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XUAN DUY THAO NGUYEN

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BY THE COMMITTEE CONSISTING OF

Dr. Dimitrios V. Papavassiliou, Chair

Dr. Sepideh Razavi, Co-Chair

Dr. Edgar A. O'Rear III

Dr. Bin Wang

Dr. Prakash Vedula

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Abstract

The stability of interfaces in the presence of surface-active agents such as surfactants and nanoparticles (NPs) is imperative in various industrial and environmental contexts. These include separation processes, enhanced oil recovery, and environmental remediation, highlighting the significance of interface stability in diverse scenarios. In stabilizing oil-water interfaces, surfactants and NPs play a vital role, but with different mechanisms in each case. NPs affect interfacial behavior by reducing the interfacial area, whereas surfactants lead to a reduction in interfacial tension of the oil-water system. Although many studies have concentrated on equilibrium conditions without considering fluid flow, industrial applications typically involve displacing immiscible fluids. Therefore, there is a need to explore the impact of flow conditions on the properties of the oil-water interface, especially in the context of the presence of surfactants and NPs. In this thesis, we investigated the effect of anionic surfactant (sodium dodecylsulfate, SDS) and nonionic surfactant (octaethylene glycol monododecyl ether, C12E8) on the oil-water interface by using Dissipative Particle Dynamics (DPD) simulation methods. In particular, SDS represented the case of a short surfactant molecule on the interface, while C12E8 was a longer molecule. Surfactants are in conjunction with NPs (homogeneous and anisotropic particles) either on the flow of oil and water in a narrow channel under Poiseuille or Couette flow conditions.

It is important first to verify the integrity of the computations by comparing the velocity profile resulting from simulations of Poiseuille and Couette flows to theoretical expectations. Based on this approach, satisfying the no-slip boundary conditions required the following: (1) creating frozen solid walls, (2) applying the bounce-back boundary condition, and (3) determining the DPD parameters necessary for ensuring that the boundary conditions were obeyed, that the oil and water viscosities were represented correctly. Moreover, the effects of surfactants at the oil-water interface and the interfacial instability under shear were investigated. A critical shear rate was found for Poiseuille flow, beyond which the surfactants desorb from the interface, forming micelles and destabilizing the interface. The surfactant-covered interface remained stable under Couette flow even at high shear rates. Besides the flat interface of oil and water, the motion of an oil droplet with and without the presence of surfactants and Janus particles (JPs) under shear was studied.

In certain cases, oil droplets are observed to be mobilized along a solid surface. To describe this phenomenon, simulations were conducted that modeled the movement of oil droplets along

solid walls. The presence of surfactants at the oil droplet surface led to the most considerable migration velocity and displacement observed under Couette flow. The surfactants affect the interfacial tension, enhancing the momentum transfer from the water to the oil and reducing the oil–water slip. When the surfactant concentration is relatively low, the effects of Marangoni stress are overwhelmed by the flow field. Concerning Janus particles (JPs), they impede the migration of droplets. This is attributed to a weaker interaction between Janus particles and the solid wall in the presence of surfactants. Consequently, the coexistence of surfactants and JPs results in a more significant displacement than in bare oil because of the smaller interfacial tension.

Additionally, the anticipation of fingering is crucial when addressing the displacement of immiscible fluids, as viscous fingering is prevalent in the oil and gas industry. This phenomenon occurs when oil and water move together in porous media close to reservoir wells, but water moves more readily than oil, leading to instabilities and the development of water fingers. While the viscous fingering phenomenon has been investigated for bare oil-water systems, the effects of surfactants or particles at the oil-water interface are yet to receive detailed investigation. Our simulations involve injecting water into an oil-filled channel to displace the oil with different types of NPs (including homogeneous particles and amphiphilic JPs), surfactants, or both JPs and surfactants before pushing the oil forward. JPs exhibiting a dual chemistry, with a polar face featuring a contact angle θ_p and an apolar compartment characterized by a contact angle θ_A , inherently possess an amphiphilic nature. The degree of amphiphilicity of JPs, denoted by $\Delta\theta = (\theta_A - \theta_p)/2$,¹ is controlled during the computations so that the range is from zero to 47.8°. The computation results suggest that an oil droplet attached to a channel wall exhibits the greatest migration distance when only surfactants are presented at the interface. The droplet demonstrates the least migration in the presence of particles alone, regardless of their wetting characteristics. The re-arrangement of the surfactant molecules and the NPs at the interface, generating weak Marangoni stresses, plays a role in the motion of the drop. The instability of the oil-water meniscus arises from water flow, resulting in fingering phenomena before the eventual full detachment of the oil drop from the channel wall. The appearance of fingers depends on the presence of NPs or surfactants, with the particles leading to longer fingers at the same fluid velocity. A critical contact angle appears to dictate the detachment of the oil droplet from the channel wall, and this remains constant whether particles are present or not. When the oil drop detaches fully from the channel

walls, the particles and the surfactant molecules reorient on the interface, modifying the shape of the droplet.

Last but not least, investigating the desorption energy of NPs at the interface of oil and water phases in the presence of surfactants and/or NPs is vital for numerous applications across various industries. The presence of surfactants alters the interfacial properties, potentially influencing the desorption behavior of NPs. Both surfactants and NP have the potential to influence the behavior of interfacial properties, which lead to variations in the desorption energy required for NPs to detach from the interface. In addition, while many studies overlook specific interactions between particles and surfactants, it is notable that surfactants can indeed interact with the surface of NPs, potentially influencing desorption energy. Hence, careful consideration of the interplay between surfactants and NPs is essential in the study of desorption energy. The thesis seeks to gain insights into the energy needed to detach a NP (including the homogeneous particle and amphiphilic JP) from the oil-water interface with the presence of NPs, and surfactants, as well as their coexistence, into one of the homogeneous phases. When examining the desorption energies of individual particles with the center of NPs as they traverse the oil-water interface, it is observed that the presence of surfactants can reduce the energy requirement, whereas the presence of NPs may lead to a challenging trend. Regarding the effect of NP type, hydrophilic NPs are favored in the water phase due to their lower desorption energy compared to the significantly higher energy required in the oil phase. Conversely, hydrophobic NPs exhibit an opposite trend. In the case of Janus NPs, the desorption energy level lies between those of homogeneous NPs.

These findings will be focused on exploring the mechanism of stabilizing the interface between oil and water using NPs and surfactants, as well as the potential implications for tuning oil and water interfacial behavior.

Chapter 1. Introduction

1.1 Immiscible fluid displacement

The displacement of immiscible fluids is a phenomenon widespread in various natural,^{2, 3} and engineered systems, with profound implications across numerous scientific disciplines and industrial applications.^{4, 5} From the migration of oil and water through porous geological formations to the manipulation of fluids in enhanced oil recovery techniques,⁶ understanding the dynamics and mechanisms of immiscible fluid displacement is significantly necessary. This process involves the displacement of one fluid phase by another that does not mix with it, leading to the complex interaction of fluid behavior at the interface. The study of immiscible fluid displacement not only clarifies the fundamental principles governing fluid flow but also holds significant relevance in fields such as environmental remediation,⁷ and biomedical sciences, especially in petroleum engineering when chemicals and water displace viscous oils.^{8, 9} In this thesis, exploring the details of immiscible fluid displacement displays opportunities for optimizing processes, mitigating environmental risks, and affecting enhanced oil recovery processes. Therefore, it becomes essential to pay attention to the study of immiscible fluid displacement.

Additionally, most studies have focused on the simple case with only two immiscible fluids in the system; in practical applications, different types of chemicals are transported with oil and water, such as surfactants, polymers, and nanoparticles (NPs). Interfacial systems comprising fluids and surface-active agents find a wide range of applications in drug delivery, food science, and the chemical industry. These systems commonly incorporate surfactant molecules and/or colloidal particles. There needs to be a careful examination of additives and impurities that could act as surface-active agents.

1.2 Surfactants

Surfactants are one of the surface-active agents that typically exhibit amphiphilic characteristics. This means that each molecule includes both a hydrophilic "water-seeking" group (the head), and a hydrophobic "water-repelling" group (the tail). When surfactant molecules are added at the oil-water interface, they tend to orient themselves with their hydrophilic heads facing toward the water phase and their hydrophobic tails facing toward the oil phase. This arrangement allows the surfactant molecules to form a monolayer at the interface, effectively shielding the oil and water from each other. As a result, the surfactant molecules disrupt the interaction forces between the oil and water molecules at the interface, reducing the interfacial tension (IFT). In

addition, there is a notable reduction in IFT, and the presence of surfactants contributes to the stabilization of emulsions,^{10, 11} alters the wettability of reservoir rocks, and facilitates the mobilization of trapped oil. Therefore, surfactants hold significance in both scientific research and industrial applications, such as the recovery and purification of raw material in the mining and petroleum sectors to enhance oil recovery (EOR) by improving the oil recovery rate and extending the productive lifespan of oil reservoirs.

There are several experimental methods to measure interfacial tension in fluid-fluid systems, such as direct measurement using a microbalance, measurement of capillary pressure, analysis of the balance between capillary and gravity forces, and analysis of gravity-distorted drops.¹² In this thesis, the IFT values (γ) with the interfacial regions arranged along the z -direction were calculated following the Kirkwood–Buff relation,¹³ expressed as

$$\gamma = \frac{1}{2} L_z \left[P_{zz} - \frac{1}{2} (P_{xx} + P_{yy}) \right] \quad (1.1)$$

where P_{xx} , P_{yy} and P_{zz} are the diagonal components of the pressure tensor, and L_z is the domain length in the z -direction.

The Critical Micelle Concentration (CMC) is the concentration of surfactant in a solution at which micelles begin to form spontaneously.¹⁴ At concentrations below the CMC, surfactant molecules exist as monomers dispersed in the solvent. However, as the concentration of surfactant molecules increases and exceeds a critical value, micelles begin to form in a solution (see **Figure 1.1**). Determining the CMC accurately is important for optimizing surfactant formulations, and selecting surfactant concentrations that maximize performance while minimizing costs, and reducing environmental impact.

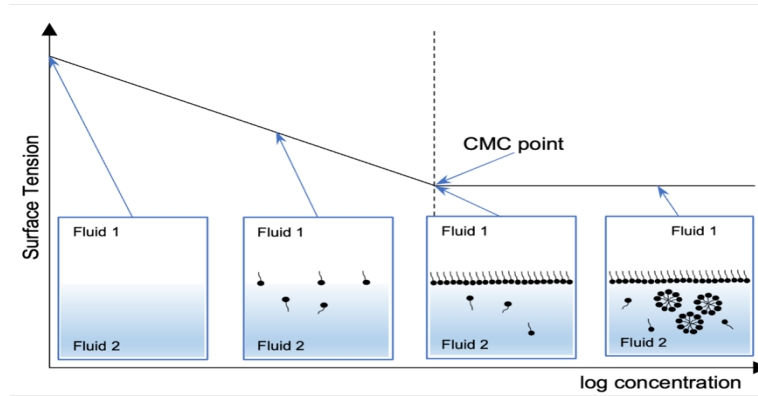


Figure 1.1. Surface tension of a surfactant solution with increasing concentration, formation of micelles

1.3 Nanoparticles

Nanoparticles (NP) also affect interfacial behavior. Because of their size, nanoparticles have a larger surface area per volume than large-scale materials and high chemical reactivity and are widely used in different areas such as transportation, medicine, food safety, energy, and environmental science.¹⁵ They are particularly appealing for enhancing oil recovery due to their distinct properties, including altering wettability, improving the mobility of trapped oil, enhancing sand consolidation, and reducing IFT.¹⁶ Vafaei et al.¹⁷ computed the effective gas-liquid surface tension in the case of nanofluids by solving the Laplace-Young equation. The study reported that the surface tension is a function of both concentration and particle size. The surface tension decreases with an increase in the nanoparticle concentration until a saturation phenomenon is reached. At this point, the surface tension cannot further decrease and an opposite trend starts to develop. Additionally, NPs are resistant to degradation in oil and gas reservoirs at high salinity and high temperature.¹⁸ These properties make them suitable for various EOR approaches. Ehtesabi et al.¹⁹ discovered that the 0.01% anatase TiO₂ NP solution demonstrated a remarkable capacity to retrieve 80% of the oil after the injection of two pore volumes. In contrast, water only succeeded in recovering 49%. The mechanism is attributed to a wettability shift favoring water wetness. The research in glass micromodel flooding systems conducted by Li et al.²⁰ exhibited that silica NPs can reduce the IFT between the oil-water interface, resulting in an enhancement in oil recovery, about 4-5% higher compared to brine flooding. In addition, Li and Tors ter²¹ studied the transportation and adsorption behaviors of various types of silica NPs through the porous media. From their results, it was found that the hydrophilic silica nano-structure particles (NSP) have a better adsorption ability compared to hydrophilic silica colloidal nanoparticles (CNP). The energetic difference when such a particle (of radius R) transitions from the bulk to the fluid-fluid interface is expressed as²²

$$\Delta E = \pi R^2 \gamma_{ow} (1 \pm \cos \theta_E)^2 \quad (1.2)$$

where R is the radius of the particle, and θ_E is the equilibrium contact angle of a particle at a fluid interface. The sign preceding the cosine is negative when referring to nanoparticle displacement into the water phase and positive when denoting displacement into the oil phase. From the thermodynamic aspect, the free energy change due to the adsorption of a nanoscale particle is on the order of $\sim k_B T$ (where k_B is the Boltzmann constant).²²

Janus nanoparticles (JP) are colloidal particles characterized by having two distinct surface regions or functionalities. These regions can have different chemical compositions, surface charges, or wetting properties. The name "Janus" comes from the Roman god with two faces, symbolizing the dual nature of these particles. Their distinctive structure permits selective functionalization on either side, facilitating customized interactions with diverse surfaces. JPs can enhance the stability of air-water or oil-water interfaces compared to homogeneous particles, and indeed, JPs exhibit more efficient adsorption to interfaces.²³ For example, JPs can be used as effective surfactants owing to their exceptional adsorption at the interface, leading to enhanced emulsion polymerizations as discussed in the research conducted by Walther et al.²⁴ The polar face of the JP is in contact with the aqueous phase, whereas, an apolar face is entirely in contact with the oil phase.

Furthermore, the complexity arises from the differing affinities of JPs dual surfaces for each fluid phase, resulting in complicated behavior at the fluid-fluid interface and differences in the calculation of adsorption energy compared to the homogeneous nanoparticle. The energy required to desorb JPs from a flat oil-water interface to a single fluid phase is described as follow:²⁵

$$\Delta E_{WI} = -\gamma_{OW}(S_{AO}\cos\theta_A + S_{PO}\cos\theta_P - S_I) \quad (1.3)$$

$$\Delta E_{OI} = \gamma_{OW}(S_{AW}\cos\theta_A + S_{PW}\cos\theta_P + S_I) \quad (1.4)$$

where γ_{OW} is the interfacial tension between oil and water; S_{AO} , S_{PO} , S_{AW} , S_{PW} are the area of the apolar and polar regions on the JP that are in contact with the oil phase (O) or water phase (W); θ_A and θ_P are the three-phase contact angles of polar and apolar particles; S_I is the area of the oil-water interface occupied by the particle when it is located at the interface.

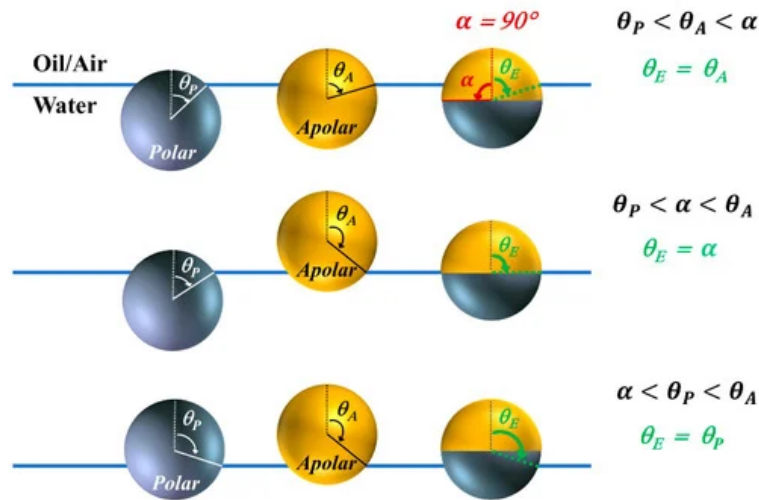


Figure 1.2. Equilibrium arrangements of a Janus particle positioned at a fluid-fluid interface ²⁶

The minimization of the free energy depends on the relation between three angles θ_A , θ_P , and α , and can have three possibilities as shown in **Figure 1.2**.

- $\theta_P < \theta_A < \alpha$, the equilibrium angle $\theta_E = \theta_A$
- $\theta_P < \alpha < \theta_A$, the equilibrium angle $\theta_E = \alpha$
- $\alpha < \theta_P < \theta_A$, the equilibrium angle $\theta_E = \theta_P$

For a spherical Janus particle the desorption energy required for NP move from the interface to the oil phase or water phase is presented by Jiang et al.²³ They assumed that Janus particles have the wettability separation line parallel to the interface, with no consideration given to their rotational dynamics. Then, the desorption energy (E_I) can be expressed as follows:

- $\theta_P < \alpha < \theta_A$

$$\Delta E_{WI} = 2\pi R^2 \gamma_{OW} [-\cos\theta_A(1 - \cos\alpha) + 0.5\sin^2\alpha] \quad (1.5)$$

$$\Delta E_{OI} = 2\pi R^2 \gamma_{OW} [\cos\theta_P(1 + \cos\alpha) + 0.5\sin^2\alpha] \quad (1.6)$$

- $\theta_P < \theta_A < \alpha$

$$\Delta E_{WI} = -2\pi R^2 \gamma_{OW} [(1 - \cos\theta_E)\cos\theta_A - 0.5\sin^2\theta_E] \quad (1.7)$$

$$\Delta E_{OI} = 2\pi R^2 \gamma_{OW} [\cos\theta_P(1 - \cos\alpha) + 0.5\sin^2\theta_E + \cos\theta_A(\cos\theta_E + \cos\alpha)] \quad (1.8)$$

Several studies have been conducted to compare the analysis of the dynamics of homogeneous and Janus particles at fluid-fluid interfaces, employing methods not only experiment^{27, 28} but also simulation methods such as molecular dynamics,²⁹ dissipative particle dynamics,³⁰ or Monte Carlo simulations.³¹

1.4 The coexistence of surfactants and nanoparticles

The coexistence of surfactant and nanoparticles on the fluid-fluid interface is more complicated than other physical processes, while having a broad range of applications in energy and environmental areas. Hence, many studies have been developed.³²⁻³⁴ While both surfactants and NPs can stabilize oil-water interfaces, their respective mechanisms vary, with the combined presence of NPs and surfactants at liquid-liquid interfaces demonstrating enhanced interfacial properties compared to either component acting alone. There are many studies that have been conducted regarding the effects of the presence of NPs and surfactants on oil-water interfacial behavior.

Nourafkan et al.³⁵ used NPs (TiO_2) as carriers for mixtures of anionic and nonionic surfactants to control the delivery of surfactants to the oil-water interface in EOR applications. As a result, the NPs reduced the surfactant adsorption on a sandstone rock surface, leading to increased oil recovery compared to chemical flooding with surfactants alone. Vu et al.³⁶ discussed the impact of NP surface chemistry on its adsorption onto a flat interface of an oil-surfactant-water system. They concluded that maintaining a constant surfactant concentration while introducing NPs resulted in decreased IFT; however, in the absence of surfactant, NPs did not affect the IFT. Tanvir et al.³⁷ investigated the impact of nonionic surfactants (sorbitan oleate) on the surface tension of ethanol and n-decane with the presence of nanofluid fuels containing suspended aluminum (Al), aluminum oxide (Al_2O_3), and boron (B) NPs. The experimental results show that at high particle concentrations, the surface tension will increase with particle concentration for all scenarios because of the increasing Van der Waals force between the accumulated particles. Luo et al.³⁸ observed that while the interfacial tension between water and trichloroethylene decreases with higher sodium dodecyl sulfate (SDS) surfactant concentrations, it remains unaffected by changes in NP concentration. Hence, the surfactants competitively dominate the interface, resulting in the depletion of NPs from the interfaces. The difference in the effect of NP and surfactant coexistence on IFT depends on the interaction between surfactant molecules, NPs, and the oil-water interface. When surfactant molecules are strongly adsorbed onto the NP surface, the surfactant concentration at the interface decreases, leading to an increase in IFT compared to the surfactant-only case. This is because of the reduced availability of surfactant molecules at the interface. Conversely, when NPs are present at the oil-water interface, a decrease in IFT is observed. This occurs because the NPs occupy space at the interface, reducing the available interfacial area for surfactant molecules to adsorb. As a result, the concentration of surfactants increases, effectively lowering the IFT. However, if the NPs settle within either the oil or water phase rather than at the interface, they do not significantly affect the IFT between the two phases. In this scenario, surfactants are the main factor influencing the IFT behavior whereas the NPs are not directly interacting with the interface.

Moreover, combining surfactants with NPs can lead to intriguing alterations in the wetting properties of surfaces, as well as influencing phase behavior and interparticle interactions at the oil-water interface. For example, NPs can enhance surface hydrophobicity or hydrophilicity, depending on the specific functional groups attached to their surface, thereby tailoring the wetting behavior of the interface. Tang et al.³⁹ investigated the influence of NPs and surfactants on the

stability and rheological behavior of polymeric nanofluids. Their findings show that the addition of NPs altered the wettability of the reservoir rock, thus changing the distribution and flow of fluid in the reservoir while the surfactants helped NPs to disperse well in the polymer solution. Harikrishnan et al.⁴⁰ have performed experiments regarding the spreading dynamics of nanocolloidal suspensions in the absence and presence of surfactants. They observed that in the case of combined colloidal systems, the dominance of surfactant-driven spreading dynamics has been noted despite the presence of both particle and surfactant effects. Zargartalebi et al.⁴¹ identified the influence of hydrophilic and slightly hydrophobic silica NPs on the properties of SDS anionic surfactant solutions, particularly focusing on surfactant interfacial and equilibrium adsorption behaviors. They found that adding a small amount of SDS resulted in stable NP suspensions, which could potentially enhance oil recovery processes.

In addition, interparticle interactions at the oil-water interface can also be significantly modified by the presence of NPs and surfactants. The effects of surfactants on controlling the final NP self-assembly were discussed in the study conducted by Crivoi et al.⁴² The added hexadecyltrimethylammonium bromide (CTAB) surfactant enlarges the positive surface charge of particles, so the repulsive force is enhanced and the ring pattern is generated. Surfactants play a vital role in preventing particle-particle agglomeration, ensuring the well-dispersion of nanofluids. Therefore, understanding the interplay between surfactants and NPs at the fluid-fluid interface is essential for designing advanced materials with tailored interfacial properties. This knowledge is valuable across various fields, where precise control over interfacial phenomena is critical for product performance and functionality.

1.5 Research Motivation

The behavior of surface-active agents, including surfactants and NPs, at the oil-water interface under non-equilibrium conditions is expected to exhibit distinct mechanisms compared to equilibrium conditions. Despite previous research efforts, there is still uncertainty regarding the interactions between surfactants and NPs at the oil-water interface. This uncertainty likely stems from the complexity of the systems involved, which include multiple components interacting simultaneously. Furthermore, we anticipate that the effectiveness of surface-active agents in stabilizing the interface and promoting emulsification will be influenced by factors such as shear rate, velocity profile, and composition gradients, highlighting the importance of understanding

their behavior in dynamic environments. Therefore, there are several specific problems that we aim to address in this thesis.

