at equilibrium.

To quantitatively characterize an extent of the gel spreading, we follow the evolution of its size and shape by calculating a radius of gyration, R_g , and a shape anisotropy, κ^2 (Fig. 1e). The shape anisotropy, κ^2 , is derived from the eigenvalues of the gyration tensor, S_p ,

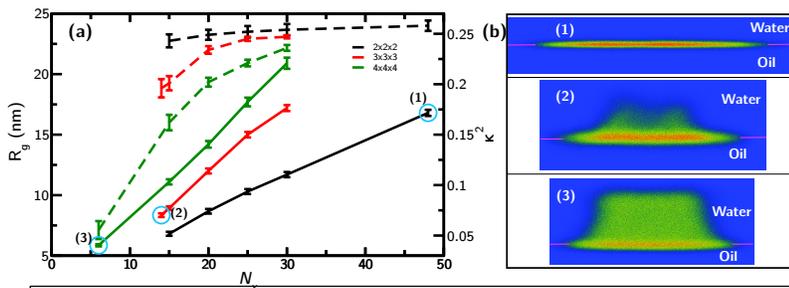


Fig. 2. (a) The shape anisotropy, κ^2 (dashed curves, right axis) and the radius of gyration, R_g , (solid curves, left axis) as a function of N_x . The circles correspond to the gel with the matching number of polymer beads. (b) The number density of gel in x-z plane integrated in y-direction.

via its first and second invariants ($I_1 = \lambda_1 + \lambda_2 + \lambda_3$ and $I_2 = \lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_3\lambda_1$) as $\kappa^2 = 1 - 3 \frac{I_2}{I_1^2}$. As long as the gel remains in the water phase, κ^2 remains close to zero, which corresponds to a shape close to spherical (Fig. 1e). As the gel approaches the interface and begins to spread over it, κ^2 increases until it reaches a value close to 0.25, which corresponds to a planar shape.

Fig. 2a summarizes the equilibrium values of the shape anisotropy, κ^2 and the radius of gyration, R_g , for the gels with various sizes and cross-link densities. The effect of the crosslink density can be clearly seen from the Fig. 2b, which shows equilibrium shapes of the gels from the most loosely cross-linked (top image) to the gel with the highest cross-link density (bottom image). The increase in the cross-link density increases an elastic contribution to the total energy of the gel, preventing

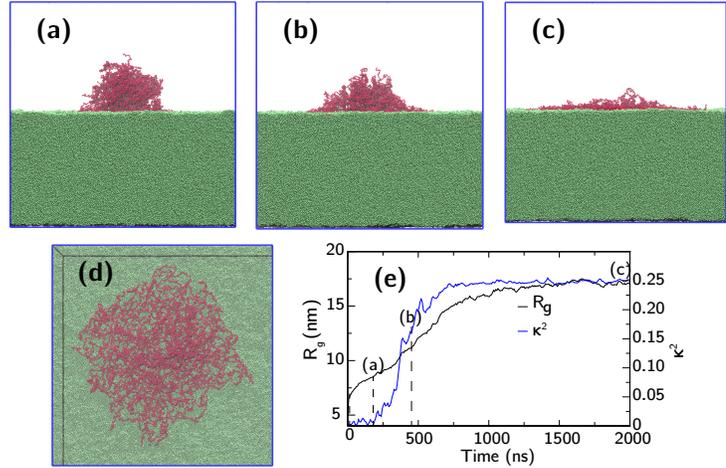
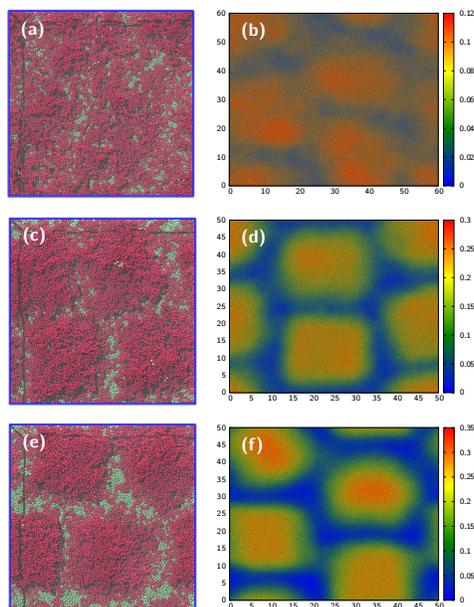