- Explore the model of non-equilibrium conditions, including Poiseuille and Couette flow phenomena. Validate simulation parameters by comparing them to theoretical expectations of bulk phase viscosities and velocity profiles within the multifluid system. The dynamic behavior of surfactants at the flat oil-water interface is also investigated.
- Investigate the presence of surface-active agents at the oil droplet interface, particularly within the context of oil droplet transport in nanochannels with solid walls that serve as rock surfaces. By simulating these processes, the dynamics of oil droplet movement and the role of surface-active agents in influencing transport behavior were studied.
- Illuminate the individual and combined behaviors of surfactants and/or different types of NPs at the oil-water interface during the displacement of two immiscible fluids within a nanochannel. Additionally, elucidates how their combined presence influences interfacial behavior and the shape of the fluid-fluid interface.
- Explore the role of NP jamming, surfactants, or the combination of NPs and surfactants located at the fluid-fluid interface on the desorption energy of NPs as they move through the bulk phase in enhancing oil recovery processes.

In addressing the identified problems related to the effects of surface-active agents on the oil-water interface under non-equilibrium conditions, we propose to use the Dissipative Particle Dynamics (DPD) simulations as a computational approach. DPD offers a coarse-grained representation of molecular systems, allowing for the investigation of dynamic phenomena at the molecular level. The details of the computational method are described in Chapter 2. The model of non-equilibrium conditions and simulation parameters for the multifluid system are studied in Chapter 3. The dynamic interface behavior of oil-water-surfactants is also discussed in this chapter with the micelle formation at a critical shear rate. The effects of surfactants, NPs and their concurrent presence at the oil-water interface on the migration of an oil droplet is discussed in Chapter 4. In Chapter 5, we explore interparticle interactions among NPs positioned at the meniscus of the oil-water interface under non-equilibrium conditions. We revealed the mechanism and the behavior of NPs when they rearrange themselves on the oil-water interface when the detachment occurs. The effect of surfactants, the coexistence of NPs and surfactants, and the wettability of solid walls on immiscible fluid displacement, resulting in fingering behavior are

studied in detail in Chapter 6. We calculated the lengths of fingers as a function of the Capillary number (Ca) to predict meniscus stability. The desorption energy of NPs as they move through the bulk phase is described in Chapter 7. In Chapter 8, the summary and recommendations for future investigation are presented.

Chapter 2. Dissipative Particle Dynamics

2.1 Force Field

Instead of individual atoms, DPD models represent clusters of molecules.⁴³ By Newton's equation of motion, it is possible to calculate the position and velocity of each DPD particle, which is often called a bead. The governing equations are as follows:

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i, \quad (2.1)$$

$$m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R), \quad (2.2)$$

where $\mathbf{r}_i$, $\mathbf{v}_i$ are the position and velocity vectors, respectively, m_i is the mass of bead i , and $\mathbf{f}_i$ is the force vector acting on bead i . The total force exerted between two DPD particles i and j includes three components: the conservative ($\mathbf{F}_{ij}^C$), dissipative ($\mathbf{F}_{ij}^D$), and random ($\mathbf{F}_{ij}^R$) forces⁴⁴. The conservative force $\mathbf{F}_{ij}^C$ is a soft repulsion acting along the line of the centers and can be calculated as follows:

$$\mathbf{F}_{ij}^C = \begin{cases} a_{ij} \left(1 - \frac{r_{ij}}{r_c}\right) \hat{\mathbf{r}}_{ij} & \text{for } r_{ij} < r_c \\ 0 & \text{for } r_{ij} \geq r_c \end{cases} \quad (2.3)$$

where a_{ij} is a maximum repulsion between beads i and j which controls the type of fluid interactions, $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, $\hat{\mathbf{r}}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/r_{ij}$, $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, and r_c is the cut-off radius indicating the distance over which a bead can affect its neighbors.

The dissipative or drag force, $\mathbf{F}_{ij}^D$, on beads i and j , is given by

$$\mathbf{F}_{ij}^D = -\gamma w^D(r_{ij}) (\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij}) \hat{\mathbf{r}}_{ij} \quad (2.4)$$

where γ represents the friction coefficient, w^D is an r -dependent weight function:

$$w^D(r_{ij}) = \begin{cases} (1 - r_{ij})^2, & \text{for } r_{ij} < r_c \\ 0, & \text{for } r_{ij} \geq r_c \end{cases} \quad (2.5)$$

The random force, $\mathbf{F}_{ij}^R$, can be determined by

$$\mathbf{F}_{ij}^R = \sigma w^R(r_{ij}) \theta_{ij} \hat{\mathbf{r}}_{ij} \quad (2.6)$$

where w^R is also an r -dependent weight function, σ controls the amplitude of random motion⁴⁵ and the term θ_{ij} is a Gaussian white noise function that is calculated as

$$\langle \theta_{ij}(t) \rangle = 0, \quad \langle \theta_{ij}(t) \theta_{kl}(t') \rangle = (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \delta(t - t') \quad (2.7)$$

where t is time and δ_{ij} is the Kronecker delta and $\delta(t - t')$ is the Dirac delta function.⁴⁶

As Espanol and Warren demonstrate,⁴⁶ the weight functions w^D and w^R are related to each other and to the dissipation parameters:

$$w^D(r) = [w^R(r)]^2 \quad (2.8)$$

and

$$\sigma^2 = 2\gamma k_B T \quad (2.9)$$

where T is the system temperature, and k_B is the Boltzmann constant.

2.2 Scaling factors

The particle mass, the temperature, and the cut-off radius (r_c) were chosen as the units of mass, energy, and length within the DPD simulations, so that $m = r_c = k_B T = 1$. Further, the bead number density was selected as $\rho = 5$ beads per unit volume. Using these parameters, the time scale was determined as $\tau = r_c \sqrt{m/k_B T}$.⁴⁷ For example, five water molecules or six water molecules were lumped together into one water bead, the mass scale, length scale, and time scale are shown in **Table 2.1**.

Table 2.1. Scaling factors for DPD computations

Density	Number of water molecules in one bead	Mass scale (10^{-25} kg)	Length scale (10^{-10} m)	Temperature scale (K)	Time scale (10^{-12} s)
5	5	1.5	9.09	298	5.48
5	6	1.8	9.66	298	6.38

2.3 Periodic boundary conditions

In this thesis, we aim to model a macroscopic system through an approximation wherein a small part of the macroscopic system represents the whole system, thus reducing the number of atoms in the simulation box. However, this approximation may lead to undesirable effects, with the edge effect being the most notable. In simulations bounded by finite boundaries, particles near the edges may experience different interactions compared to those in the bulk due to the absence of neighboring particles beyond the boundary. To minimize these edge effects, a periodic boundary condition (PBC),⁴⁸ can be used to ensure that each particle interacts with a consistent environment, regardless of its position within the simulation box. In detail, the single simulation cell is infinitely

replicated in the three Cartesian dimensions once the periodic boundary condition is applied. As a consequence, when a particle exits the simulation cell, it re-enters from the opposite side, maintaining a constant total number of particles in each cell (see **Figure 2.1**). Overall, periodic boundary conditions are a fundamental aspect of DPD simulations, enabling the study of large-scale systems while minimizing boundary effects, maintaining the representativeness of the simulated environment, and reducing the computational cost.

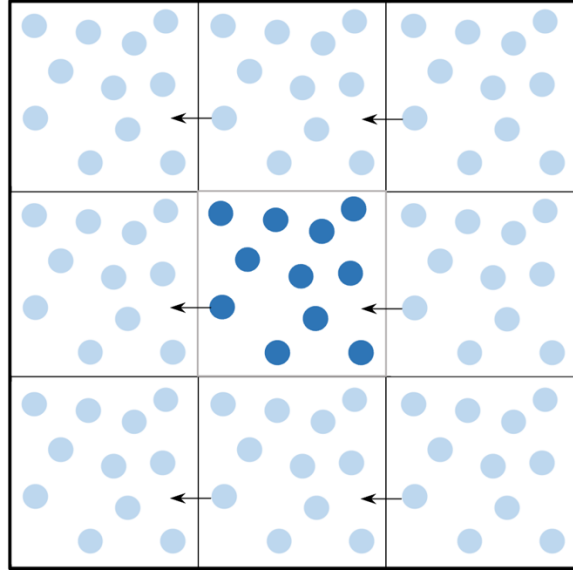


Figure 2.1. Periodic boundary conditions. Applying periodic boundary conditions in one dimension is equivalent to replicating the simulation cell (displayed in gray) in that dimension.

In the figure, the cell is periodic in two dimensions.

2.4 No-slip boundary condition

The no-slip boundary condition at the walls needs to be obeyed for fluid flow in a nano channel. The solid walls were created by freezing the DPD wall beads, while bounce-back boundary conditions were used on the surface of the walls to prevent any fluid (water or oil) beads from penetrating into the solid domain. Since the soft potential used in DPD does not prevent penetration, one needs to be aware of this issue. Therefore, the no-slip boundary condition was obtained by satisfying three conditions: (1) freezing the DPD beads of the walls relative to each other to create solid walls, (2) applying bounce-back boundary conditions not exactly at the walls but at a distance of 0.1 DPD unit away from the walls to prevent fluid beads from moving through the solid domain, and (3) increasing the friction coefficient for the solid-fluid interactions to be twice that of the fluid-fluid.

2.5 Umbrella sampling for free energy calculations

The umbrella sampling method, developed by Torrie et al.,⁴⁹ is a powerful technique used in enhanced sampling methods, to overcome barriers and explore rare events in complex systems. The fundamental idea behind umbrella sampling is to use a biasing potential to sample different simulations (windows) along the chosen reaction coordinate. This potential usually takes the form of a harmonic restraint that guides the system along the desired reaction coordinate.

The external bias potential ω_i of the window i is added to the simulated system, which depends only on the reaction coordinate ξ :

$$E^b(r) = E^u(r) + \omega_i(\xi) \quad (2.10)$$

where $E^b(r)$ is the potential energy of the biased simulation, $E^u(r)$ is the potential energy of the unbiased simulation.

In each window, a bias function is applied to keep the system close to the reference point ξ_i^{ref} of the respective window i . K is a force constant defining the restraint potential. The harmonic bias potential added to the system is expressed as

$$\omega_i(\xi) = \frac{K}{2} (\xi - \xi_i^{ref})^2 \quad (2.11)$$

In many cases, a reaction coordinate (ξ), a continuous parameter that provides a distinction between two thermodynamic states, can be defined. The probability distribution $Q(\xi)$ of the system along ξ can be calculated according to

$$Q(\xi) = \frac{\int \delta[\xi(r) - \xi] \exp(-\beta E) d^N r}{\int \exp(-\beta U) d^N r} \quad (2.12)$$

where E is the potential energy, $\beta = \frac{1}{k_B T}$.

In order to calculate the unbiased free energy, we need to obtain the unbiased distribution of the reaction coordinate, according to the following equation:

$$P_i^u(\xi) = \frac{\int \delta[\xi^{ref}(r) - \xi] \exp[-\beta E(r)] d^N r}{\int \exp[-\beta E(r)] d^N r} \quad (2.13)$$

The unbiased probability $P_i^u(\xi)$ could be determined by:

$$P_i^u(\xi) = P_i^b(\xi) \exp[\beta \omega_i(\xi)] \exp[-\beta \omega_i(\xi)] \quad (2.14)$$

The free energy of the window could be conducted by:

$$E^u(r) = -\left(\frac{1}{\beta}\right) \ln P_i^b(\xi) - \omega_i(\xi) + F_i \quad (2.15)$$

with

$$F_i = -k_B T \ln \langle \exp[-\beta \omega_i(\xi)] \rangle \quad (2.16)$$

Finally, the unbiased free energy could be combined by all the windows to generate the complete free energy landscape along the reaction coordinate.

In brief, the change in free energy within each window is calculated from the sampled distribution along the reaction coordinate, with the purpose of creating more uniform probability distributions, and the construction of histograms to represent the distribution of positions along the conformational pathway. An illustrative depiction of the umbrella sampling process is presented in **Figure 2.2**. If the overlap between their tails is sufficient, the free energy along any path in conformation space, known as the Potential of Mean Force (PMF), can be determined from these histograms through a technique known as the Weighted Histogram Analysis Method (WHAM).

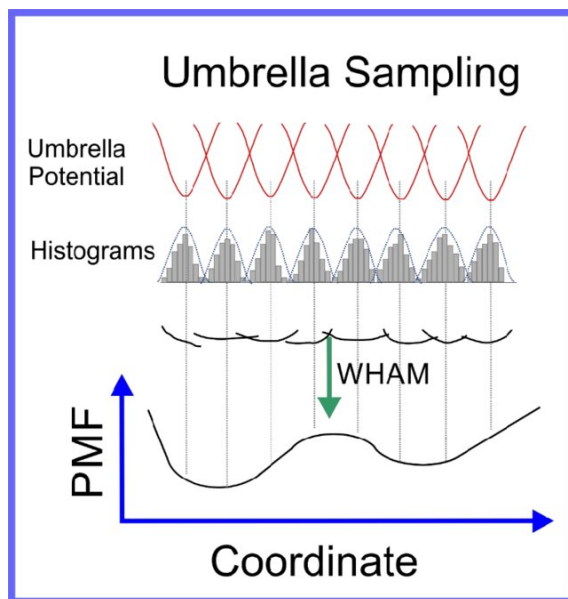


Figure 2.2. Schematic representation of umbrella sampling algorithm.⁵⁰

2.6 Software Package

To perform all calculations, the software package Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)⁵¹ was used in our study. A visual molecular dynamics (VMD) software program was used to visualize the system snapshots.⁵² The three-phase contact angle of a drop on a flat surface is calculated based on its density profile and using the sphere, ellipse, and

sphere approximations by using ImageJ software.⁵³ The PMFs are calculated by using the weighted histogram analysis method (WHAM) as implemented by Grossfield.⁵⁴

Chapter 3. Coarse-Grained Modeling of Multiphase Flows with Surfactants

Abstract*

Coarse-grained modeling methods allow simulations at larger scales than molecular dynamics, making it feasible to simulate multifluid systems. It is, however, critical to use model parameters that represent the fluid properties with fidelity under both equilibrium and dynamic conditions. In this work, dissipative particle dynamics (DPD) methods were used to simulate the flow of oil and water in a narrow slit under Poiseuille and Couette flow conditions. Large surfactant molecules were also included in the computations. A systematic methodology is presented for determining the DPD parameters necessary for ensuring that the boundary conditions were obeyed, that the oil and water viscosities were represented correctly, and that the velocity profile for the multifluid system agreed with theoretical expectations. Surfactant molecules were introduced at the oil-water interface (sodium dodecylsulfate and octaethylene glycol monododecyl ether) to determine the effects of surface-active molecules on the two-phase flow. A critical shear rate was found for Poiseuille flow, beyond which the surfactants desorb from the interface, and affecting the stability of the interface by forming micelles; the surfactant-covered interface remained stable under Couette flow even at high shear rates, while Couette flow was stable even at high shear rates.

3.1 Introduction

The interfacial behavior of immiscible fluids is important for understanding, predicting, and controlling systems that involve oil–water or oil–gas flows. Multilayer coating applications, separation applications, environmental remediation of contaminated regions in the subsurface, and petroleum engineering applications for oil mobilization are examples where such flow systems are important.⁵⁵⁻⁵⁸ In addition to experiments, computations that are focused on the molecular scale, such as molecular dynamics (MD) simulations, can be used as tools to probe multifluid flows, flows with large molecules (i.e., polymers or surfactants), particulate flows, and interfacial phenomena.⁵⁹⁻⁶² However, MD techniques are computationally expensive and even unfeasible when investigating large-scale systems or systems with very large molecules because of the very small length and time scales employed (on the order of Angstroms and femtoseconds,

* Material in this chapter has been published in Nguyen, T. X., Vu, T. V., Razavi, S., & Papavassiliou, D. V. (2022), *Polymers*, 14(3), 543.

respectively). In contrast to MD, coarse-grained modeling techniques, such as dissipative particle dynamics (DPD), can meet the need for larger particle sizes and longer time steps.⁶³ Coarse-graining can provide a bridge between modeling and real-world applications.⁶⁴ In DPD, several atoms or molecules are consolidated in groups called *beads* that interact with each other based on Newton's equation of motion. The forces acting on these beads depend on the type of molecules in the system. In non-equilibrium computations, when there is a flow, the theoretically expected behavior (such as the satisfaction of no-slip boundary conditions at the fluid-solid interfaces) and the fluid physical properties (such as viscosity) should be replicated with fidelity by the computational results. For flow over a flat plate, a computational protocol has been developed to satisfy the no-slip boundary condition,^{45, 58, 65, 66} which could not be obtained with DPD unless the equivalent force between the wall and the fluid DPD beads was adjusted. Additional issues emerge when considering dynamic behavior for the flow of multiple fluids since the fluid beads interact with beads of the same fluid and also with beads of the other fluid phase. In multifluid flow cases, an accurate representation of the viscosity of each fluid is imperative, and a systematic determination of the DPD model parameters that dictate the macroscopic viscous behavior of the fluids in such systems is needed.⁶⁷ Detailed computational protocols for obtaining these DPD model parameters are not common in the DPD literature.

In this work, we focus on the velocity distribution of two immiscible fluids (heptadecane and water) in the presence of surface-active molecules (surfactants). One of the DPD model parameters, the dissipative parameter, determines the friction between interacting DPD beads, between beads of the same fluid, between beads of different fluids, and between the fluids and the solid walls. Poiseuille flow and Couette flow are used to compare fluid velocities to theoretical expectations and to verify the computational results. In addition, after the model interaction parameters were obtained, we computed flow fields in the presence of surfactants at the oil-water interface. Two types of common surfactants were added at the oil-water interface. Nonionic surfactants exhibit salinity tolerance, and they are often used as co-surfactants with anionic surfactants.⁶⁸ Herein, we investigated the effect of sodium dodecylsulfate (SDS, an anionic surfactant) and octaethylene glycol monododecyl ether (C12E8, a nonionic surfactant) on the oil-water interface. In particular, SDS represented the case of a short surfactant molecule on the interface, while C12E8 was a longer molecule. Both of these surfactants have been employed in

our prior work for oil-water-nanoparticle computations,^{69, 70} and they have been employed in industrial oil-water systems such as flooding of oil reservoirs for EOR.^{71, 72}

The contributions of this chapter are in (a) developing a detailed procedure for the modeling of the flow of two multiphase flows with a coarse-grained approach, (b) demonstrating the effects of DPD model parameters on the physical properties of multifluid systems, and (c) probing the effects of surfactants at the oil-water interface and the interfacial instability under shear that leads to micelle formation in the bulk of one of the two phases.

3.2 Materials and Methods

3.2.1 Velocity distribution of two immiscible liquids in nanoslits

While a coarse-graining model is a molecular scale model, its results should agree with theoretical and experimental predictions at larger scales, where the continuum assumption can be made. The system chosen to model two-phase flow is shown in **Figure 3.1**. Two immiscible fluids (fluids I and II) with different viscosities μ^I and μ^{II} , respectively, flow in a nanoslit. One can assume that $\mu^I < \mu^{II}$ and that the flow is in the x -direction between a pair of horizontal plates. The slit is filled with fluid I and fluid II with h^I and h^{II} are the corresponding heights. These can be adjusted by changing the ratio of the flow rate of fluid I to fluid II. The slit dimension in the z -direction is $2h$, where h is the distance from the center of the channel to the wall. For the Poiseuille flow conditions (see **Figure 3.1a**), the driving force for the flow is a pressure gradient in the x -direction, while for the Couette flow conditions, the driving force is the shear applied to the fluids when the top wall of the nanoslit moves in the x -direction with velocity v (see **Figure 3.1b**).

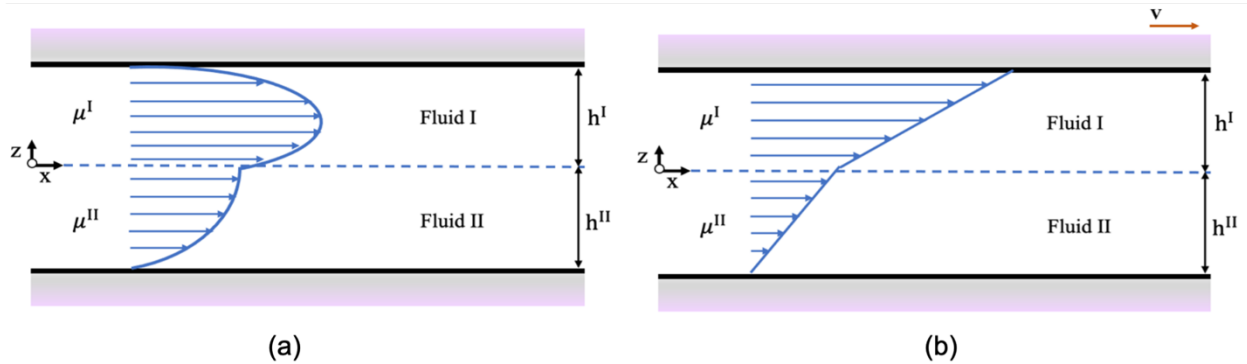


Figure 3.1. The flow of two immiscible fluids between a pair of plates under (a) Poiseuille and (b) Couette flow conditions.

The theoretical solution for this system in Poiseuille flow conditions, i.e., with Newtonian fluids, fully developed flow, steady state, $h^I = h^{II}$, and under the driving force of a pressure gradient has been known.⁷³ In the case of $h^I \neq h^{II}$, it is a trivial mathematical exercise to demonstrate that the fluid velocity profile is given as:

$$v^I = -\frac{\rho g}{2\mu^I} z^2 - \frac{C_1}{\mu^I} z + C_2 \quad (3.1)$$

$$v^{II} = -\frac{\rho g}{2\mu^{II}} z^2 - \frac{C_1}{\mu^{II}} z + C_2 \quad (3.2)$$

where ρ is the fluid density, ρg is the pressure gradient, which is applied in the DPD simulation as a body force in the flow direction, g_x , and the constants of integration C_1 and C_2 found with the application of the no-slip boundary condition at the walls and the application of the continuity of stresses at the fluid-fluid interface are as follows:

$$C_1 = \frac{\rho g}{2} \frac{(h^{II})^2 \mu^I - (h^I)^2 \mu^{II}}{\mu^{II} h^I - \mu^I h^{II}} \quad \text{and} \quad C_2 = \frac{\rho g}{2} \frac{h^I}{\mu^I} \left(h^I + \frac{(h^{II})^2 \mu^I - (h^I)^2 \mu^{II}}{\mu^{II} h^I - \mu^I h^{II}} \right)$$

In plane Couette flow the upper wall moves at a constant velocity v , whereas the lower wall is stationary. The fluid velocity profile for Couette flow in a channel is expressed by

$$v^I = v \left(\frac{C_1}{\mu^I} z + C_2 \right) \quad (3.3)$$

$$v^{II} = v \left(\frac{C_1}{\mu^{II}} z + C_2 \right) \quad (3.4)$$

where

$$C_1 = \frac{\mu^I \mu^{II}}{\mu^{II} h^I + \mu^I h^{II}} \quad \text{and} \quad C_2 = \frac{\mu^I h^{II}}{\mu^{II} h^I + \mu^I h^{II}}$$

3.2.2 Simulation details

In this work, five water molecules were lumped together into one water bead (W) when simulating oil-water systems and oil-water with SDS systems. The oil phase was represented by heptadecane ($C_{17}H_{36}$) molecules, and each molecule included three oil beads (O) to represent the same volume of fluid as each one of the water beads. The first surfactant was SDS, where each molecule contained one head (H) and two tail (T) beads, while four head and two tail beads were used for modeling C12E8 as the second surfactant. The schematic configuration of each molecule in the DPD simulations is shown in **Figure 3.2**. For the simulations of oil-water with C12E8, six water molecules were lumped in one DPD bead with the purpose of keeping comparable volumes

of beads in the computations for all molecules. In addition, for the surfactant C12E8, the angle potentials that were applied between beads need to be considered. Based on the C12E8 molecular structure, the tail-tail-head angle was fixed at 180° and all other angles were kept at 130° in order to meet the need for interfacial stability when surfactant was added.⁶⁹

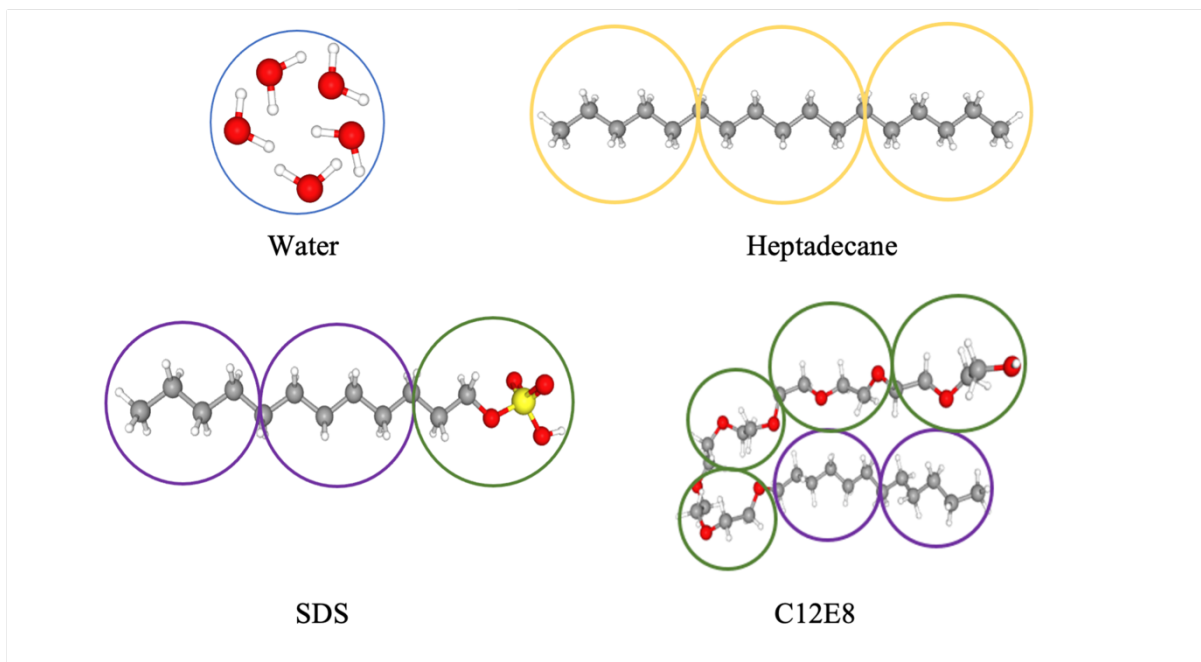


Figure 3.2. Schematic configuration of heptadecane, water, SDS and C12E8 surfactant molecules as beads of the DPD simulations. Hydrogen, carbon, oxygen, and sulfur molecules are shown as white, gray, red, and yellow spheres, respectively. The circles represent the DPD beads that group atoms or molecules together.

Conversion of time and length scales from DPD units to physical units in the case of C12E8 simulations was conducted using the same approach as for the SDS, and is shown in **Table 3.1**

Table 3.1. Scaling factors for DPD computations.

Type of Surfactant	Density	Number of water molecules in one bead	Mass scale (10^{-25}kg)	Length scale (10^{-10}m)	Temperature scale (K)	Time scale (10^{-12}s)
SDS	5	5	1.5	9.09	298	5.48
C12E8	5	6	1.8	9.66	298	6.38
None	5	5	1.5	9.09	298	5.48

The details for the selection of the interaction parameters a_{ij} representing the repulsion between the different types of beads (water, oil, surfactant tail, surfactant head) have been published previously and are adopted herein.⁶⁹ Groot and Warren⁴⁴ have shown that the repulsion parameters between the fluid-fluid (the same type of beads) should be:

$$a_{ii} = 75 \frac{k_B T}{\rho} \quad (3.5)$$

Therefore, when the number density is $\rho = 5$ and $k_B T = 1$, the value of the interaction parameter is $a_{ii} = 15$. All the interaction parameters between oil, water and wall beads are listed in **Table 3.2** for simulations with oil and water only.⁶⁹

Table 3.2. Interaction parameters (a_{ij}) used in the DPD computations.

	W	O	Wall
W	15	90	15
O		15	20
Wall			15

While the repulsion interactions between beads depend on the type of molecules in the simulated system, the focus here is on investigating the dynamic behavior of the fluids. Regarding the DPD beads, there is not a single rule that can be used to determine their size. Instead, the physical system and the goals of the research project should help to define the size of the beads and how a molecule should be split into different beads. In the present case, where surfactant molecules are simulated in the system, the use of separate beads that represent the head and the tail behavior is needed. The main rule is that the beads for all simulated components should

represent atoms or molecules that have the same volume in physical dimensions. In prior work, we have explored the effects of coarse-graining level (i.e., how many water molecules should be in a bead) on the DPD parameters of a system with water and carbon nanotubes.⁷⁴ We found that macroscopically observed hydrodynamic behavior (i.e., slip length and drag coefficient) agreed with findings from molecular dynamics when the interaction parameter appearing in the conservative force was modified. The procedure was a trial and error procedure, so a general rule was not obtained. However, a larger level of coarse-graining led to larger lengths and time scales (for example, in⁷⁴ the maximum number of water molecules in the largest bead was 273, corresponding to beads with a diameter equal to the diameter of the carbon nanotubes at 2.5 nm). In general, increasing the size of the entities that the beads represent could affect the results, and modifications of the model parameters might be needed.

The experimentally determined micelle aggregation number for SDS and C12E8 in an aqueous solution was used to obtain the repulsion parameters for the surfactant interactions between themselves and water, and the IFT was used to obtain the oil-water interactions. The surfactant-oil interactions were obtained by matching the IFT in the DPD system at different surfactant concentrations at the interface with the experimentally obtained values of IFT as a function of the surfactant interfacial concentration. The key to that approach was to use the theoretically expected amount of surfactant molecules on the interface at the critical micelle concentration (CMC) and at fractions of the CMC, in order to obtain the IFT within reasonable computational time. If the surface concentration was chosen randomly, the high concentration of surfactant could push some surfactant molecules out of the interface[27]. In DPD units, 1.61 SDS surfactant molecules per $1 r_c^2$ area was used as the number for SDS molecules on the water-heptadecane interface. Similarly, 1.47 molecules per $1 r_c^2$ area in DPD units was applied for the system of C12E8 on a water-heptadecane interface.⁶⁹ According to this procedure, the repulsion parameters in the case of SDS at the oil-water interface are listed in **Table 3.3**, and the repulsion parameters for C12E8 are listed in **Table 3.4**

Table 3.3. Set of repulsion parameters used in the water-oil-SDS simulations. H and T represent the head and tail beads of SDS surfactant, while W and O denote water and oil, respectively.

	H	T	W	O	Wall
H	20	42	10	50	35
T		15	25	12	15.5
W			15	90	15
O				15	20
Wall					15

Table 3.4. Details of parameters used in the water-oil-C12E8 simulations. H and T represent the head and tail of C12E8 surfactant, while W and O denote water and oil, respectively.

	H	T	W	O	Wall
H	15	25	14	25	35
T		15	54	14.5	15.5
W			15	100	15
O				15	20
Wall					15

Both Poiseuille and Couette flow simulations were performed in a rectangular box of size $20 \times 20 \times 21 r_c^3$, as seen in **Figure 3.1**. The initial positions of the DPD beads were randomly selected between two parallel solid plates, and the computational domains were assumed to be periodic in the streamwise x -direction and the spanwise y -direction, the boundary condition on the two solid plates is no slip in z -direction. The computational domain consisted of 1,250 wall beads and 41,600 fluid particles to maintain a density of 5. To determine the viscosity of two immiscible fluids under the Poiseuille flow condition, a body force was chosen as $g_x = 0.01$, while the velocity of the walls was set equal to zero. This body force is the way to introduce the pressure drop that drives the Poiseuille flow. The effect of surfactants on the velocity profile and the critical shear rate that could create micelles were also examined. Based on the calculations above, the numbers of surfactant molecules at the oil-water interface at the CMC were approximately 644 and 588 for SDS and C12E8, respectively, equal to 1,932 and 3,528 surfactant beads. The

duration of the simulations was 10^6 timesteps with $\Delta t = 0.02$ in DPD units. Simulations were performed with 2×10^6 , 3×10^6 and 5×10^6 time steps, and the results did not change – the desorbed micelles were observed to be stable in all computations. Simulations were further performed for larger box size, with dimensions $L_x \times L_y \times L_z = 20 \times 20 \times 51 r_c^3$, to examine the influence of box size on the velocity profile and the magnitude of critical shear rate for the creation of micelle.

3.3 Results and Discussion

3.3.1 Single phase flow and determination of fluid viscosity

The results for single fluid flow simulation for water are shown in **Figure 3.3**, and are compared to the Poiseuille flow equation for the fluid velocity profile (the dotted lines). First, we simulated the case with the bounce-back boundary condition and kept the dissipative parameter between water-water and between water-wall beads the same, $\gamma = 4.5$. The velocity profile for water flow (yellow line) is higher than expected when compared to the parabolic Poiseuille flow solution, resulting in a large slip of the fluid at the walls. From this finding, it can be concluded that using the same friction coefficients between different types of materials would not result in an accurate representation of the system if one wanted to prevent fluid particles from entering the wall domain. If the dissipative parameter for water-wall interactions was reduced by one-half that of water-water, the velocity profile for water flow (green line) is also greater than expected and a large slip is still present.

When the dissipative parameter for water-wall interactions was increased to twice that of water-water (red line), the no-slip condition was satisfied. The normalized error ($\bar{e}_{L_2}$) can be used to quantify the difference between the theoretical and the simulation results, calculated as follows:

$$\bar{e}_{L_2} = \frac{\|v^{\text{theory}} - v^{\text{simulation}}\|_{L_2}}{\|v^{\text{theory}}\|_{L_2}} = \frac{\left[\frac{1}{N} \sum (v^{\text{theory}} - v^{\text{simulation}})^2\right]^{\frac{1}{2}}}{\left[\frac{1}{N} \sum (v^{\text{theory}})^2\right]^{\frac{1}{2}}} \quad (3.6)$$

where N is the number of observations. From **Figure 3.3**, the maximum velocity was 2.063, and the parabolic velocity profile (in DPD units) was

$$V_x = \frac{\rho g}{2\mu} h^2 \left[1 - \left(\frac{z}{h}\right)^2\right] = 2.063 \left[1 - \left(\frac{z}{10.4}\right)^2\right] \quad (3.7)$$

The viscosity of water can be obtained based on the velocity maximum so that $\mu_{\text{water}} = 1.31$ in DPD units.

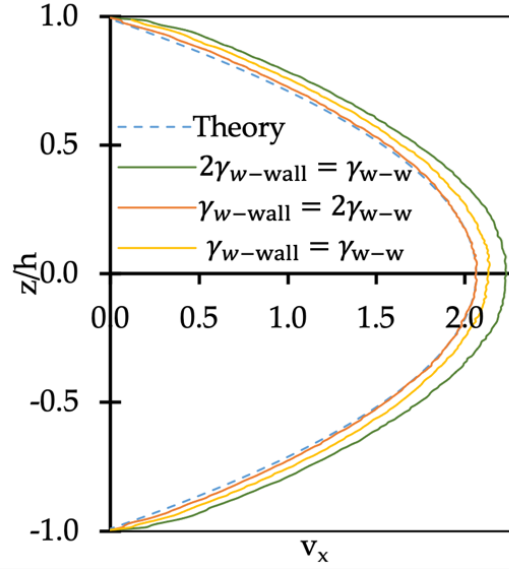


Figure 3.3. Poiseuille flow velocity profile for water with different dissipative parameter values between the wall and the water beads.

In fact, the dynamic viscosity of water and heptadecane are $8.9 \times 10^{-1}(\text{mPa.s})$ and $4.21(\text{mPa.s})$,⁷⁵ which is equivalent to 1.31 and 6.24 in DPD units, respectively. In order to estimate the correct value of the dissipation parameter for oil flow dynamic simulations, single phase flow computations for oil in Poiseuille flow were conducted for different values of the body force g_x acting on the oil beads. The maximum velocity of the parabolic profile was found, and from that the viscosity of the oil phase. Finally, in **Figure 3.4a** the effect of the dissipative parameter on the oil viscosity is presented. The results of the simulations are in good agreement with the theoretical velocity.⁷⁶ A straight line can be fitted to the simulation results, so that

$$\mu_{\text{oil}} = 0.21 \gamma_{\text{oil-oil}} + 1.51 \quad (3.8)$$

Therefore, the dissipative parameter for oil-oil, which yields the reported dynamic viscosity of the oil ($\mu_{\text{oil}} = 6.24$) is equal to $\gamma_{\text{oil-oil}} = 22.5$ and the dissipative parameter for the oil-wall interaction is twice that, and equal to $\gamma_{\text{oil-wall}} = 45.0$, since we apply the same rule as for the water-wall case. The Poiseuille flow velocity profile for oil was also verified with the parabolic flow theoretical solution, as seen in **Figure 3.4b**. There is agreement with the theoretical velocity profile, and we conclude that the dissipative parameters for single phase of oil ($\gamma_{\text{oil-oil}}$) and water ($\gamma_{\text{water-water}}$) in the system of two immiscible fluids should be dissimilar. This is important when dynamic simulations are conducted instead of computations at equilibrium.

It is important to comment here on the Newtonian character of the results for the computations. One would expect a parabolic velocity profile for Poiseuille flow when the fluid is Newtonian. Long n-alkanes however exhibit non-Newtonian behavior at high shear rates. The transition to shear-thinning can be estimated based on the inverse of the alkane chain relaxation time, given as $\gamma_c = \frac{1}{\tau}$, where τ is the characteristic relaxation time from the Rouse model for polymer dynamics.⁷⁷ Specifically, $\tau = \frac{12M\mu}{\pi^2\rho RT}$,⁷⁸ where M is the molecular mass and R is the ideal gas constant. Calculations for pure heptadecane show that the relaxation time based on the Rouse model is 640 ps, meaning that the shear rate for the case of Poiseuille flow was below the critical shear rate. For Couette flow, when the velocity of the top wall of the narrow slit was 5, the shear rate was one order of magnitude above the critical shear rate. However, even in that case, a Newtonian fluid behavior was observed. The reason might be that the Rouse model and the transition to shear thinning account for the entanglement and disentanglement of the n-alkane chains. In the present case of coarse graining, the chain of the alkane is represented with three beads so that disentanglement of chains does not occur.

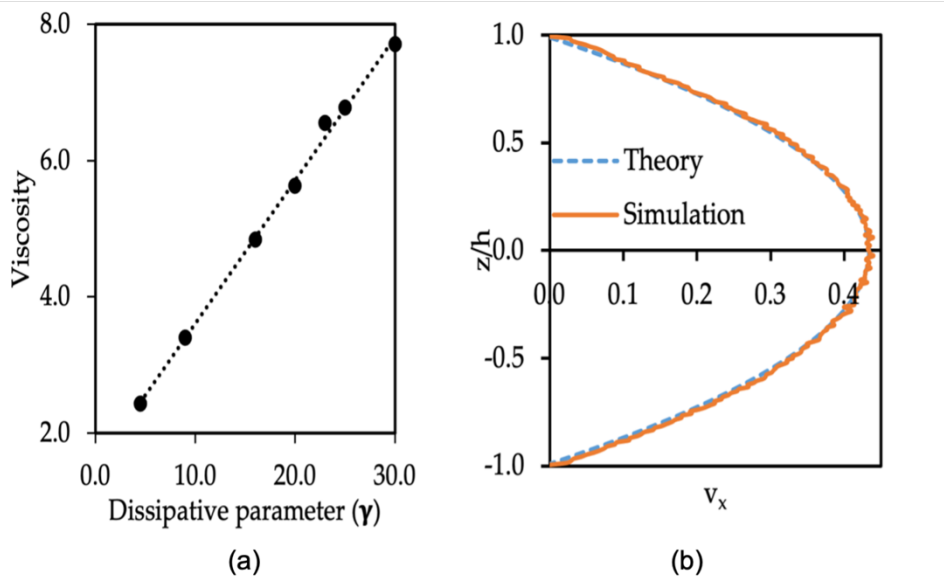


Figure 3.4. (a) Relation between the dissipative parameter and computed fluid viscosity, and (b) Poiseuille flow velocity profile for oil flow when $\gamma_{oil-oil} = 22.5$ and $\gamma_{oil-wall} = 45.0$

3.3.2 The flow of two immiscible fluids

In **Figure 3.5** we show the velocity profile across the nano slit when immiscible oil and water flow through it. The ratio of oil to water flow varied from 100% of water to 100% of oil

under Poiseuille and Couette flow conditions. The velocity profile shown in **Figure 3.5a** was obtained after the Poiseuille flow was fully developed with no boundary condition applied at the oil-water interface. The result in the case of 45.4% of oil was in good agreement with the analytical solution of Bird et al.⁷³ (see equations (3.1) and (3.2)). For the cases of 0.0%, 28.8%, 65.6%, and 100.0% of oil in the system, the slope and the shape of the velocity profiles are different at the dividing streamline between the oil and water interface. Moreover, the normalized error $\bar{e}_{L_2}$ between the theoretical and the computational results is shown in **Table 3.5**. The Couette flow field was obtained by applying a constant force to the top wall of the nano-slit so that the velocity of the top wall was equal to 5.0 (in DPD units), while the bottom wall was kept stationary. The same simulation parameters as for the single phase of oil and water in Poiseuille flow were applied to satisfy the no-slip boundary conditions. As expected, when the ratio of oil over water increased, the interface velocities increased (see **Figure 3.5b**).

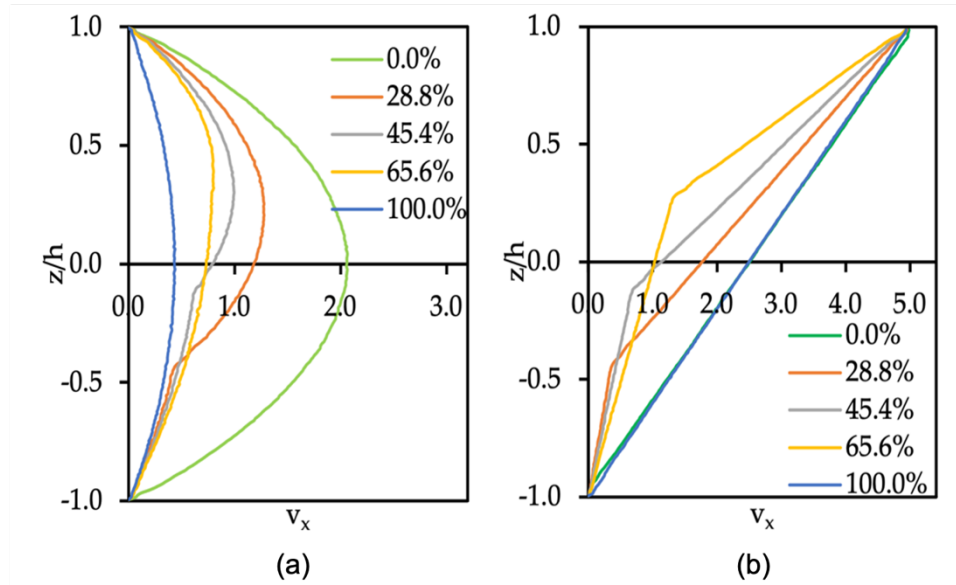


Figure 3.5. Velocity profile for two immiscible fluids with various percentages of oil (0.0%, 28.8%, 48.4%, 65.6%, and 100.0%) under (a) Poiseuille and (b) Couette flow conditions. The oil flows through the bottom side of the channel and the water through the top side of the channel since the gravitational effect was not accounted in our simulation.

Table 3.5. Errors for two-phase flow velocity profile

Percentage of oil	0.0%	28.8%	45.4%	65.6%	100.0%
Normalized error $\bar{e}_{L_2}$ (Poiseuille flow)	0.024	0.023	0.032	0.029	0.022
Normalized error $\bar{e}_{L_2}$ (Couette flow)	0.007	0.009	0.017	0.021	0.007

3.3.3 Dynamic oil-water system with surfactants

The two surfactants, SDS and C12E8, were selected because of their different molecular size and characteristics and because they have been commonly used in experiments and applications. In this work, they are used to probe the interfacial behavior of the oil-water system under shear. **Figure 3.6** is a visual illustration of the SDS and C12E8 surfactant molecules at the oil-water interface between two parallel solid plates. The external force $g_x = 0.01$ was applied to create the Poiseuille flow while the walls were stationary. As can be seen, all the surfactant molecules stay on the interface with the hydrophilic head beads (green beads) facing toward the aqueous phase, whereas the hydrophobic tail beads (purple beads) tend to face the oil phase.

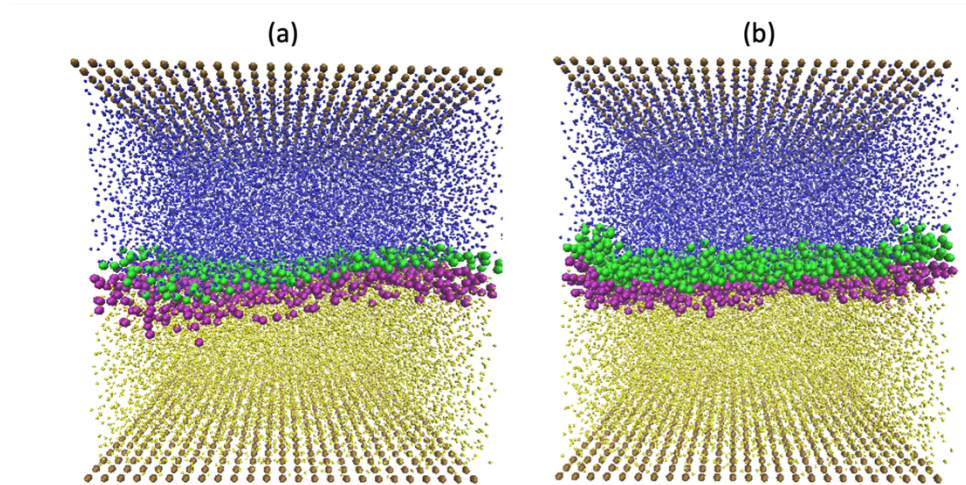


Figure 3.6. Snapshots of (a) SDS and (b) C12E8 surfactant at the oil-water interface with 50% of oil and water between two solid walls under Poiseuille flow. The wall, water and oil beads are shown as ochre, blue, and yellow, respectively. The surfactant tails are purple, while green beads represent the head beads of the surfactants.

3.3.3.1 Velocity profile of oil-water system with surfactants

The influence of surfactants located at the oil-wall interface on the velocity profile under Poiseuille and Couette flow configurations is shown in **Figure 3.7a** and **Figure 3.7b**, respectively. It is seen that the presence of surfactant at the interface leads to a reduction of the water phase velocity, while it also leads to increased velocity of the oil phase. The most drastic change of velocity for either Poiseuille or Couette flow conditions was observed when C12E8 was present. To clarify the contribution of surfactants on the velocity profile, we changed the number of surfactants (both SDS and C12E8) for the Poiseuille flow. In such a system, the presence of the surfactants may affect the viscosity of the oil phase since the surfactant molecules are large. The surfactants also change the oil-water interfacial tension, but the observation that C12E8, which is the larger molecule, has a stronger effect on the velocity profile leads to the hypothesis that this behavior is a viscosity-related effect. For a mixture of fluids, one can define an effective viscosity (μ_{eff}) that depends on the fluid components and their mole fraction in the mixture. The formula for μ_{eff} of liquids incorporates the mole fraction of the fluids in the mixture and a weighted average of the viscosities,⁷⁹ as follows:

$$\ln \mu_{eff} = \sum_{i=1}^N x_i \ln \mu_i \rightarrow \ln \left(\frac{\mu_{eff}}{\mu_2} \right) = ax_1 \ln \left(\frac{\mu_1}{\mu_2} \right) \quad (3.9)$$

If this is the case here, we would expect a linear function of the logarithm of the effective viscosity and the surfactant mole fraction in the oil phase and water phase. The effective viscosity in the oil phase and water phase was determined from the velocity profile and equation (3.1) and (3.2). The mole fraction x_i is the ratio between the moles of surfactant tails and oil or the ratio between the moles of surfactant heads and water.