Fig. 1. Gel adsorption onto the oil/water interface at times: (a) 306 ns, (b) 452 ns, (c-d) 3064 ns. (e) Radius of gyration (R_g , black curve) and shape anisotropy (κ^2 , blue curve).



(low temperature gradient in (a) and high in (b)), the top view and a side view are shown. **Fig. 3.** Adsorption of multiple gels onto the interface. (a),(b), and (c) spreading of 2x2x2, 3x3x3 and 4x4x4 gel in a confined box, respectively.

Our results show that temperature gradient controls pattern formation; by variations in gradients one can tailor the surface topology of the confined hydrogels and their permeability.

Utilizing copolymers to increase the thermal stability of enzymes. Among the current EOR approaches is enzyme EOR or (EEOR)⁸. High temperatures in deep wells makes the thermal stability of the enzymes essential for these applications. Together with concurrent experimental studies, we focused on a novel conjugation approach that has a potential to be applicable to a wide range of enzymes.⁹ Our results show a significant increase in the structural stability of the lysozyme at high temperatures. We find that controlling the phase separation in the vicinity of the enzymes plays a critical role in improving their thermal stability.¹⁰

Different aspects of this work were presented by all the participants in the project: by O. Kuksenok at the invited lecture at ACS National Meeting, New Orleans, LA, March 18–22, 2018; by C. K. Choudhury at the MRS 2017 Fall Meeting, Boston, MA, Nov 26–Dec 1, 2017, and by Yao Xiong at the 2018 SEM Annual Conference, Greenville, SC, Jun 4–7, 2018.

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high extent of spreading over the interface and leading to the irregular shapes, which simultaneously maximize the coverage of the interface and hold the original shape of the portion of the gel remaining in water. Finally, we focus on the interfacial coverage in the case of multiple gels (Fig. 3). We show that the dynamics of spreading is affected by the interaction with the neighbors only in the cases of high coverage, which corresponds to the cases of loosely crosslinked gels (the number of polymer beads is kept constant and the cross-link density increases from the top to the bottom row in Fig.3).

Simulations of confined gels in temperature gradients. Herein we focus on understanding critical dynamics of three-dimensional gels on larger length scales. The initial size of the thermoresponsive gel membrane shown in Fig. 4 is $200\mu\text{m}\times 23\mu\text{m}\times 3\mu\text{m}$, the rest of the parameters are set as described in Ref.⁷ We use 3D gLSM³ to model these systems. We considered gels in heterogeneous confinements and in temperature gradients. Our studies show that for the samples constrained by the sidewalls along the long edges (Fig. 4), the types of patterns developing strongly depend on the magnitude of the temperature gradient. The color in Fig. 4 indicates an average polymer volume fraction across the membrane, with blue corresponding to the highest values. In both cases

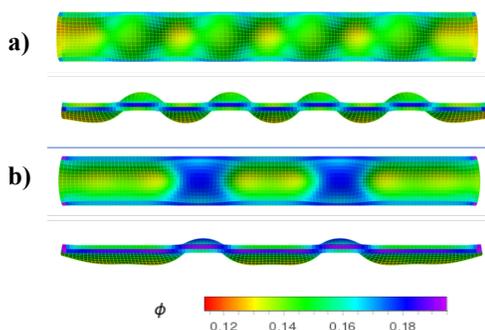


Fig. 4 Confined gel membrane in temperature gradients, $T_H=23^\circ\text{C}$ in (a) and 33°C in (b).