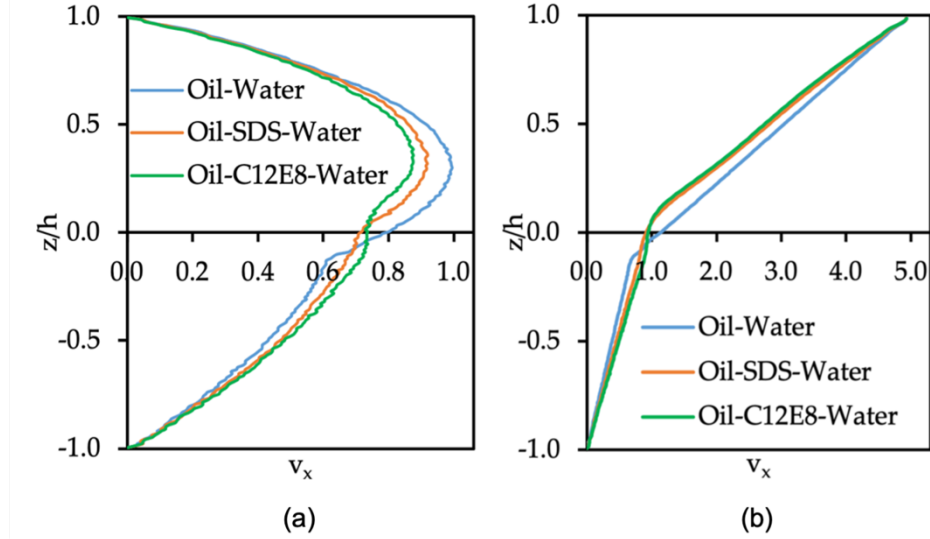


Figure 3.7. Velocity profile of oil-SDS-water and oil-C12E8-water in (a) Poiseuille and (b) Couette flows. The oil flows in the bottom side of the channel ($z/h < 0$) and the water flows through the top side ($z/h > 0$). The results are for a computational box of size $20 \times 20 \times 21 r_c^3$.

As can be seen from **Figure 3.8a**, with a very high number of SDS, the effective viscosity of the oil phase decreased significantly. In this figure, results from both the small ($20 \times 20 \times 21 r_c^3$) and the large ($20 \times 20 \times 51 r_c^3$) computational box sizes are included. The most interesting point is that the relationship between the surfactant mole fraction and the natural logarithm of the ratio of effective viscosity to the viscosity of oil can be represented by a linear function. When the surfactant mole fraction is zero, the linear fit has to pass through the point $\frac{\mu_{eff}}{\mu_{oil}} = 1.0$ and $\ln(\mu_{eff}/\mu_{oil}) = 0.0$. As the concentration of SDS increased, the effective viscosity of the oil phase decreased significantly. The investigation of effective viscosity in the case of C12E8 led to a similar conclusion (shown in **Figure 3.8b**). In addition, a linear function of $\ln(\mu_{eff}/\mu_{water})$ and mole fraction of surfactant heads in the water phase was observed in **Figure 3.8c** and **Figure 3.8d**. In summary, the presence of surfactants exerts an influence on the behavior of two immiscible fluids flowing between two parallel plates. The natural logarithm between effective viscosity and viscosity of oil or water changes linearly with the surfactant tails or heads mole fraction.

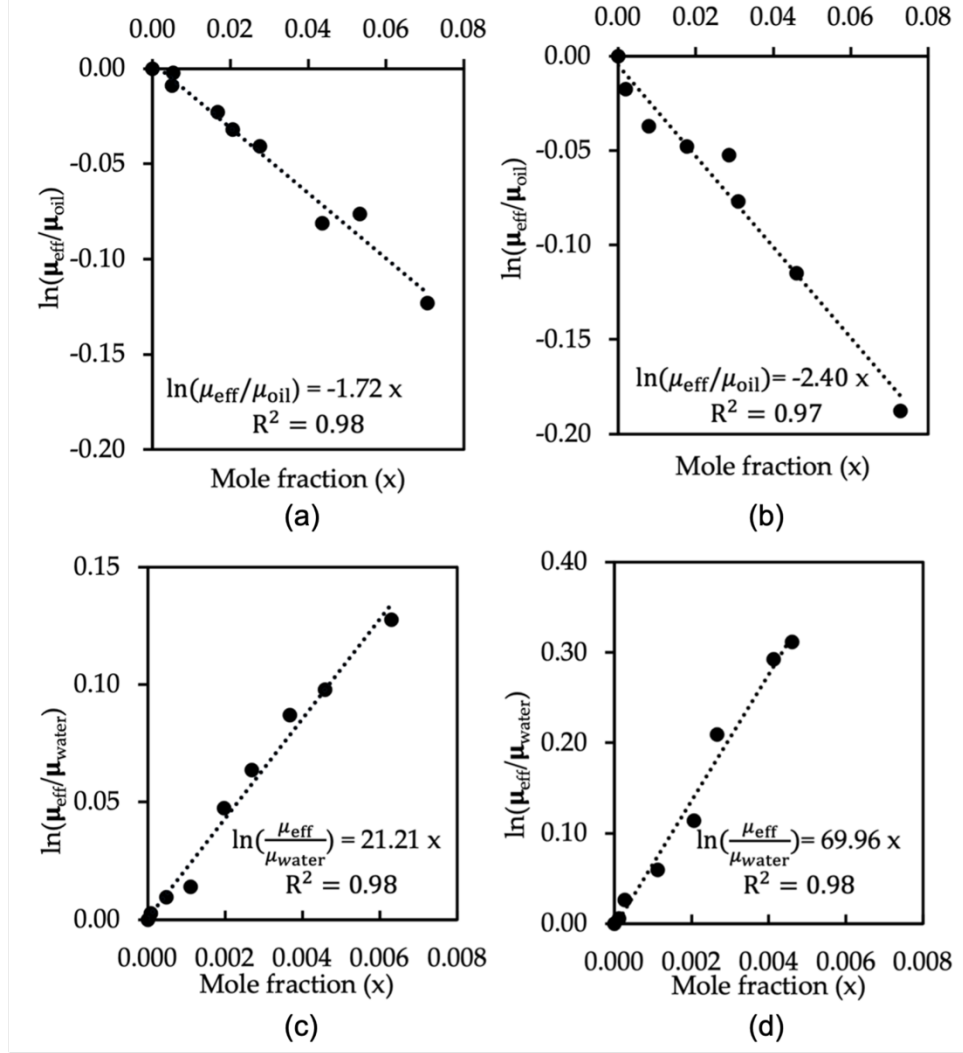


Figure 3.8. $\ln(\mu_{eff}/\mu_{oil})$ as a function of mole fraction x_i of (a) SDS and (b) C12E8 used to stabilize the oil-water interface in the case of oil phase. And $\ln(\mu_{eff}/\mu_{water})$ as a function of mole fraction x_i of (c) SDS and (d) C12E8 in the case of the water phase.

3.3.3.2 Micelle formation

Changes in the shear rate applied in the flow fields were obtained by changing the streamwise body force in Poiseuille flow and by changing the velocity of the moving wall in Couette flow. The motivation was to investigate the stability of the oil-water interface, and the results are presented in **Figure 3.9**. The shear rate, γ_S , is given as

$$\gamma_S = \left| \frac{dv_x}{dz} \right| \quad (3.10)$$

For Poiseuille flow, the shear rate is maximum at the top and bottom walls, and it has different values in the case of multifluid flow because of the difference in the viscosity of the two fluids. The minimum shear rate is reached at the position corresponding to the maximum velocity of the water flow, which can be seen in **Figure 3.9a** and **Figure 3.9d**. In addition, **Figure 3.9c** and **Figure 3.9f** show the effect of shear rate on creating micelles when the surfactants desorbed from the oil-water interface and moved into the water phase. In the case of SDS at the CMC, there appeared to be a critical value of shear rate for the desorption of micelles, which formed when the value of the body force of Poiseuille flow g_x was greater than 0.038. **Figure 3.9a** showed the maximum value of the shear rate at the interface was 0.265 (in DPD units), while the critical value of the shear rate for the oil phase in the case of Couette flow was 0.063 (**Figure 3.9b**). In the case of C12E8, the maximum value of the shear rate at the interface was 0.261, the body force of Poiseuille flow $g_x = 0.038$ was shown in **Figure 3.9d**, and the critical value of shear rate for the oil phase under Couette flow was 0.059 (**Figure 3.9e**). This observation is not an initial condition effect since the system was allowed to reach equilibrium without flow, the body force or the shear were applied later.

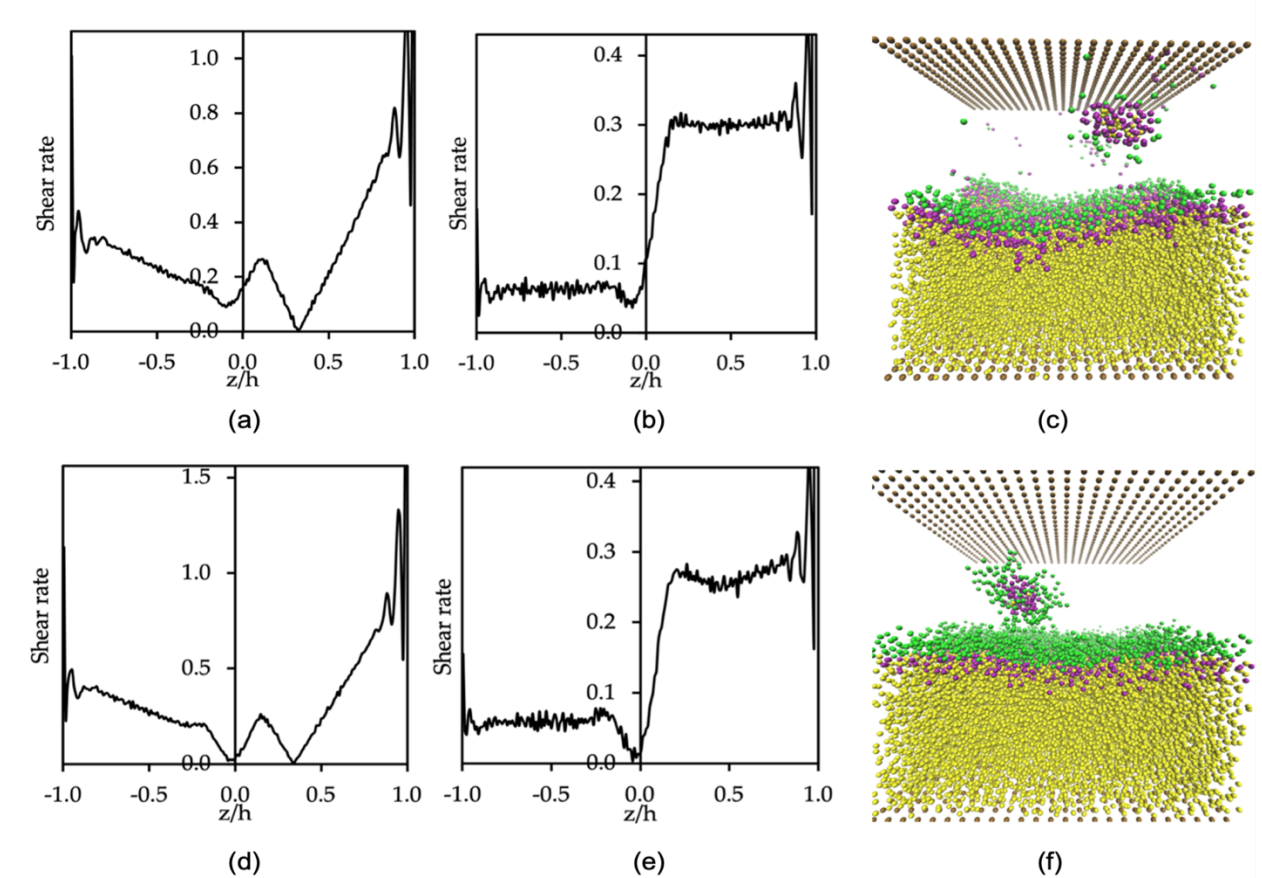


Figure 3.9. Shear rate and fluid behavior of Poiseuille flow for (a, c) oil-SDS-water and (d, f) oil-C12E8-water, and Couette flow for (b) oil-SDS-water and (e) oil-C12E8-water (box size $20 \times 20 \times 21r_c^3$). The color code for the DPD beads in (c, f) follows the colors in **Figure 3.6**.

To quantify the effect of surfactant concentration on the critical shear rate for the formation of micelles under Poiseuille and Couette flows, we modified the concentration of the SDS and C12E8 at the interface. For Poiseuille flow, when the concentration of surfactants located at the interface was reduced, we still observed the formation of micelles. The reason is that Poiseuille flow between two parallel plates can be unstable as the fluid is driven by a pressure gradient, and there is a possibility to generate waves at the interface between two different viscous and immiscible fluids.⁸⁰ At the CMC, micelles can be formed and the micelles partition into the water phase. However, why do we observe surfactant desorption even when the surfactant concentration is below the CMC at the interface? The answer is that the concentration increases locally. As can be seen from **Figure 3.10**, the waves at the interface between the two fluids generate a change in the local concentration of the surfactant. The surfactant molecules tend to concentrate downstream from the crest of the wave; the concentration can locally become comparable to the CMC, and then micelles can partition in the water phase (see **Figure 3.10a** and **Figure 3.10b**) for SDS and C12E8 behavior, respectively. The formation of micelles below the CMC can also be observed from studies on Micellar-enhanced ultrafiltration (MEUF) on aqueous solution applied in separation processes.^{81, 82} In conclusion, when the interface is unstable, surfactants tend to assemble locally (see **Figure 3.10c** and **Figure 3.10d**). Once the concentration becomes large enough, desorption and micelle formation will occur even when the surfactant concentration is lower than that at CMC.

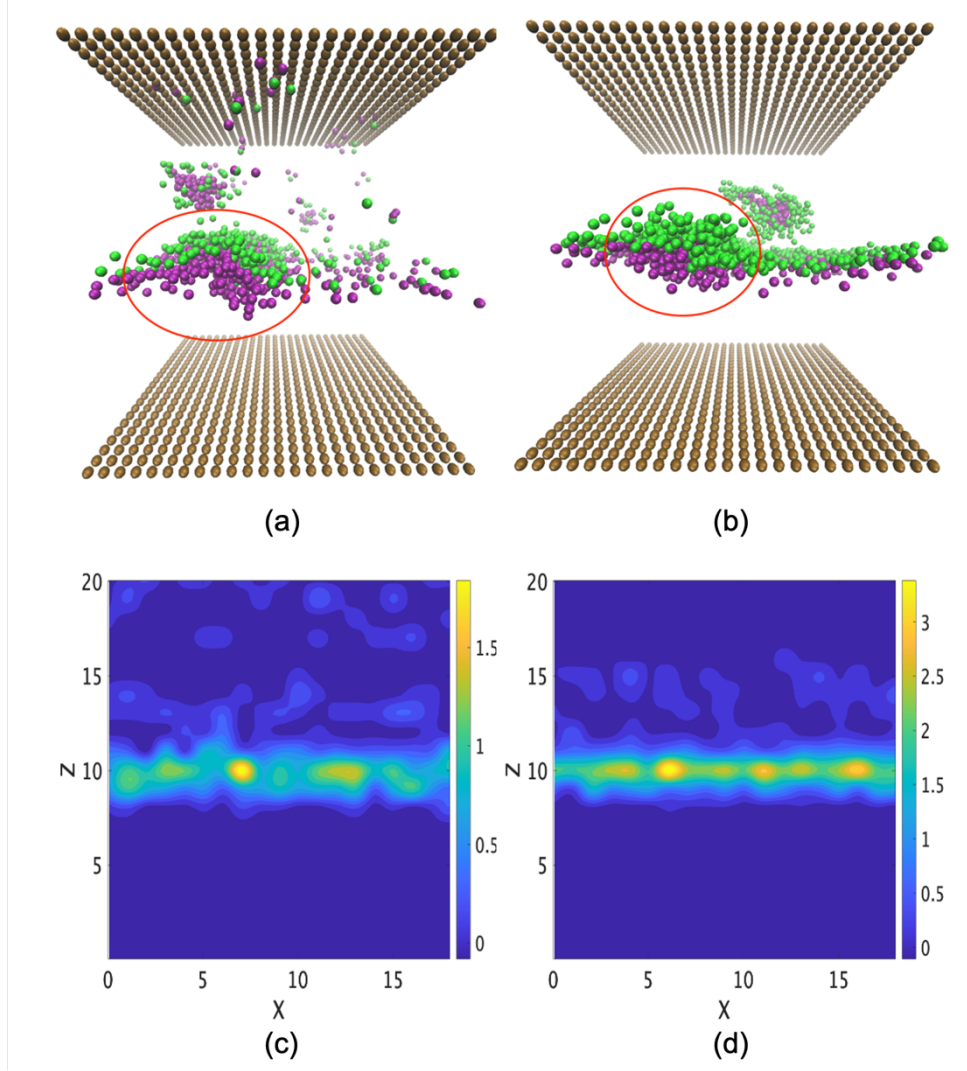


Figure 3.10. Fluid behavior of Poiseuille flow for (a) oil-SDS-water ($C_{SDS} = 50.3\%$ CMC; $g_x = 0.09$) and (b) oil-C12E8-water ($C_{C12E8} = 55.1\%$ CMC; $g_x = 0.17$). The color code for the DPD beads follows the colors in **Figure 3.6**. Water and oil beads have been hidden. Notice the high local concentration of the surfactants in the circled areas. The contour plots of the density of SDS surfactant and C12E8 surfactant are presented in (c) and (d) to show the local increase in surfactant concentration along the interface.

For Couette flow, we have not found any micelle formation when the concentration of surfactant was lower than CMC. Plane Couette flow is unconditionally stable based on linear stability analysis for single phase flows, and it has been found to be stable for multiphase flows as well. In other words, since the Couette flow is more stable, the waves do not form, and the

surfactants do not aggregate in one location to create micelles.⁸⁰ DPD simulation has been criticized for artifacts, especially in dynamic behavior, as the Schmidt number in standard DPD is close to 1, ideal for gases. An alternative to standard DPD has been suggested as LA-DPD,^{83, 84} but using the standard DPD does not appear to be the reason for micelle formation below the CMC observed herein. For no flow or for Couette flow, the surfactants do not aggregate in one location of the interface to create micelles. However, for Poiseuille flow, the surfactants tend to assemble, and once the local concentration becomes large enough, desorption in the form of micelles was observed. Hence, the micelles can appear if the concentration is comparable to the CMC locally.

3.3.3.3 The effect of computational box size

The effects of the computational box size on the fluid velocity were investigated by increasing the height of the nano-slit. The reason for probing the channel height effects was the fact that the C12E8 molecule is rather long (6 DPD units) relative to the channel height (20.8 DPD units) and the number of surfactant beads in the computation affects the viscosity of the oil or the water. The computational box height was increased from $L_z = 21$ to $L_z = 51$, and oil-water flow with the presence of surfactants was simulated. The same external body force as in the case of the small box ($L_z = 21$), $g_x = 0.01$, was imposed on each fluid particle in the x-direction to drive the Poiseuille flow. The top wall was set to move with velocity $v = 5.0$ to create the Couette flow. In **Figure 3.11**, it can be seen that the shape of the velocity profile looks like the one in the smaller box.

For Poiseuille flow, there was about a six-fold increase in the value of the velocity at the interface (at $z = 0$) in the case of SDS added on the oil-water interface when L_z increased from 21 to 51. The maximum velocity of Poiseuille flow depends on the height of the channel, as can be seen from equation (3.1) and (3.2). For Couette flow, the bigger size of the box in the z-direction did not have a significant effect on the magnitude of velocity, as expected from equation (3.3) and (3.4). In addition, the value of velocity in oil phase in the system of oil-C12E8-water is higher than the velocity of the oil-SDS-water system, hence, this result is the same as the one we discussed previously (small box: $20 \times 20 \times 21r_c^3$).

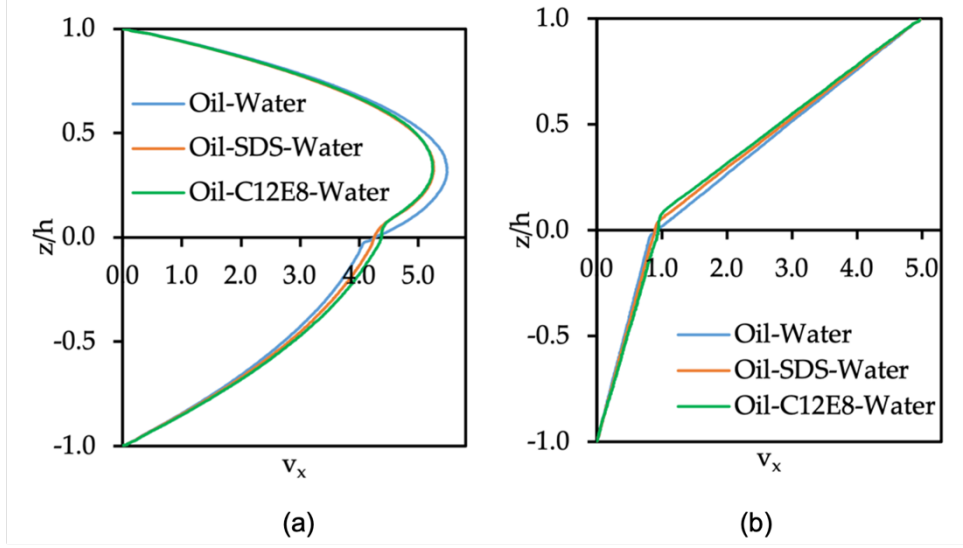


Figure 3.11. Velocity profile of SDS or C12E8 surfactant at the interface of oil-water flow with computational box size $20 \times 20 \times 51 r_c^3$ under (a) Poiseuille flow and (b) Couette flow configurations.

We also investigated the formation of micelles in the big box ($20 \times 20 \times 51 r_c^3$). SDS surfactant desorbed from the interface when the shear rate increased up to 0.226 (as shown in **Figure 3.12a**) under the Poiseuille flow condition, while **Figure 3.12b** shows that the shear effect in Couette flow led to elongated shapes for the micelles, which did not appear in the case of top wall velocity less than 8.8 (shear rate for oil phase was 0.058). For C12E8, as can be seen from **Figure 3.12c**, the critical shear rate was 0.151, equivalent to the external body force $g_x = 0.008$. In addition, the top wall moved with a velocity of 5.6 (Couette flow), corresponding to a shear rate of approximately 0.039 for the oil phase, while it increased abruptly at the oil-water interface and went up slightly within the water phase (see **Figure 3.12d**). As a result, the formation of micelles in the water phase was also observed when surfactants were present in the bigger simulation box.

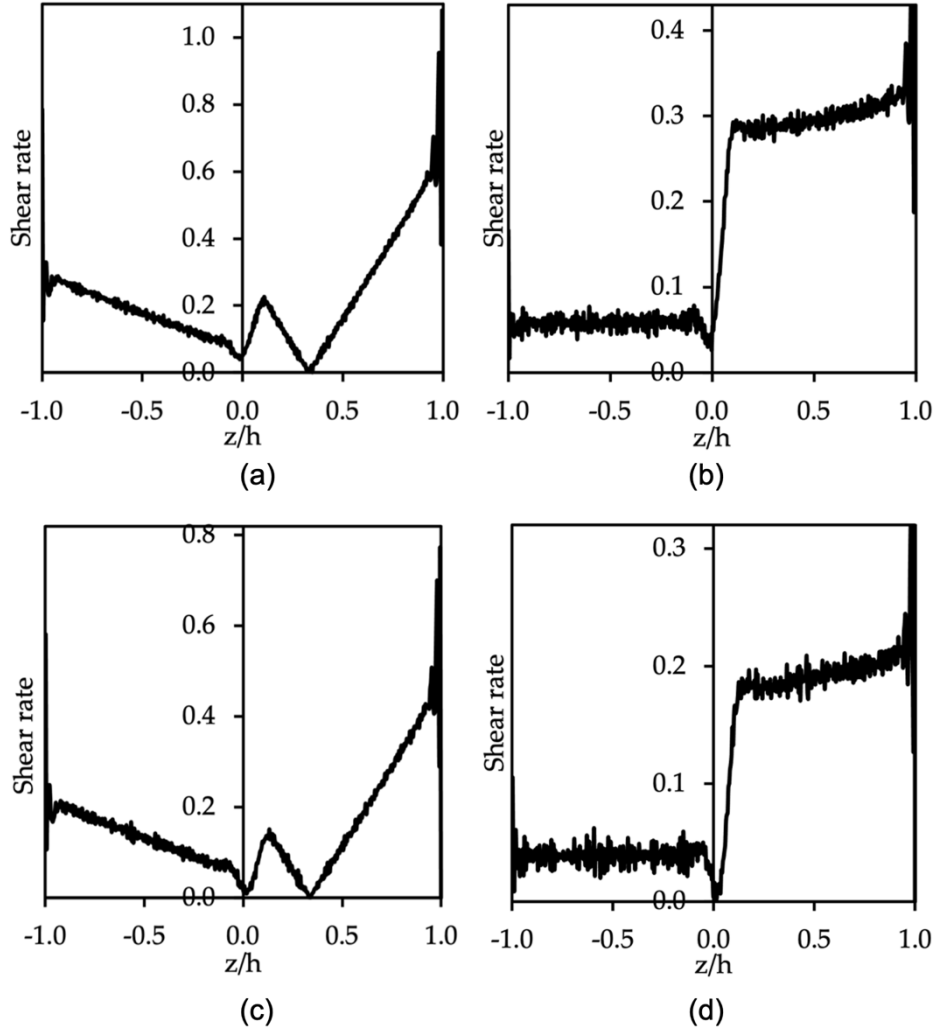


Figure 3.12. Shear rate and fluid behavior of Poiseuille flow for (a) oil-SDS-water and (c) oil-C12E8-water, and Couette flow for (b) oil-SDS-water and (d) oil-C12E8-water (box size $20 \times 20 \times 51 r_c^3$). Oil flows through the left side of the channel and water through the right side of the channel. The inset is a density plot with the y-axis as density of the oil-surfactant-water system.

3.4 Conclusions

In summary, we have investigated the multi-fluid dynamic behavior for immiscible fluids during Poiseuille or Couette flow and the interaction of surfactants with the oil-water interface under shear using the DPD simulation method. While the repulsion interactions between beads depend on the type of molecules in the simulated system, the focus here is on investigating the dynamic behavior of the fluids. Regarding the size of the DPD beads, there is not a single rule that

can be used to determine their size. Instead, the physical system and the goals of a research project should help to define the size of the beads and how a molecule should be split into different beads. The no-slip boundary condition was satisfied by using frozen wall particles and the bounce-back boundary condition. In this way, the fluid-wall interface did not allow any water or oil beads to penetrate the wall. Moreover, the dissipative parameter for each fluid should be different to model the difference in the viscosity of the fluids before conducting simulations of the multiphase system under flow.

Selecting the appropriate dissipation parameters for the DPD model for each fluid was important. When successful, an accurate model for the viscosity of each of the two different fluids led to results that were in excellent agreement with the analytical solution of Bird et al.⁷³ for the case of ~50% oil and water. In addition, the results for other cases with different ratios of oil to water agreed with the theoretical predictions quite well.

Under shear flow, the presence of surfactants located at the oil-water interface affected the velocity profile. The presence of the surfactants modified the effective viscosity of the oil phase and water phase and led to a change in fluid velocity for the same pressure drop. Furthermore, it was demonstrated that the surfactant can desorb from the interface when the shear rate increases above a critical value. The shear led to an unstable oil-water interface in Poiseuille flow, leading to local increases in the surfactant concentration followed by surfactant desorption into the aqueous phase. Plane Couette flow was stable for immiscible fluids, so localized increases in the surfactant concentration did not occur in that case. The phenomenon of micelle formation below CMC only occurred in the case of Poiseuille flow because of the appearance of waves and the resulting increase in local surfactant concentration. Finally, it must be noted that the effects of viscosity and shear rate in the case of surfactants were confirmed with calculations in a simulation box that was twice as wide.

Chapter 4. Janus Nanoparticle and Surfactant Effects on Oil Drop Migration in Water under Shear

Abstract[†]

The effects of surface-active nanoparticles and surfactants on the behavior of oil–water interfaces have implications for a variety of industrial processes related to multiphase flows including separation processes, enhanced oil recovery, and environmental remediation. In this work, the migration of an oil droplet in shear flow is investigated with the presence of surface-active molecules and nanoparticles at the oil–water interface. Pure oil (heptadecane) in water and oil with the presence of Janus nanoparticles (JPs) and/or octaethylene glycol monododecyl ether, a nonionic surfactant, were examined using coarse-grained computations. The shear flow field was created utilizing a Couette flow, where the top wall of a channel moved with a specified velocity and the bottom wall was kept stationary. The dissipative particle dynamics (DPD) method was applied. The oil drop was placed on the stationary wall, and its displacement was recorded over time. When surfactants were added at the oil–water interface, the slip of the water over the oil drop was reduced, leading to a larger displacement of the drop. Moreover, surfactant molecules tended to concentrate toward the rear side of the oil drop rather than the front as the drop moved in the flow field. The presence of only JPs on the oil–water interface resulted in slower droplet migration. In the presence of both JPs and surfactants, the effect of JPs on the oil–surfactant–water system was investigated by changing the number of JPs on the drop surface while keeping the concentration of the surfactant constant. Under the same shear rate, the droplet’s migration speed increased in the presence of both surfactants and JPs compared to the case of bare oil. The JPs appeared to follow a repeated pattern of motion while residing close to the solid substrate–oil drop contact line. These findings elucidate the contribution of both surfactants and JPs on oil drop displacement for enhanced oil recovery or remediation of an oil-contaminated subsurface.

4.1 Introduction

The motion of liquid droplets is important to a broad range of process industries,⁸⁵⁻⁸⁷ especially the petrochemical sector, where oil and water are often produced and transported

[†] Material in this chapter has been published in Nguyen, T. X., Razavi, S., & Papavassiliou, D. V. (2022), *The Journal of Physical Chemistry B*, 126(33), 6314-6323.

together.^{88, 89} Several techniques can be exploited to make droplets move, such as electrostatic actuation,^{90, 91} surface energy gradient,^{92, 93} or external forcing by shear flow,⁹⁴⁻⁹⁷ and several studies regarding the transportation of droplets have been performed either experimentally^{94, 95} or computationally.^{97, 98} Notably, most previous studies focused on the motion of droplets or bubbles in a cylindrical capillary.⁹⁹⁻¹⁰¹ For non-cylindrical geometries, Horwitz et al. studied the effect of the dimensionless parameters (Reynolds number and capillary number) and the viscosity ratio between the droplet and the carrier fluid on droplet deformation in a square duct.¹⁰² More recently, Luo et al.⁹⁷ used a three-dimensional front-tracking finite-difference method to study the effects of surfactant, including the reduced surface tension and the Marangoni stress, on the motion of a droplet in a square microchannel.

An important aspect that needs examination is the presence of additives or impurities, which may play the role of surface-active species. For instance, surfactants are conventionally used for flushing residual oil in hydrocarbon reservoirs through chemical flooding in EOR processes. In particular, C12E8 is a common nonionic surfactant used for EOR.⁷² In our prior research studies, this surfactant has been employed to explore the effects of surfactants on flat oil-water interfaces,⁶⁹ in the case of compression of flat interfaces¹⁰³ and on the behavior of the multiphase flow.¹⁰⁴ Nanoparticles also affect interfacial behavior, as prior research has demonstrated that nanoparticles can stabilize emulsions,¹⁰⁵ affect substrate wettability,^{106, 107} and increase the oil recovery rate for EOR.¹⁰⁸ JPs which are a class of nanoparticles possessing amphiphilicity, are also shown to impact the properties of fluid-fluid interfaces and their response to applied stresses.^{1, 109-115}

The coexistence of surfactants and nanoparticles on the oil-water interface has broad applications in energy and environmental areas.³²⁻³⁴ However, most studies have focused on equilibrium conditions when there is no flow in the system.^{116, 117} Under shear flow conditions, computations based on the lattice Boltzmann method have shown that nanoparticles or surfactants adsorbed at the droplet interface display exciting behavior.¹¹⁸ In this study, the drops were suspended in the middle of a channel, and the motion of nanoparticles on the drop interface and their clustering under shear were investigated. The particles were spherical, neutrally wetting particles, which did not distribute homogeneously over the droplet surface and were found to not affect surface tension. The effects of shear on the migration of drops attached to a wall have not been investigated when both surfactants and nanoparticles are present and when the oil-water

interface is modified. In this work, we seek to quantify the behavior of surfactants when they adsorb on an oil droplet and examine the displacement of this droplet immersed in water and under shear flow, with or without the presence of JPs. The dissipative particle dynamics coarse-graining computational method is applied to simulate a shear flow under controlled conditions. The main research contributions are (a) to probe the effects of surfactants located at the oil-water interface on the migration of an oil droplet, (b) to examine the effects of JPs on the migration process, and (c) to understand the physical mechanisms of drop motion in the presence of both surfactant and JPs.

4.2 Simulation details

A plane Couette flow was established in a channel with a height of $21 r_c$ (in dimensionless DPD units). The driving force for the flow was applied by moving the top wall of the channel with a constant relative velocity v , while the bottom wall did not move. Using this process, a well-controlled shear flow field was generated. The no-slip boundary condition at the walls needed to be obeyed, while periodic boundary conditions were applied in the other two directions. The DPD beads representing water, oil ($C_{17}H_{36}$), and surfactants ($C_{12}E8$) were modeled identically to the description provided in Chapter 3. Regarding the NP, the JPs were considered spherical particles, consisting of two faces with distinct wetting properties. The distance between neighboring NP beads was set at $0.30 r_c$, and the diameter of the particles was set to $4.7 r_c$ (~ 3.64 nm).¹⁰³ The NP was crafted to possess hollow structures, with vacant spaces inside. The conversion of time and length scales from DPD units to physical units is shown in **Table 4.1**. The NVE ensemble was used with temperature rescaling every 200 time steps, and the Mach number for the computations was always less than 0.12. The schematic configuration of all species used in the DPD simulations is shown in **Figure 4.1**.

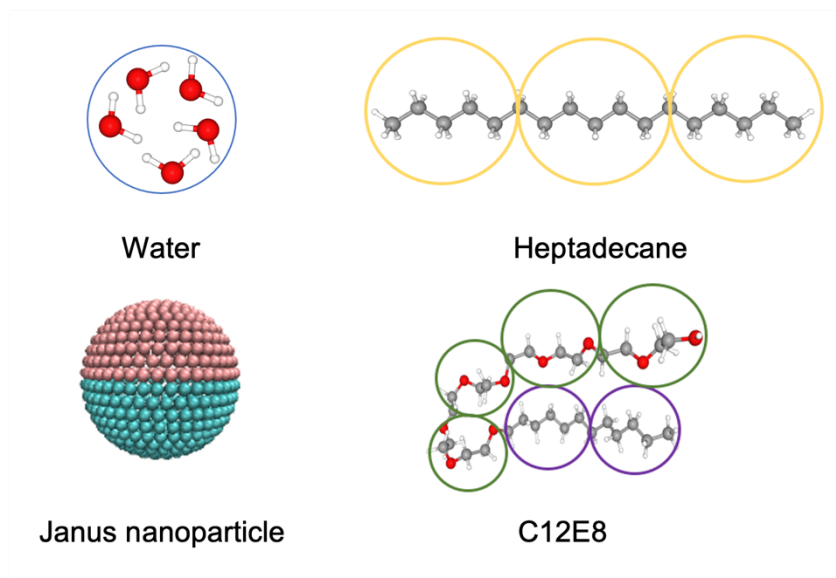


Figure 4.1. Schematic configuration of water, heptadecane, Janus particle and C12E8 surfactant molecule as beads of the DPD simulations. Oxygen, hydrogen, and carbon are shown as red, white, and gray spheres, respectively. Cyan is the hydrophilic and pink is the hydrophobic surface of JP beads.

Table 4.1. Scaling factors for DPD computations

Additive on the interface	Density	Number of water molecules in one bead	Mass scale (10^{-25} kg)	Length scale (10^{-10} m)	Temperature scale (K)	Time scale (10^{-12} s)
C12E8	5	6	1.80	9.66	298	6.38
C12E8+JPs	5	6	1.80	9.66	298	6.38
JPs	5	5	1.50	9.09	298	5.48
None	5	5	1.50	9.09	298	5.48

When the surfactant surface concentration is high, some surfactant molecules can partition out of the interface and create micelles in the water phase.¹¹⁹ Following the procedure detailed in our earlier work,⁶⁹ the repulsion parameters used in the present study for the case of C12E8 at the oil-water interface and the JPs at the oil-water interface, are listed in **Table 4.2**.

Table 4.2. Details of the various repulsion parameters (a_{ij}) used in the simulations*

	H	T	W	O	Pho	Phi	Wall
H	15	25	14	25	54	15	35
T		15	54	14.5	15	54	15.5
W			15	100	54	15	25
O				15	15	54	20
Pho					15	54	15.5
Phi						15	35
Wall							15

* H and T represent the head and tail of C12E8 surfactant, while W and O symbolize water and oil, respectively. The JPs include hydrophobic (Pho) and hydrophilic (Phi) beads.

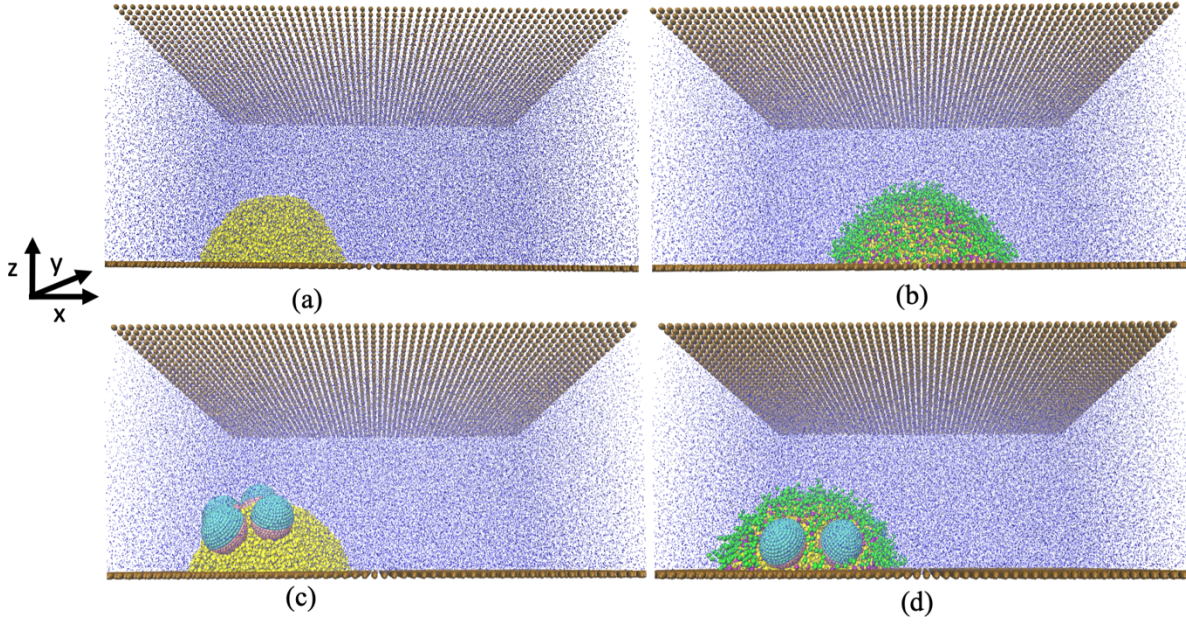


Figure 4.2. Snapshot of the oil droplet in the channel for various systems studied: (a) oil in water; (b) oil, water, and surfactant; (c) oil, water, and Janus nanoparticles; (d) oil, Janus nanoparticles, surfactants, and water system. The wall, water, and oil beads are shown as ochre, blue, and yellow, respectively. Cyan color represents the hydrophilic part of the JP, while pink is used for the hydrophobic face. Purple and green represent the tail and head beads of the surfactant, respectively.

The Couette flow simulations were performed in a computational box with dimensions $50 \times 30 \times 21 r_c^3$, in the x, y, z directions (see **Figure 4.2**). The DPD water beads were placed

between the two parallel solid plates in random locations. The computational domain shown in **Figure 4.2** consisted of 4,788 wall beads and 156,000 fluid beads, the density of the fluid in DPD units was 5 (i.e., the number of DPD beads per 1 unit volume of the simulation).⁴⁴ The surfactants and JPs were added to the surface of the oil droplet. The simulation time step was set to $\Delta t = 0.02$ in DPD units, and the total number of steps was 1,000,000 with an additional 10,000 time steps for the start-up period to reach equilibrium with no flow.

4.3 Verification of Computations: Contact angle and size of oil droplet

The contact angle of a droplet is typically used to quantify the wetting of a solid by a liquid. Here we present the contact angle for the oil droplet on the solid substrate; therefore, when the contact angle for the oil and the solid is smaller than the right angle ($\theta_{oil} < 90^\circ$), the surface is hydrophobic; if the droplet has a large contact angle ($\theta_{oil} > 90^\circ$), the oil droplet does not wet the solid wall and the surface is hydrophilic.

The surface tension between the fluids and the solid is related to the contact angle with the Young's equation as follows:

$$\gamma_{SW} - \gamma_{SO} = \gamma_{OW} \cos\theta_{oil} \quad (4.1)$$

where γ_{SW} is the solid wall-water surface tension, γ_{SO} is the solid wall-oil surface tension, γ_{OW} is the oil-water surface tension and θ_{oil} is the equilibrium three-phase contact angle of the oil drop on the solid substrate surrounded by water.

Separate DPD simulations were conducted to calculate the surface tensions in equation (4.1). Layers of oil and water were distributed in a periodic box; thus, two oil-water interfaces were employed to calculate the surface tension between oil and water, γ_{OW} , using equation (1.1).¹⁹ The solid-fluid surface tensions were not calculated directly, instead their difference shown on the left-hand side of equation (4.1) was calculated. Two simulations were conducted for this purpose, one with the oil phase only and another with the water phase only between two solid walls, to obtain the quantity shown on the right-hand side of equation (1.1) for each of the cases of wall-oil and wall-water. The difference between these two, which is the quantity on the left-hand side of equation (4.1), was then calculated. Following the start-up period for each of these simulations, the interfacial tension values were determined every 100 time steps of the simulation and then averaged for 1,000,000 steps. These results were converted from the DPD units to real world units using a scaling factor κ determined as $\kappa = \frac{\text{mass scale}}{\text{time scale}^2} = 4.98 \text{ mN/m}$. As a result, the interfacial

tension value of heptadecane-water was computed as $\gamma_{ow} = 53.33$ mN/m, which compares well with the experimentally reported value of $\gamma_{ow} = 53.20$ mN/m,¹²⁰ while $\gamma_{sw} - \gamma_{so} = 8.42$ mN/m. Using these values and equation (4.1), the contact angle for the oil droplet on the solid wall was calculated to be $\theta_{oil} = 80.9^\circ$.

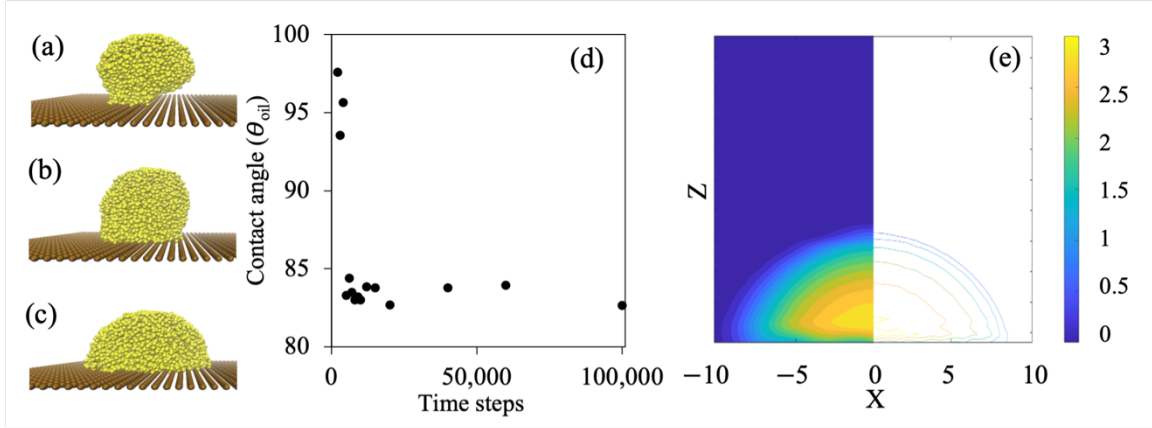


Figure 4.3. Equilibration of an oil drop (1,944 oil molecules) on a solid wall at different stages of the DPD computation. (a) Drop after 500 time steps, (b) 1,000 time steps, and (c) 10,000 time steps; (d) contact angle of oil droplet in water phase during the simulation time and (e) contour plot of oil droplet density at equilibrium.

To validate the computations, the contact angle of the oil droplet was also determined from the steady-state results of the DPD. The contact angle value for the oil drop reached equilibrium within 10,000 time steps in the computations (see **Figure 4.3a-d**). Finally, the contact angle of a drop on a flat surface was calculated directly from the density profile of the droplet and by using the sphere approximation and the ellipse approximation using the ImageJ software.⁵³ As seen in **Figure 4.3e**, the value of the contact angle was found to be $\theta_{oil} \approx 82.8^\circ \pm 1.1$, in good agreement with the value of the contact angle determined from Young's equation (i.e., 80.9°).

The contact angle when using a larger or smaller oil drop and a different simulation box size was also investigated, as shown in **Figure 4.4**. In **Figure 4.4a**, the contact angle was $\theta_{oil} = 82.0^\circ \pm 1.6$ for all cases studied with the number of oil molecules increasing from 972 to 6,048 molecules. As shown in **Figure 4.4b**, the size of the computational box does not affect the contact angle calculations, as expected when the properties of the fluids and the wall do not change. Therefore, we chose the biggest box for our simulations, while the number of oil molecules was set at 1,944 molecules (i.e., twice the number of oil molecules required to measure the contact

angle). The contact angle for this case ($\theta_{oil} = 82.8^\circ$) had the smaller difference with that obtained from Young's equation.

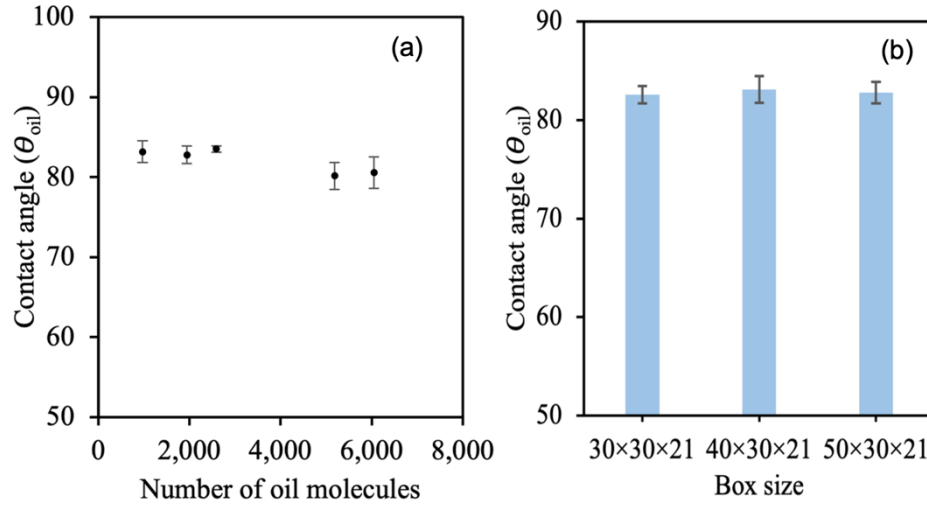


Figure 4.4. Dependence of the oil drop contact angle on the solid wall on (a) the number of oil molecules (box size: $x \times y \times z = 50 \times 30 \times 21$) and (b) the size of the simulation box (1,944 oil molecules).

4.4 Results and Discussion

4.4.1 Effect of surfactants located at the oil-water interface

Surfactants lower the IFT between oil and water, stabilizing the drop interface. To study the effect of their presence at the interface on drop migration, we added C12E8 molecules to the oil-water interface and subjected the drop to shear flow. The number of molecules added to the oil-water interface in these studies was determined as follows: The interfacial concentration of C12E8 on the heptadecane–water interface, corresponding to the critical micelle concentration (CMC), is $2.60 \times 10^{-10} \text{ mol/cm}^2$.¹²¹ In DPD units, this translates to 1.47 molecules per $1 r_c^2$ of interfacial area for the system of C12E8 on an oil–water interface. Since we did not observe surfactant adsorption on the solid surface, the surface concentration of C12E8 at CMC was calculated as $N_{CMC} = 1.47 \times S_0 = 1.47 \times 2\pi \frac{h^2}{1 - \cos\theta_{oil}} \approx 540$ molecules, where S_0 is the area of the spherical cap that constitutes the oil–water interface. The drop interfacial area calculation was based on the measurement of the distance, h , from the solid wall to the highest point of the oil drop, and θ_{oil} used here is the equilibrium contact angle for the oil drop in the absence of surfactant molecules. The interfacial tension γ_{OW} and the three-phase contact angle of the oil droplet in the

presence of surfactants at interfacial concentrations up to the value corresponding to CMC are plotted in **Figure 4.5a-b**, respectively. It was assumed that the number of C12E8 surfactant molecules per 1 r_c^2 for the case of heptadecane-water and hexadecane-water is approximately the same;⁶⁹ hence, the IFT at CMC for the case of C12E8 with hexadecane-water can be used for comparing with the case of hexadecane-water. The IFT for hexadecane-water at CMC of C12E8 was $\gamma_{ow} \approx 3.33 \text{ mN/m}$,¹²¹ which was very close to our simulation result for hexadecane-water $\gamma_{ow} \approx 3.55 \text{ mN/m}$ (see **Figure 4.5a**). In addition, it is seen that both γ_{ow} and θ_{oil} decreased significantly with the concentration of surfactant on the oil-water interface. Thus, the droplet spread more on the solid surface.

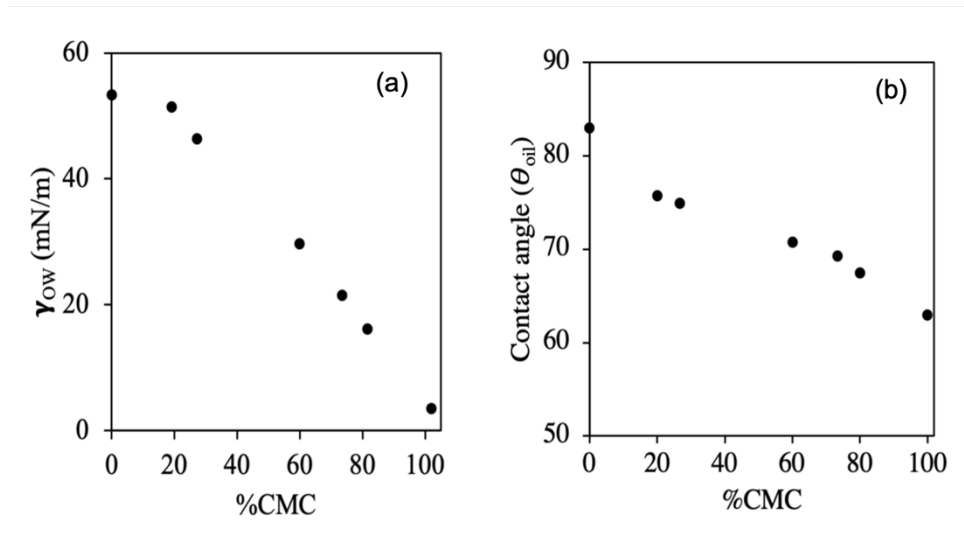


Figure 4.5. (a) Dependence of interfacial tension γ_{ow} and (b) contact angle (θ_{oil}) on the surface concentration of C12E8 normalized with its value at the CMC.

The drop migration results are provided in **Figure 4.6** as a function of γ_{ow} , where the concentration of C12E8 surfactant was increased up to the CMC, and the IFT was reduced accordingly (**Figure 4.5a**). The displacement of the drop was measured as the distance traveled by the drop center of mass (COM) during the simulation. The oil migration velocity, V_o , was calculated based on the drop displacement and the time of the simulation (1,000,000 time steps after reaching equilibrium). Thus, it is the average migration velocity of the drop for the time duration simulated. The velocity designated as V_w is the carrier fluid (water) velocity at a distance from the channel wall equal to the z location of the drop center of mass. The velocity profile for a plane Couette flow of a Newtonian fluid (water) is also known from theory to be changing linearly

as a function of the distance from the stationary channel wall.¹²² The velocity V_w was calculated from the DPD data at the z location that corresponds to the center of mass of the oil drop. Any difference between these two velocities (V_o and V_w) indicates that the oil is lagging the surrounding water, and this difference is a measure of the slip between the two phases. As can be seen from **Figure 4.6a**, increasing the surfactant concentration (and decreasing the interfacial tension) led to an increase in the oil droplet displacement. For the case when the velocity of the top wall was 1.0, the displacement reached a maximum when the interfacial tension was $\gamma_{ow} \approx 20.84$ mN/m. This interfacial tension corresponded to surfactant concentration at the interface equal to 73.33% of CMC. Increasing the surfactant concentration further led to a slight decrease in the oil displacement until the concentration reached the CMC. The same trend was observed for the case of the top wall velocity $v = 0.8$.

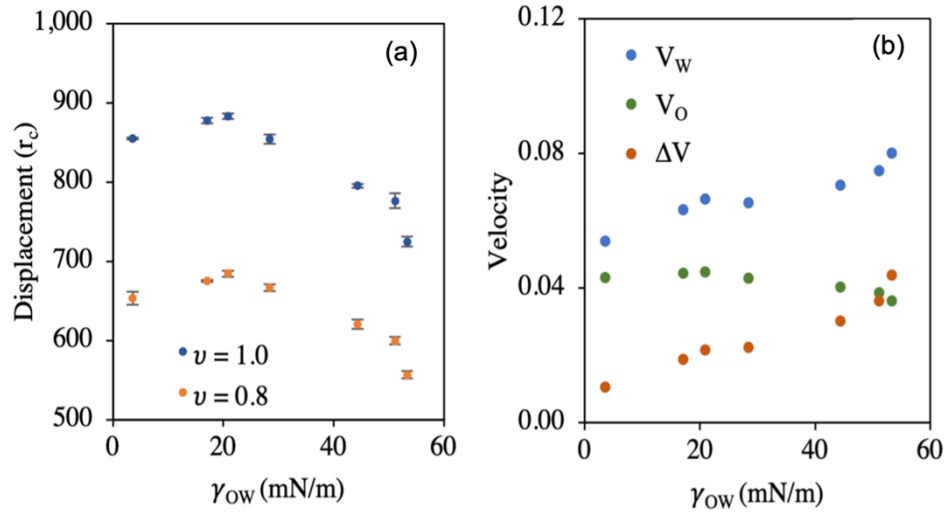


Figure 4.6. Effect of the oil-water interfacial tension (γ_{ow}) on the oil drop migration. The γ_{ow} changes with the addition of more surfactant to the interface; the highest γ_{ow} corresponds to the case of oil-water with no surfactant in the system, and the lowest γ_{ow} represents the case with surfactants at the CMC. (a) Displacement of the oil droplet for the duration of the simulation.

Error bars indicate the standard deviation around the average value. (b) The slip velocity between the oil droplet and the water.

These results can be explained by comparing the slip velocity between the oil droplet and the water as shown in **Figure 4.6b**. When the γ_{ow} decreased from 53.33 mN/m (no surfactant) to 3.55 mN/m (at the CMC), the value of V_w went down because the drop shape changed. In order

words, the center of mass of the droplet moved closer to the stationary channel wall in the z direction as the drop spread out on the surface, and the three-phase contact angle of the oil droplet reduced (see **Figure 4.5b**). The actual velocity of the droplet V_O was found to increase up to a point, and then it remained almost constant as the surfactant concentration reached CMC. The slip velocity ΔV decreased with a reduction in γ_{OW} values in the presence of higher surfactant concentrations. As the γ_{OW} decreased, the transfer of momentum between the two immiscible fluids became more efficient. Applying a linear fit between the γ_{OW} and the slip velocity ΔV between the oil droplet and water, it is found that $\Delta V = 0.0006 \gamma_{OW} + 0.0083$. Although the value of the coefficient of determination is not extremely high ($R^2 \approx 0.94$), it is accepted to use a simple linear relationship since there is no physical justification for using a high-order polynomial fit. The presence of a local maximum in the displacement as a function of γ_{OW} is also important to probe; therefore, we investigated the distribution of surfactant concentration on the droplet surface. Under the applied shear flow, the surfactant molecules moved from the front side (receding) to the rear side (advancing) on the drop surface, which results in low concentration at the front side and high concentration at the rear side. This migration generated a concentration gradient and a subsequent interfacial tension gradient on the oil drop-water interface, leading to Marangoni effects. The gradient in surfactant concentration can be observed clearly by examining snapshots of the surfactant distribution on the drop surface, as depicted in **Figure 4.7**. At high surfactant concentration ($C_{C12E8} > 75\%$ CMC), a reduction of the oil droplet displacement occurred (shown in **Figure 4.6a**) because the Marangoni stress created fluid motion at the interface. The driving force towards achieving a uniform surfactant distribution at the interface generated an interfacial velocity on the oil drop that was in the opposite direction to the shear flow (**Figure 4.7a**). Thus, the oil droplet tended to resist the flowing water due to the interfacial flow from high to low surfactant concentration, causing a smaller displacement. In contrast, when the concentration of C12E8 was small, the surfactant concentration was more nonuniform on the surface of the oil drop (see **Figure 4.7b**); meanwhile, the influence of shear flow on the migration of the droplet was dominant. Hence, the effect of Marangoni flow was overwhelmed by the increase in momentum transfer and decrease in slip velocity. The main driving force of the oil movement was the impact of the water flow. This result agrees with previous reports.^{59, 123}

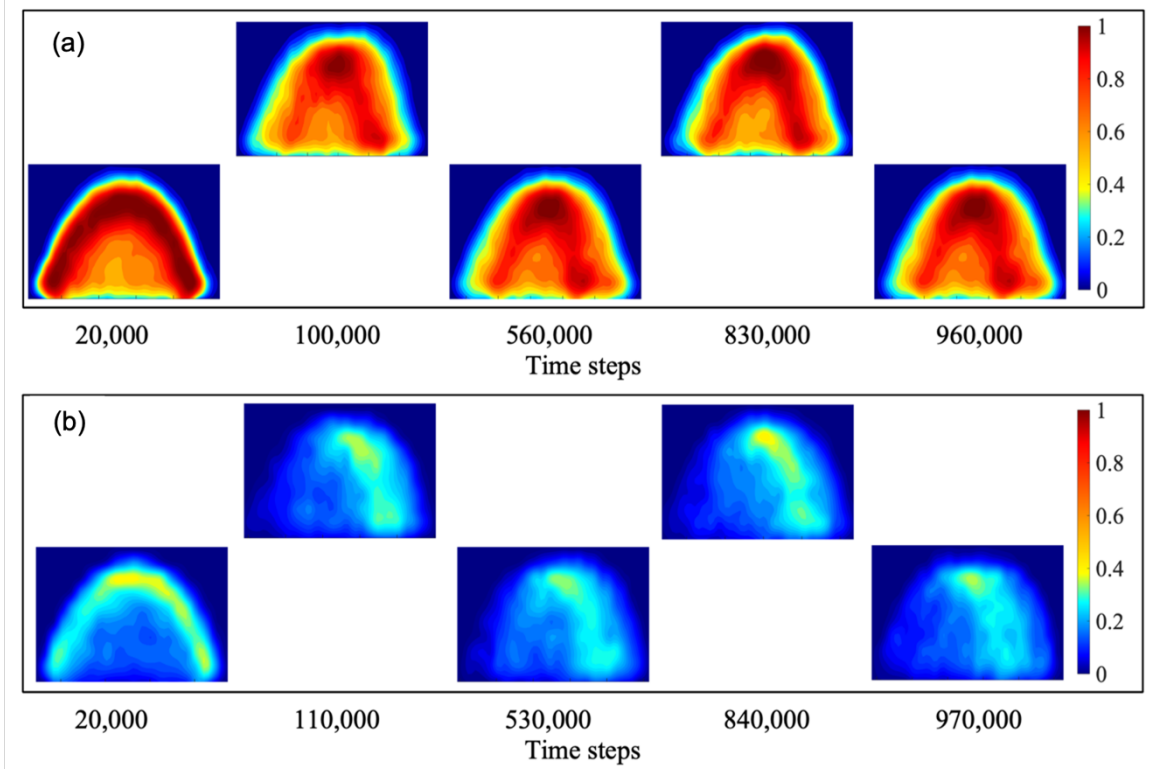


Figure 4.7. Color maps for the density of surfactant at various times during the simulation for the case of surfactant concentrations at (a) CMC and (b) 26.67% CMC when the top wall moved with velocity $v = 1.0$. The start-up period is included in the time steps. Surfactants did not adsorb on the surface .

4.4.2 Effects of Janus particles and surfactants on the oil-water interface

To gain further insights into the physical mechanisms underlying the combined effects of the presence of Janus particles and surfactants on the drop motion in the microchannel, we conducted a detailed analysis of the JP particle motion on a drop surface with and without surfactant. The number of C12E8 surfactant molecules was chosen to correspond to 73% of the CMC for the oil-water interface (i.e., 396 surfactant molecules added). There were two reasons for this choice. First, this concentration corresponded to the maximum drop displacement, as described in the previous Section, while mitigating the Marangoni effects. The second reason was to prevent surfactant molecules from desorbing from the oil-water interface to the aqueous phase and to avoid the creation of micelles. Such surfactant desorption could happen since the presence of JPs at the drop interface would decrease the interfacial contact area between oil and water.³⁶ Taking this into consideration, the effective surfactant concentration at the interface could exceed

the surface concentration corresponding to the CMC if more than 396 surfactant molecules were used.

In **Figure 4.8** we show the position of JPs relative to the center of mass (COM) of the oil droplet. The difference between the COM of a Janus particle i and the COM of the oil drop, Δ_i , was calculated as a function of simulation time as follows:

$$\Delta_i = COM_{JP_i} - COM_{oil} \quad (4.2)$$

When the value of Δ_i is negative, the i -th JP is at front of the oil drop (as seen for JP1 in **Figure 4.8**), and when $\Delta_i > 0$, the JP was at the rear of the oil drop (see JP2 in **Figure 4.8**) and was set free to rotate. As the drop migrated, the JPs would move on the interface following specific patterns.

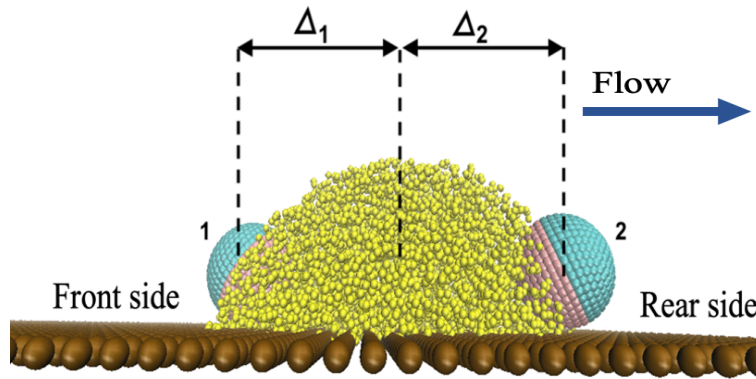


Figure 4.8. Position of Janus particles (JPs) compared to center of mass (COM) of oil droplet. Δ_1 is the distance between the COM of JP1 on the front side, while Δ_2 is the distance between the COM of the drop and the COM of JP2 on the rear side of the drop.

The relative position of each JP on the drop interface is plotted in **Figure 4.9** as a function of time. Without surfactant, the JPs would end up either at the front or at the rear of the drop and would remain close to each other because of the JP-JP interactions. The preferred location was close to the wall, at the oil-water-solid contact line, since JPs extending out of the drop experienced a hydrodynamic drag and moved away from the top of the drop and towards the drop sides. This behavior is seen in the top row of **Figure 4.9**, where all the JPs are seen to settle at either negative or positive Δ . In marked contrast, when surfactants were also present at the interface, JPs tended to move from the front to the rear of the droplet and come back again in a periodic motion. The surfactant molecules were selected to minimize the Marangoni effect, as mentioned above. Although surfactant remains in the oil drop, it still causes the interfacial velocity to be reversed

when it is added. Janus particles and surfactants can move freely under Marangoni flow while shear flow externally imposed moves in the opposite direction, resulting in periodic movements for JPs. This is seen in **Figure 4.9d-f**, where Δ changed sign periodically. We can speculate that the reason for this periodic motion is the competition between hydrodynamic effects and Marangoni effects. The surfactant molecules move toward the front of the drop, but they also keep the JPs separated from each other. When JPs are at the front side of the drop, hydrodynamic resistance moves the JPs to the rear side of the drops (as was the case when the JPs were present without surfactants). When the JPs arrive at the rear side of the drop, the surfactants between the JPs cause them to stay separated from each other and to be at locations away from the hydrodynamic stagnation point at the rear side of the drop. The hydrodynamic forces and the Marangoni motion of surfactants then push the JPs to the front and the cycle is repeated. The ratio of the projection of a single JP on the direction of the flow over the projection of the oil drop in the direction of the flow is about 6%, so smaller JPs relative to the oil drop would experience smaller hydrodynamic forces. However, as the number of JP coverage increases, the periodic motion is manifested more clearly indicating that the surfactants keep the JPs separated and away from the stagnation point at the rear side of the oil drop.

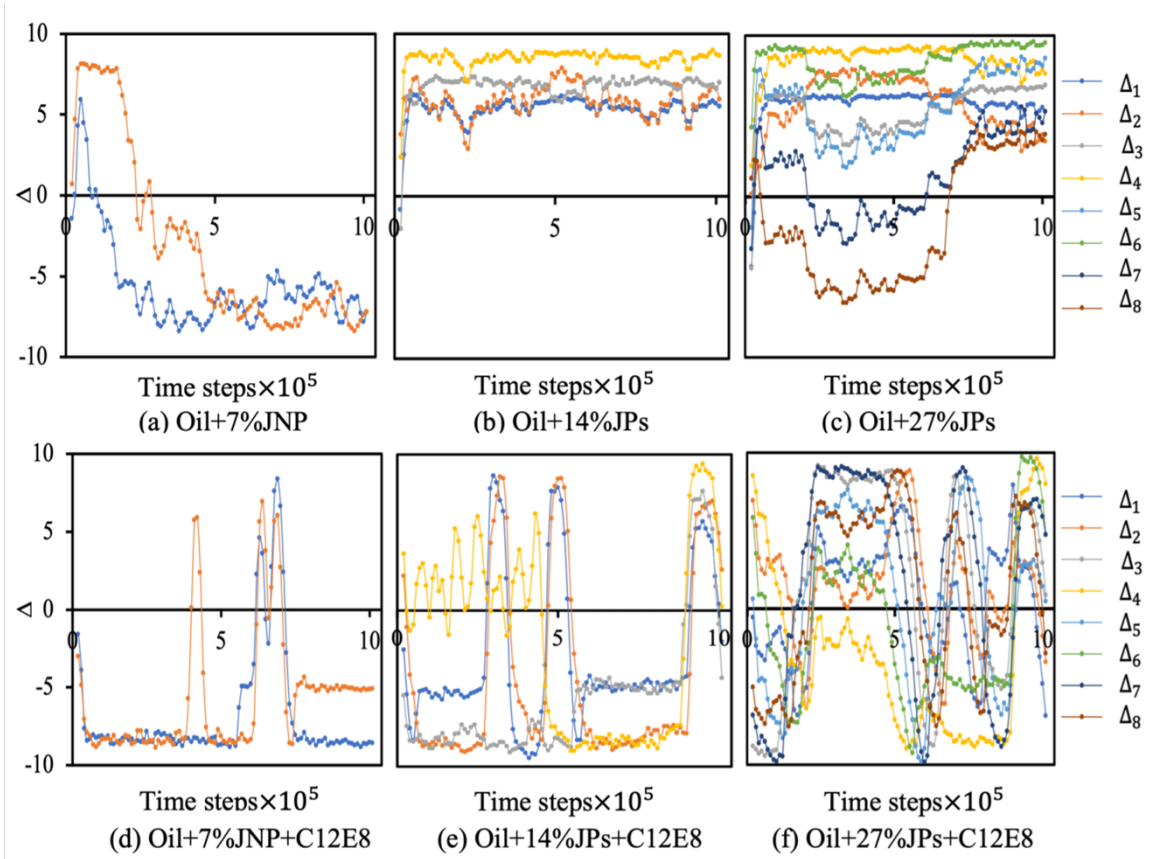


Figure 4.9. Trajectories of each JP relative to the center of mass of the droplet. Top row: No surfactant present and different JP coverage. Bottom row: 396 molecules of C12E8 present at the interface and different JP coverage.

Because of how JPs moved with or without the presence of surfactants, they had different JP-bottom wall potential energy. The total potential energy of all JPs relative to the bottom wall was calculated and averaged over 1,000,000 time steps (shown in **Figure 4.10**). For every single case with the same number of JPs present, it is seen that the total JP-bottom wall potential energy in the case of only JPs is larger than the case when JPs co-existed with surfactants. Therefore, the motion of the droplet would become more difficult in the case of only Janus particles present at the oil-water interface. Furthermore, when particles are assembled at the three-phase contact line of the drop with the bottom wall, the friction between them and the wall impedes the drop displacement. In comparison, surfactants can move freely, which helps to prevent the aggregation of JPs. As a result, the presence of surfactants aided the motion of Janus particles and resulted in a decrease in particle interaction with the wall.

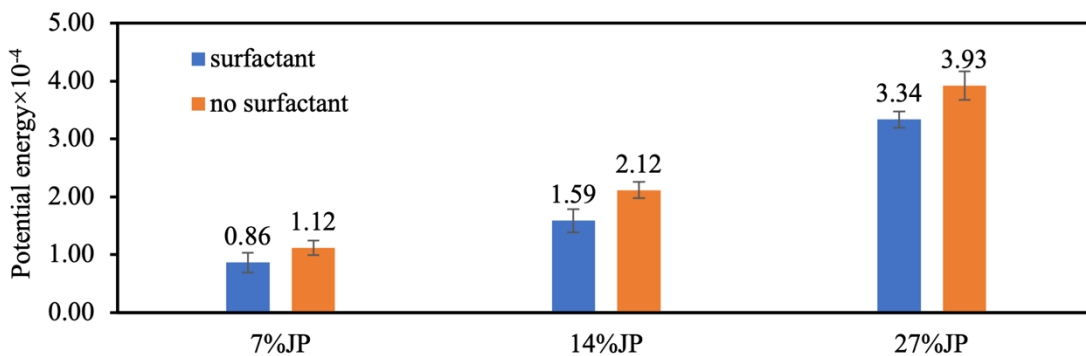


Figure 4.10. The total average potential energy of Janus particles and the solid bottom wall with C12E8 (blue) or without C12E8 (orange) at the interface between oil and water. The potential energy is in the DPD unit.

Finally, the displacement of the oil droplet was calculated for all cases examined under Couette flow and plotted in **Figure 4.11**. These included an oil droplet migrating in the water phase (designated as Oil in **Figure 4.11**), an oil droplet with surfactant with a concentration at 73% of the CMC (designated as Oil+C12E8), oil droplets with Janus particles at three different concentrations (designated as Oil+7%JPs, Oil+14%JPs, Oil+27%JPs), and oil droplet-surfactant-Janus particles at 73% of the CMC and different JP concentrations (designated as Oil+C12E8+7%JPs, Oil+C12E8+14%JPs, Oil+C12E8+27%JPs). Each of these drops was subjected to the same shear flow conditions and for the same duration. It can be seen that the drop migrated farther in the presence of both surfactants and Janus particles at the interface compared to the case of a bare oil droplet under shear. This was the case for both cases of top wall velocity in the Couette flow channel. Moreover, the more Janus particles were added to the oil droplet, the less the drop displacement. In addition, JPs experience lower water velocity around them when they assemble close to the oil-solid contact line, leading to a decrease in the speed of the particles.¹²⁴ Therefore, when more Janus particles were added, the displacement decreased.

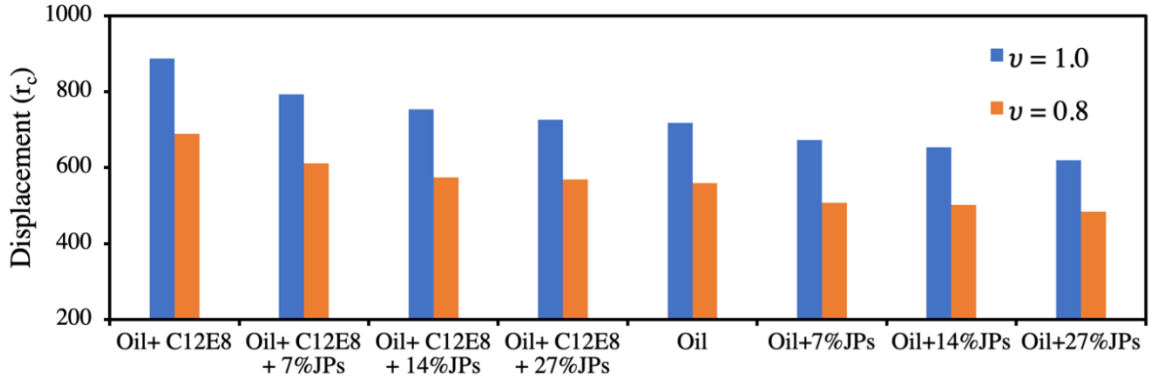


Figure 4.11. Displacement of the oil droplet in various cases.

4.5 Conclusions

In this study, we have numerically investigated the motion of an oil droplet with and without the presence of surfactant and Janus particles under shear flow conditions (Couette flow) by using the DPD simulation method. Under Couette flow, the presence of surfactants at the oil droplet surface leads to the largest migration velocity and displacement observed. The surfactants affect the interfacial tension, enhancing the momentum transfer from the water to the oil and reducing the oil-water slip. A linear relationship appears to apply between the slip velocity and the interfacial tension. Marangoni stresses tend to generate a motion of oil in the direction opposite to the direction of the shear flow, thus retarding the drop motion as a whole. However, with a relatively small surfactant concentration, the effects of Marangoni stress are overwhelmed by the flow field.

It is demonstrated that Janus particles assemble at the drop-solid contact line, increasing the friction between the drop and the wall and increasing the potential energy for the interactions between the Janus particles and the wall. Hence, JPs slow down the drop migration. Finally, the displacement of the oil droplet in the presence of both Janus particles and surfactants at the interface was compared to the case of a bare oil droplet. Since Janus particles have less interaction with the solid wall in the presence of surfactants, and since the interfacial tension, in this case, is smaller than in the bare oil case, the co-existence of surfactants and Janus particles leads to higher displacement than the case of bare oil.

Chapter 5. Effects of Nanoparticle Wettability on Meniscus Stability of Oil-Water Systems: A Coarse-Grained Modeling Approach

Abstract[‡]

A coarse-grained modeling approach is employed to probe the effect of nanoparticles and their wettability on the stability of the interface between two immiscible fluids. In this study, pure oil (dodecane) and water are placed side by side in a nanochannel, forming a meniscus. Homogeneous hydrophilic nanoparticles, Janus particles, and homogeneous hydrophobic nanoparticles are placed at the oil-water interface and their dynamics are studied as they rearrange at the oil-water interface. The results show that when the water is set in motion two instabilities occur: the formation of fingers and the detachment of water from the channel wall. It is observed that the formation of fingers is affected by the wettability of the nanoparticles. The second instability may lead to the formation of a drop that propagates through the channel. However, it is found that the wetting properties of the nanoparticles do not affect the critical flow rate for the detachment of the water from the wall. Therefore, detachment occurs at the same three-phase contact angle, regardless of the nanoparticle wetting properties. These findings can be important for industrial applications, such as enhanced oil recovery, separation technologies, and microfluidic and nanofluidic technologies.

5.1 Introduction

In recent years, the applications of nanotechnology have grown in several areas, such as environmental remediation,¹²⁵⁻¹²⁷ pharmaceuticals,^{128, 129} and food processing.¹³⁰ In the petroleum exploration and production industry, nanoparticles (NPs) have gained a significant presence in EOR since they can affect the characteristics of both the rock where oil is found and the residual oil.^{11, 131, 132} The utilization of NPs in EOR techniques has several advantages, such as adjusting the rheological characteristics of the involved fluids, flexibility in selecting the size and shape of NPs, and chemical modification of the NP surface in order to tune fluid and interfacial properties.¹³³ Several laboratory studies on NP-enabled EOR have taken place during the past

[‡] Material in this chapter has been published in Nguyen, T. X., Razavi, S., & Papavassiliou, D. V. (2024), The Journal of Physical Chemistry B, 128(12), 3016-3026.

decade. One area of study revolves around investigating the application of hydrophilic silica nanoparticles. Ju et al.¹³⁴ indicated that injecting NPs resulted in their adsorption onto pore surfaces, changing the surface wettability and significantly improving oil recovery.

In addition to their impact on surface wettability, NPs can influence the rheological properties of fluid-fluid interfaces depending on their size, shape, surface roughness, and anisotropy,^{1, 110-115, 135, 136} which can be employed in tuning the stability of emulsions and foams.^{105, 137} Among different types of NPs, Janus particles (JPs) stand out as they combine surface anisotropy and amphiphilicity into a single particle. Because one face of the JPs is hydrophilic and the other hydrophobic, they exhibit special properties at fluid interfaces. For instance, the desorption energy from the interface is up to three times higher than for homogeneous nanoparticles.¹³⁸ Since the surface anisotropy of JPs can be controlled, the resulting interfacial properties of the particle network can be tuned. Razavi et al.¹¹² showed that the amphiphilicity of JPs controlled their collapse behavior at the air-water interface under applied compressive stress, a behavior that was attributed to the orientation of particles and interparticle capillary interactions as the JP amphiphilicity was modified.¹³⁶ In addition to experimental investigations, simulations may offer an opportunity to carry out numerical experiments, allowing systematic changes in NP properties and leading to significant contributions to the study of NP characteristics.

Immiscible fluid displacement is widely used in industrial applications,^{5, 139, 140}, especially in the oil and gas industry, where chemicals and water are used in EOR.^{8, 9} The method involves injecting a fluid, such as water or gas, into an oil reservoir to displace the oil and push it toward production wells. The displaced oil is then recovered, which increases the overall production rate. There is a tendency for water to move more readily than oil, leading to instabilities and the development of water fingers. The phenomenon is known as viscous fingering or Saffman-Taylor instability.^{141, 142} The Saffman–Taylor instability occurs when a fluid pushes a more viscous fluid in a confined space. This is commonly encountered in situations involving porous media or within the gap between two parallel plates (i.e., Hele–Shaw cell¹⁴³). It is essential to predict fingering when dealing with immiscible fluid displacement because it can affect the efficiency of any oil displacement process. However, most studies regarding this instability have been done for two immiscible liquids, whereas, in reality, a system consists of many components, such as oil, water, additives, and surface-active species. The establishment of viscous fingering depends on several factors, such as the viscosity ratio of wetting and non-wetting fluids, the capillary forces, and the

injection rate.¹⁴⁴ Several technologies have been developed to avoid fingering, including the modification of the rock wettability by injecting low salinity after high salinity water;¹⁴⁵ varying the pressure gradient or the flow rate of the displacing fluid;¹⁴⁶ changing the wettability of the injection fluid by conducting core flood experiments on water-wet and oil-wet cores;¹⁴⁷ and using surfactants to modify the interfacial tension.¹⁴⁸ Moreover, when viscous fingering occurs, it can create poor sweep efficiency. Thus, polymers are employed as a viscosity control agent, but often degrade in a reservoir with harsh conditions.^{149, 150} NPs have been proposed to enhance the viscosity of the polymers in the injection fluid by strengthening the thermal stability of the polymer solution and reducing degradation. Numerical simulations by the Lattice Boltzmann method have also been used to investigate viscous fingering, breakthrough times, as well as gravity considerations.¹⁵¹

However, the fundamental understanding of the impacts NPs have on the viscous fingering phenomenon still needs to be improved. In particular, the effects of NP wettability on immiscible fluid displacement and resulting fingering behavior have not been investigated in detail. In this study, we used computations to simulate the flow of water that displaced oil (dodecane) in a nanochannel using the dissipative particle dynamics (DPD) coarse-graining computational method. The contributions of this chapter are to (a) probe how homogeneous particles (hydrophobic or hydrophilic) influence the meniscus at the oil-water interface under equilibrium and non-equilibrium conditions and compare their behavior to the case when amphiphilic JPs are employed and (b) examine viscous fingering in the presence of NPs at the interface, where the low-viscosity fluid (water) displaces the high-viscosity fluid (oil).

5.2 Simulation details

Figure 5.1 is a schematic configuration of all species used in the DPD simulations and **Table 5.1**, shows the time and length scales for converting DPD units to physical units.

Table 5.1. Scaling factors for DPD computations.

Bead density (beads/volume)	Number of water molecules in one bead	Mass scale (10^{-25} kg)	Length scale (10^{-10} m)	Temperature scale (K)	Time scale (10^{-12} s)
5	6	1.80	9.66	298	6.38

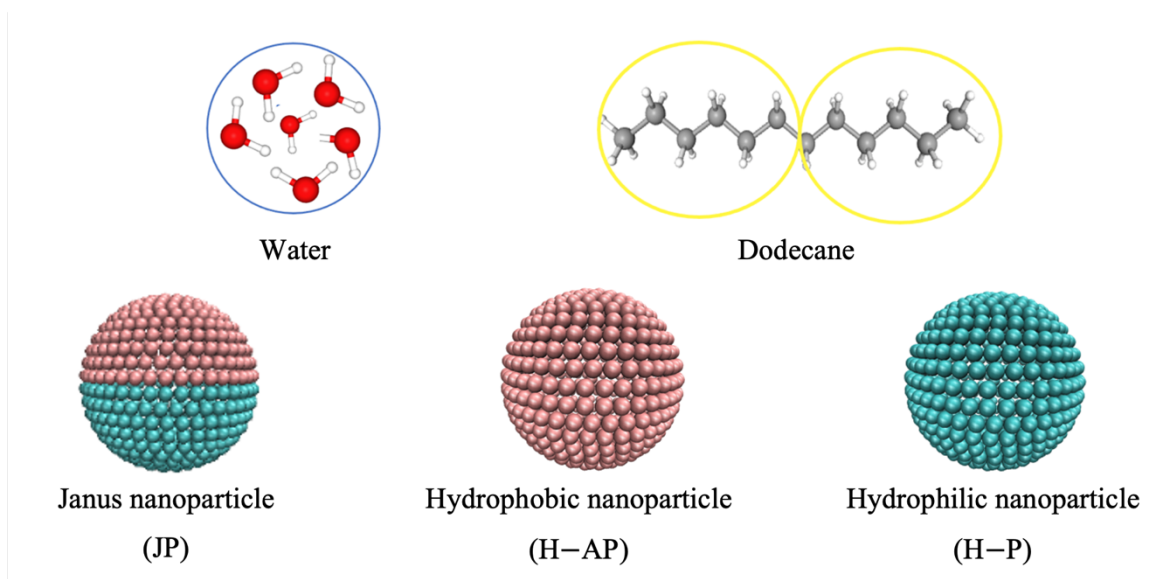


Figure 5.1. A schematic representation of the beads generated by simulations of DPD with water, dodecane, Janus particles, and homogeneous particles (hydrophilic and hydrophobic nanoparticles). Red, white, and gray spheres represent oxygen, hydrogen, and carbon, respectively. Cyan color represents the hydrophilic part, while pink is used for the hydrophobic face of the nanoparticles.

Figure 5.1 shows that each water bead (W) consisted of six water molecules, and each dodecane molecule ($C_{12}H_{26}$) contained two oil beads (O). The dimensions of the nanochannel were $90 \times 10 \times 31 r_c^3$ (using dimensionless DPD units in the x, y, z directions), with the fluid density set as 5 in DPD units (i.e., 5 DPD beads per unit volume of the simulation).⁴⁴ Therefore, 138,600 fluid beads in the computational domain and 2,938 wall beads were added to the system. The interaction parameter between oil and water was determined based on the IFT between these two fluids achieved by aligning the simulation results with experimental findings. The dodecane-water IFT was calculated with separate calculations utilizing a system with two flat oil-water interfaces. The simulation box size was $90 \times 10 \times 31 r_c^3$ (using dimensionless DPD units in the x, y, and z directions). Instead of using two solid walls in the z-direction, periodic boundary conditions in all directions were applied. Over a period of 500,000 steps, the interfacial tension values were averaged during 100 time steps of the simulation. The final interfacial tension was calculated by averaging these values further. With the interaction parameter of dodecane and water

$a_{o-w} = 129$, the value of interfacial was computed as $IFT = 52.64 \pm 0.9$ mN/m which compares well with the experimentally reported value of $IFT = 52.55$ mN/m.¹⁵²

The dynamic viscosity of water and dodecane are 8.9×10^{-1} (mPa.s) and 1.36 (mPa.s),¹⁵³ which is equivalent to 1.31 and 1.97 in DPD units, respectively. Based on the results of previous research,¹⁰⁴ the velocity profile of the water phase can be shown in **Figure 5.2**. The no-slip condition was satisfied when the dissipative parameter for interactions between water and walls was raised to twice the value of water-water interactions.

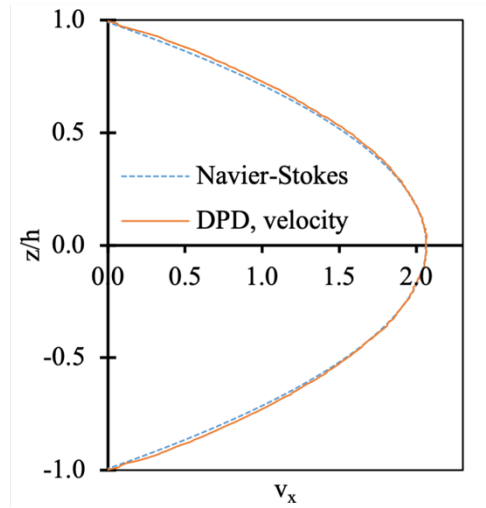


Figure 5.2. Poiseuille flow velocity profile for water flow when $\gamma_{water-water} = 4.5$ and $\gamma_{water-wall} = 9.0$

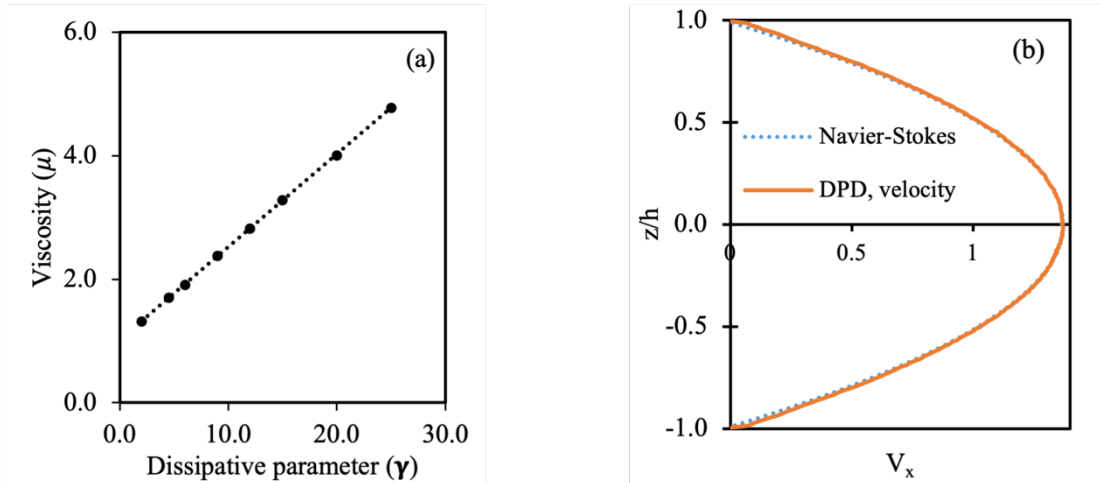


Figure 5.3. (a) Relation between the dissipative parameter and computed fluid viscosity, and (b) Poiseuille flow velocity profile for oil flow when $\gamma_{oil-oil} = 6.4$ and $\gamma_{oil-wall} = 12.8$

Moreover, the relationship between viscosity and dissipative parameter γ is linear. For the case of dodecane, this relationship is to be:

$$\mu_{\text{oil}} = 0.15 \gamma_{\text{oil-oil}} + 1.02 \quad (5.1)$$

Therefore, the dissipative parameter for oil-oil, $\gamma_{\text{oil-oil}} = 6.4$, and the dissipative parameter for the oil-wall interaction equals to $\gamma_{\text{oil-wall}} = 12.8$. **Figure 5.3a** presents the effect of the dissipative parameter on the oil viscosity. The Poiseuille flow velocity profile for oil was also verified by comparing it to the parabolic flow theoretical solution, as seen in **Figure 5.3b**. There is an agreement with the theoretical velocity profile. Therefore, we chose these dissipative parameters for two immiscible fluids and applied them to all simulations.

By adjusting the interaction coefficient a_{ij} , different types of NPs can be generated, including hydrophilic or hydrophobic nanoparticles and JPs with hydrophilic and hydrophobic phases. The NPs were placed on the oil-water interface. The interaction parameters used in the present study are listed in **Table 5.2** and **Table 5.3**. In the case of JPs, our study simulates a particular JP type where one facet corresponds to an amidine polystyrene latex (APSL) surface, while the opposing facet represents the wettability of a gold surface. The interaction parameters with the oil and the water have been determined by matching the available experimental data on the three-phase contact angle of particles at the oil-water interface.¹⁰³ This case was marked as the nanoparticle F; for the rest of the JP cases, the interaction parameter between each face of the Janus particle and the fluid phases was altered in order to simulate JPs with different degrees of amphiphilicity.¹⁵⁴ The hydrophobic NPs (type A) and hydrophilic NPs (type G) used in our simulation represent APSL and gold, respectively, exhibiting the surface characteristics corresponding to JP type F.

Table 5.2. Values of the repulsion parameter (a_{ij}) used in the simulations*

	O	W	Phi	Pho	Wall
O	15	129	a**	c**	20
W		15	b**	d**	30
Phi			15	25	35
Pho				15	15.5
Wall					15

*W and O represent water and oil, respectively, while the NPs include hydrophilic (Phi) and hydrophobic (Pho) beads.

** The values of a, b, c, and d that represent the interaction parameters of hydrophilic-oil (Phi-O), hydrophilic-water (Phi-W), hydrophobic-oil (Pho-O), and hydrophobic-water (Pho-W) beads, are provided in **Table 5.3**.

Table 5.3. Values of the repulsion parameters (a_{ij}) for different types of nanoparticles.

Type of nanoparticle	Phi-O (a)	Phi-W (b)	Pho-O (c)	Pho-W (d)
A (Hydrophobic nanoparticle)			15	50
B (3528–2530)	35	28	25	30
C (3530–2540)	35	30	25	40
Janus nanoparticle				
D (5530–2540)	55	30	15	40
E (5530–2580)	55	30	25	80
F (2520–1550)	25	20	15	50
G (Hydrophilic nanoparticle)	25	20		

The configuration of JPs and their corresponding alignment at the interface was investigated by measuring the angle between the orientation alignment vector and the interface.¹⁰³ The polar angle (α) is defined as the angle between the normal vector $\vec{k}$ that is perpendicular to the oil-water interface and the vector $\vec{n}$ connecting the particle center and a selected bead (top or bottom) on the surface of the particle (see **Figure 5.4**). This angle could take values from 0 (i.e., a Janus NP with its cap up) to 180° (i.e., Janus cap down).

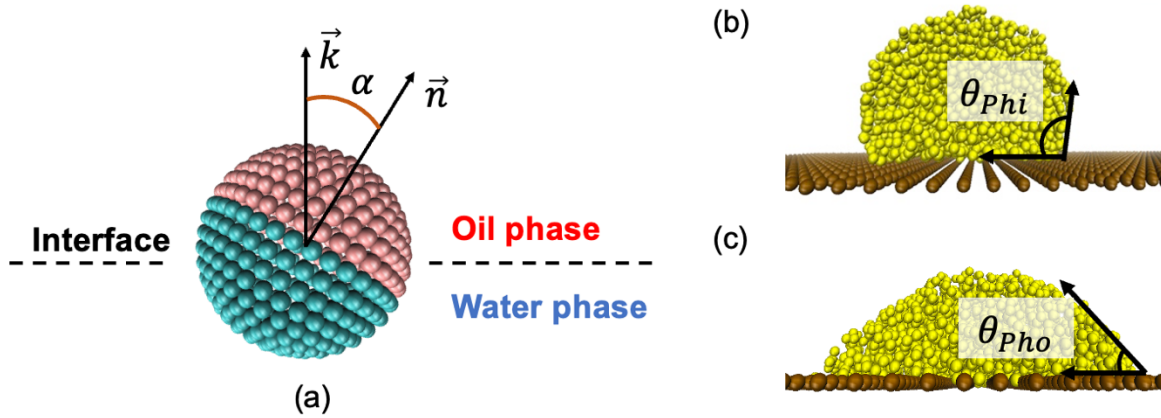


Figure 5.4. (a) Schematic illustrating the polar angle (α) between the vector $\vec{n}$ perpendicular to the Janus cap and vector $\vec{k}$ normal to the oil-water interface. The three-phase contact angle

formed by the oil droplet on a solid flat surface that exhibits the same wetting behavior as the hydrophilic facet of the JP is referred to as θ_{phi} and is shown in (b). The three-phase contact angle formed by the oil droplet on a solid flat surface that exhibits the same wetting behavior as the hydrophobic facet of the JP is referred to as θ_{pho} and is shown in (c). Color code is the same as that in **Figure 5.1**, the water beads are removed for clarity.

The difference in wettability between the two surfaces determines the degree of amphiphilicity of a JP. It is defined as $\Delta\theta = \frac{\theta_{phi} - \theta_{pho}}{2}$, where θ_{phi} and θ_{pho} describe the contact angle between an oil droplet and a flat surface with the same wettability as the hydrophilic and the hydrophobic faces of the Janus particle, respectively, as seen in **Figure 5.4b-c**.¹¹² As was shown in previous research,¹⁵⁵ the three-phase contact angle of the oil droplet on a flat surface; i.e., θ_{phi} or θ_{pho} , can be determined from the density profile of the droplet. The amphiphilicity of the Janus particle can be tuned by modifying the wetting behavior of the two opposing JP facets. In our simulations, this adjustment was achieved by enhancing the affinity of each JP facet for the water phase, resulting in the modification of $\Delta\theta$, which in turn impacted the polar angle α , seen in **Figure 5.4a**. For example, a homogeneous particle (zero amphiphilicity) has $\Delta\theta = 0^\circ$, while an anisotropic JP with strong amphiphilicity is expected to align its equator with the interface, and result in a polar angle $\alpha = 0^\circ$.

To set up the computations in the nanochannel, first, a viscous fluid (oil) was placed in the channel, surrounded by a lower-viscosity fluid (water), so a meniscus was formed across the nanochannel (see **Figure 5.5a**). After reaching equilibrium, a body force was applied to the lower viscosity fluid so that it might displace the higher viscosity fluid in the channel (see **Figure 5.5b**). In this study, a Poiseuille flow was used, driven by a pressure gradient applied in the DPD simulation as a body force in the x -direction. No-slip boundary conditions had to be applied at the inner solid surface of the channel (z -direction) and periodic boundaries were applied in the other two directions (x and y -directions).

The system was initially run with the NVE ensemble (i.e., constant number of particles, volume, and energy) to attain thermal equilibrium before further analysis. This was applied for 10,000 time steps. Recognizing the possibility of temperature fluctuations under non-equilibrium conditions, we employed a direct temperature rescaling thermostat for the subsequent time steps

by rescaling the velocities of the particle every 200 time steps. This rescaling affected only the translational degrees of freedom. As a result, the temperature remained constant at $T=1$, employing the DPD units of temperature. The simulation time step was set to $\Delta t = 0.02$ in DPD units. The total number of time steps was 1,000,000.

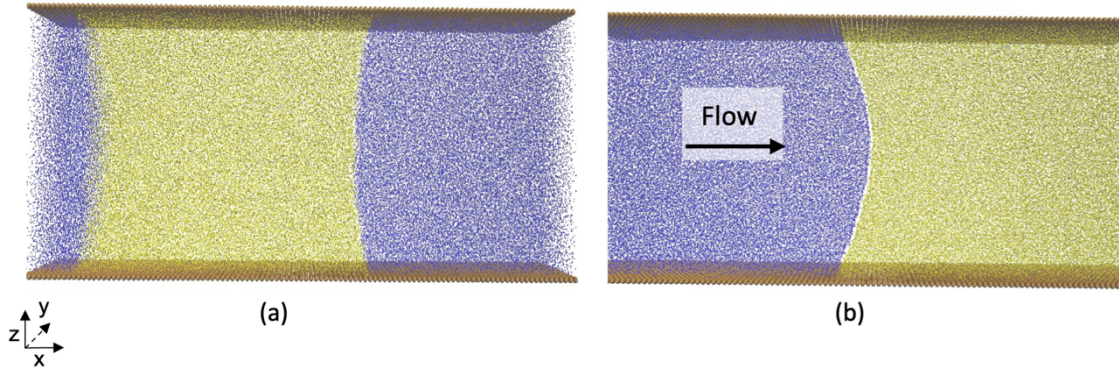


Figure 5.5. Two snapshots of the DPD model depict the oil and water meniscus located between two solid walls under (a) no flow and (b) a Poiseuille flow. The color scheme remains consistent with **Figure 5.1**.

5.3 Results and Discussion

5.3.1 Characteristics of nanoparticles and their behavior at the oil-water interface

In order to verify that the computations accounted for the physical behavior of the system, the NP behavior at the oil-water interface was investigated first. The rotation of JPs when placed at a flat interface with different initial conditions is shown in **Figure 5.6**. The NPs were initially placed at the oil-water interface with various orientations denoted by the angle α . At time step $t = 0$, the polar angle α was set to the value of $\alpha = 0^\circ$ (**Figure 5.6a**); $0^\circ < \alpha < 180^\circ$ (**Figure 5.6d**), and $\alpha = 180^\circ$ (**Figure 5.6g**). Over the simulation time, a single NP commenced rotating (**Figure 5.6b,e,h**) until it rested in its preferred position at equilibrium (**Figure 5.6c,f,i**). It is thus confirmed that the hydrophilic side of the JP tends to be in contact with the water phase, whereas the hydrophobic face exhibits an affinity for the oil phase, regardless of the initial orientation of a particle at the interface.

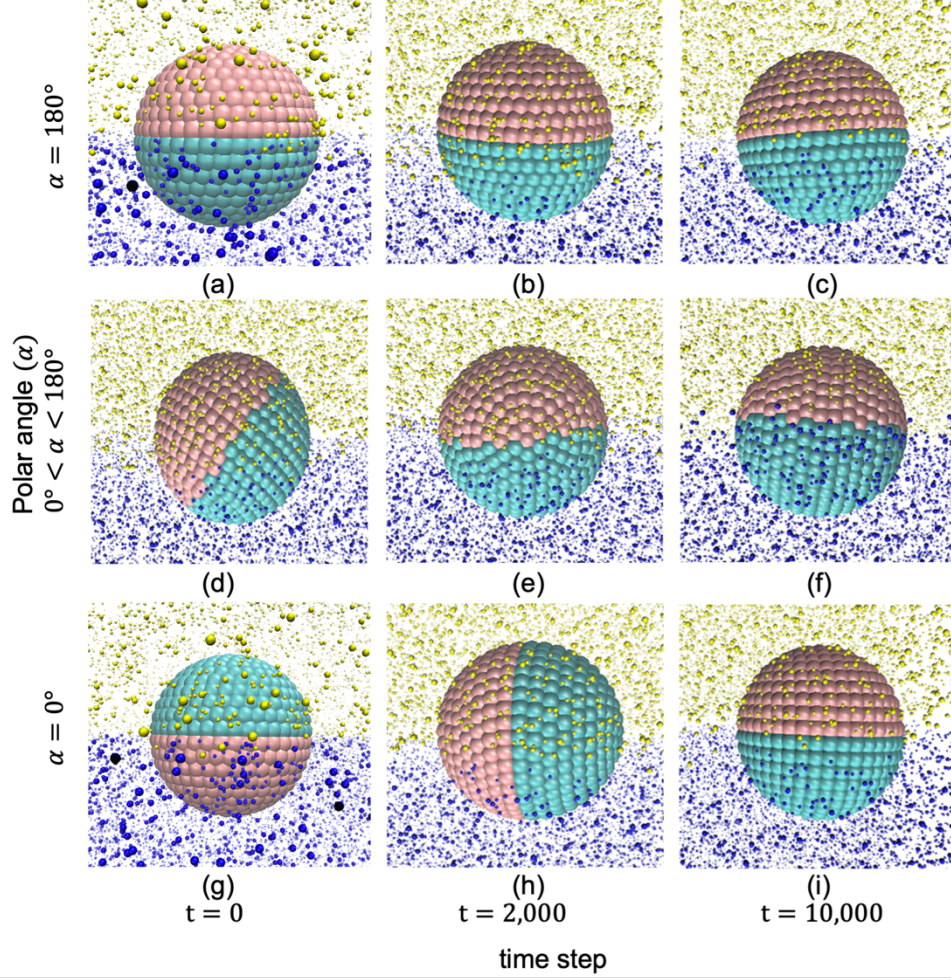


Figure 5.6. Janus particle type F (see **Table 5.4**) with different initial α -angle residing on the flat interface and the progression of its configuration during the DPD simulation. (a-c) representing the scenario where $\alpha = 180^\circ$ through time steps from 0 to 10,000. (d-f) illustrating the condition where $0^\circ < \alpha < 180^\circ$ across time steps from 0 to 10,000, respectively. (g-i) depicting the case of $\alpha = 0^\circ$ at time steps from 0 to 10,000. The color scheme is consistent with **Figure 5.1**.

Measurements of the three-phase contact angle of oil droplets in the water phase were carried out to evaluate the wettability of hydrophilic and hydrophobic surfaces of NPs on solid surfaces mimicking the JP faces. Using the example of the JP (Case F), it was determined that the average droplet contact angle on the surface of a solid wall was $\theta_{phi} \approx 95.6 \pm 2.6^\circ$ on the hydrophilic side, whereas oil was spreading on the hydrophobic surface corresponding to $\theta_{pho} \approx 0^\circ$. The degree of amphiphilicity can be estimated as $\Delta\theta = \frac{\theta_{phi} - \theta_{pho}}{2} \approx 47.8^\circ$. The results for each

Janus particle are summarized in **Table 5.4**. Altering the interaction parameter between the faces of the Janus particle and the fluid phases results in a change in the JP amphiphilicity. Two types of homogeneous nanoparticles (i.e., no amphiphilicity) were considered, in addition to five types of JPs where the degree of amphiphilicity was altered.

Table 5.4. The amphiphilicity of different types of nanoparticles.

Type of nanoparticle		$\Delta\theta$
A (Hydrophobic nanoparticle)		0°
Janus nanoparticle	B (3528–2530)	$10.7 \pm 1.0^\circ$
	C (3530–2540)	$13.9 \pm 1.5^\circ$
	D (5530–2540)	$17.3 \pm 1.5^\circ$
	E (5530–2580)	$31.0 \pm 1.0^\circ$
	F (2520–1550)	$47.8 \pm 1.3^\circ$
G (Hydrophilic nanoparticle)		0°

The change in the orientation of JPs at the interface with their amphiphilicity can be examined by placing the particles at a flat oil-water interface to study the effect independent of the curvature of the meniscus. The meniscus curvature might be affected by the width of the nanochannel and/or the wetting behavior of the channel walls. It is clearly shown in **Figure 5.7** that the particle configuration at the flat interface depends on the difference in amphiphilicity when no flow is present. The homogeneous particles rotated freely at the interface with large fluctuations in orientatin angle (α); in contrast, the rotational freedom of JPs is limited (**Figure 5.7a**). These results agree with previous findings that JPs of high amphiphilicity are expected to have limited orientational freedom.¹¹² There is a slight decrease in the angle α as the amphiphilicity of the JPs is enhanced, while there is no preferred orientation angle as the homogeneous particles are freely rotating at the interface, as displayed in **Figure 5.7b**. Moreover, this trend is observed regardless of the number of particles present at the interface. A minor variation in orientation degree is shown for the case of NPs that cover 65% of the interface area and when only one NP is present at the interface. This is likely a result of the interaction between NPs. The percentage of NP coverage at the oil-water interface (c_{NP}) was determined as follows: $c_{NP} = n \times \frac{\pi \times R_{NP}^2}{S}$, where n is the total

number of NPs, R_{NP} is the radius of NP, and S is the total interfacial area between the oil and water phases.

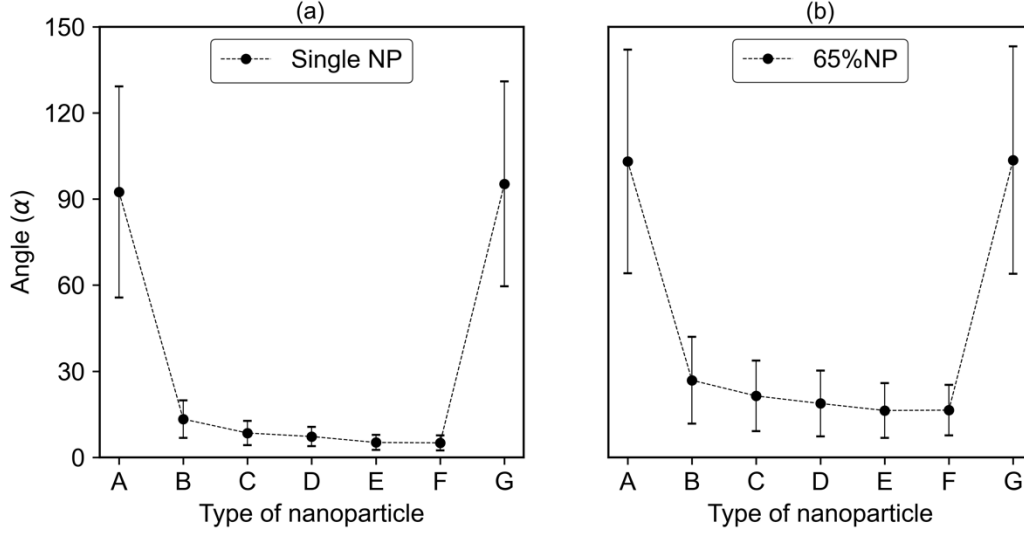


Figure 5.7. The impact of particle amphiphilicity on its orientation alignment at the interface for (a) a single nanoparticle and (b) 65% nanoparticle coverage. The error bars represent two standard deviations obtained in each case.

Next, the impact of NPs on the stability of the oil-water interface and the role of amphiphilicity was examined. 65% of the interfacial area was covered by the NPs at the oil-water interface. The initial finger length at equilibrium, L_0 , is the maximum distance between the apex of the meniscus and the 3-phase point of contact at the nanochannel wall in the x-direction (see **Figure 5.8**). The contact angle θ_{CA} is the three-phase contact angle between the oil phase and the solid wall (**Figure 5.8a**). If the contact angle θ_{CA} is altered, the length of the finger will change. Assuming that the meniscus is the arc of a circle, the three-phase contact angle and the L_0 are related as follows:

$$\theta_{CA} = \frac{\pi}{2} - \arctan\left(\frac{\frac{H}{2}}{r - L_0}\right) \quad (5.2)$$

where H is the height of the channel, and r is the radius of the water droplet forming the meniscus,

$$r = \frac{\frac{H}{2}}{\sin\left(\frac{\pi}{2} + \theta_{CA}\right)}.$$

Figure 5.8b-c depicts a snapshot of the oil-water system without and with NPs in a channel, respectively. The change of the length of the meniscus at equilibrium, L_0 , as a function of particles amphiphilicity is plotted in **Figure 5.8d**. There were no significant changes observed due to the fact that the oil-water IFT does not change (see **Figure 5.9**), in accordance with the findings of previous studies.^{36, 156, 157} This indicates that the length of the meniscus is not influenced by the presence of NPs at equilibrium.

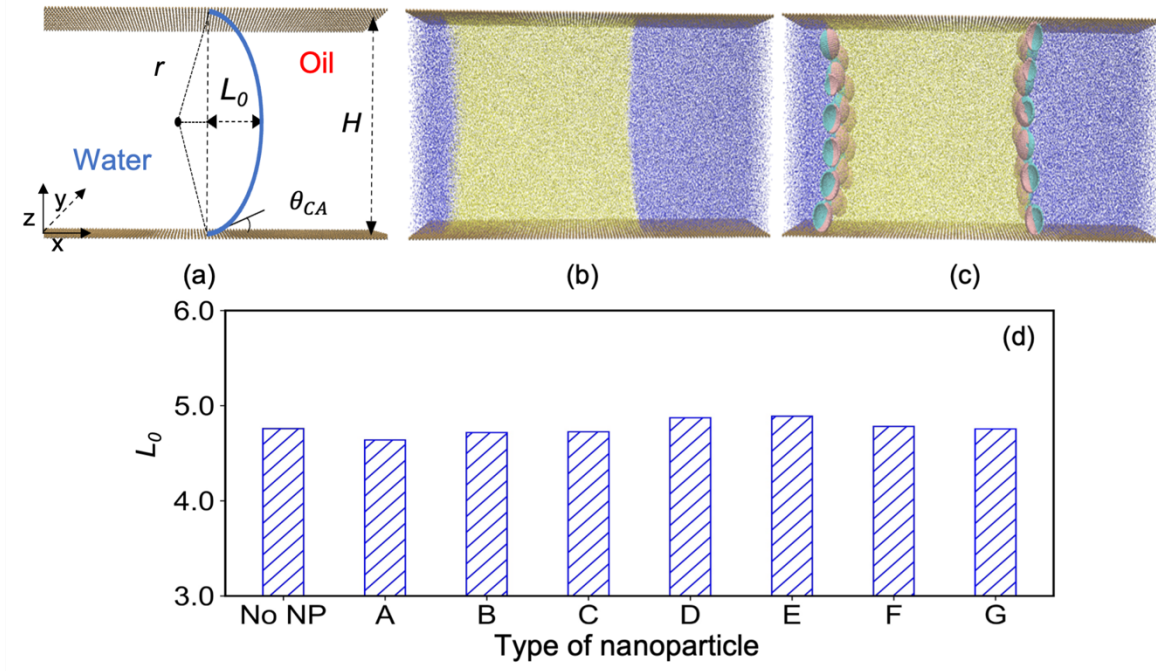


Figure 5.8. (a) Schematic illustration of simulation geometry for an oil-water meniscus confined between two solid walls. Equilibration of an oil droplet on a solid wall at different stages of the DPD computation for a system with (b) oil and water, and (c) oil, water, and nanoparticles at equilibrium. (d) Comparison of the finger length between different cases. The color scheme corresponds to that of **Figure 5.1**.

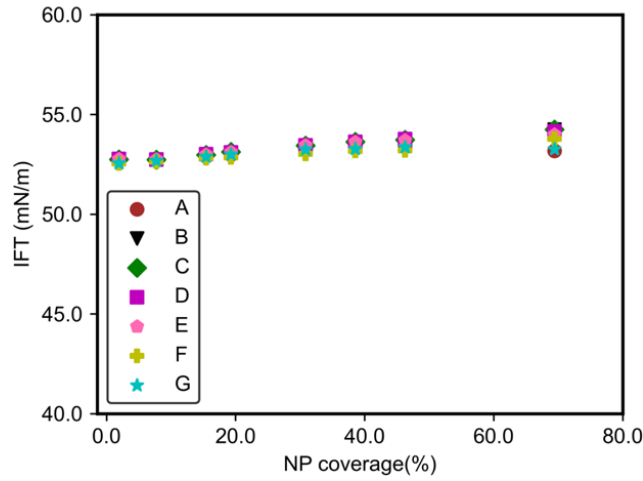


Figure 5.9. Change in the oil-water IFT as a function of nanoparticle coverage at the interface calculated for different types of nanoparticles. A, B, C, D, E, F, and G were represented for different types of NPs as shown in **Table 5.3**

5.3.2 Meniscus stability under flow

Fingering. Water is a low-viscosity fluid compared to oil. When water displaces a higher viscosity fluid, fingering may be observed, depending on the flow conditions. In the simulations, the velocity of the water phase was increased up to the point at which droplets appeared, to allow for the determination of finger length. The development of fingering instabilities at the meniscus can be characterized by dimensionless numbers, typically the Capillary number, expressed as $Ca = \frac{\mu \times V}{IFT}$, where μ is the dynamic viscosity of the displacing fluid (water), V is the velocity of water, and IFT is the interfacial tension between the oil and water phases. Although the IFT did not change when NPs were added at the oil-water interface, the Ca was affected by viscosity, velocity, and the different wetting properties of NPs. In this study, the maximum velocity of water was increased by changing the external body force, which created the Poiseuille flow, resulting in the rise of Ca number.

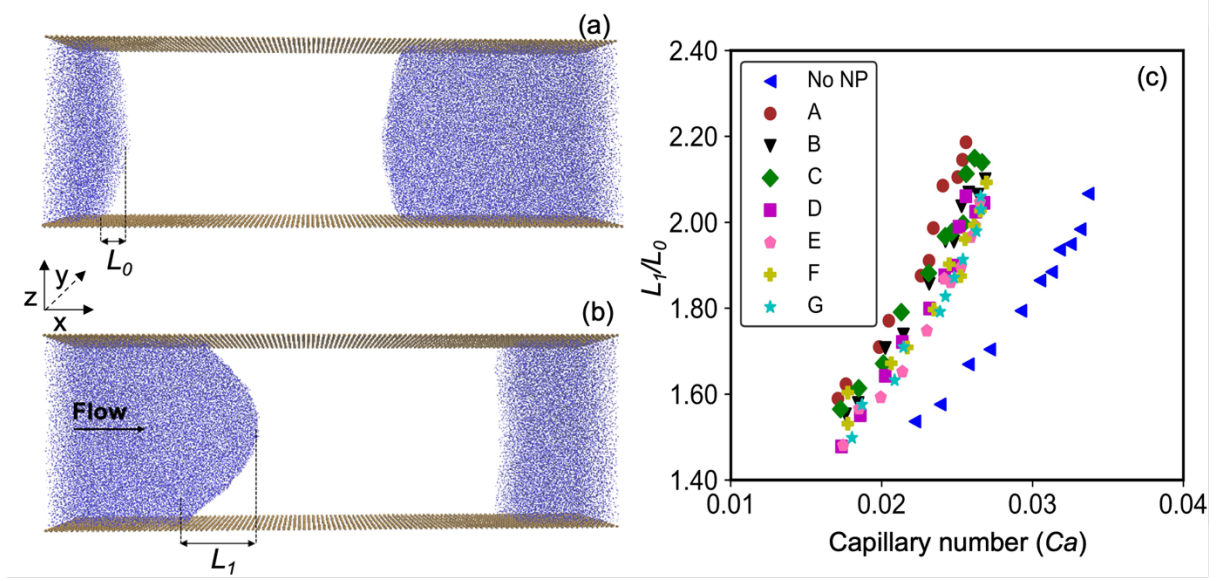


Figure 5.10. Illustration of the finger pattern (a) L_0 at $10,000^{th}$ time step in the absence of flow, and (b) L_1 at $34,000^{th}$ time step in the presence of a Poiseuille flow with a body force of $g_x = 0.0057$. The wall and water beads are depicted using ochre and blue, respectively. (c) The ratio of finger lengths $\left(\frac{L_1}{L_0}\right)$ as a function of the Capillary number (Ca) with different nanoparticle amphiphilicity.

As shown in **Figure 5.10a**, the equilibrium finger length (L_0) is determined by a computation without flow, whereas **Figure 5.10b** illustrates the dynamic finger length (L_1) calculated in the presence of flow. The instability of the meniscus is influenced by the presence of NPs located at the oil-water interface, resulting in a change in $\frac{L_1}{L_0}$ ratio. **Figure 5.10c** is a plot of the dependence of the finger length ratio, $\frac{L_1}{L_0}$, on the Capillary number. As expected, an increase in the Ca leads to a corresponding increase in the length of the finger. A straight line can be fitted to the simulation data for different cases, providing an equation of the following form:

$$\frac{L_1}{L_0} = m \times Ca + n \quad (5.3)$$

The slope of the line (m), the y-intercept (n), and the coefficient of determination (R^2) for all different cases simulated are listed in **Table 5.5**.

Table 5.5. The coefficients appearing in equation (5.3) and the coefficient of determination (R^2)

Case	m	n	R^2
Hydrophobic NP	68.4	0.4	0.97
All types of JPs	59.8	0.5	0.93
Hydrophilic NP	60.1	0.4	0.97
No NPs	44.0	0.5	0.98

In **Table 5.5**, it can be seen that when NPs are present in the system, there is a higher slope of the line compared to the case with no NPs. Therefore, the presence of particles at the fluid interface, either JPs or homogenous NPs, has an impact on the fingering phenomenon. The deformation of the meniscus exhibits variation depending on the type of nanoparticles. The bigger difference is observed for homogeneous NPs, particularly in the case of hydrophobic NPs with $m = 68.4$, while for hydrophilic NPs the slope is $m = 60$, driven by disparities in their surface wetting characteristics. The JP amphiphilicity, however, does not appear to affect the slope of the line, as seen in **Figure 5.10** and **Table 5.5**. The effects of NPs on the stability of the oil-water interface are also examined by comparing the Ca at the point of significant fingering, identified as the point at which the length of finger L_1 is at least twice the value of L_0 ; i.e., the ratio of $\frac{L_1}{L_0}$ is greater than 2. As seen in **Figure 5.11**, if the NPs are present in the oil-water system, the Ca needed to reach the same finger length was smaller when compared to the bare oil-water system. This phenomenon occurs because NPs lead to a change in the shape of the deformed meniscus when adsorbed onto the oil-water interface. Therefore, the oil-water meniscus is more stable in a system without NPs. In other words, a much higher water velocity is required to observe the same ratio of finger length when NPs are not present.

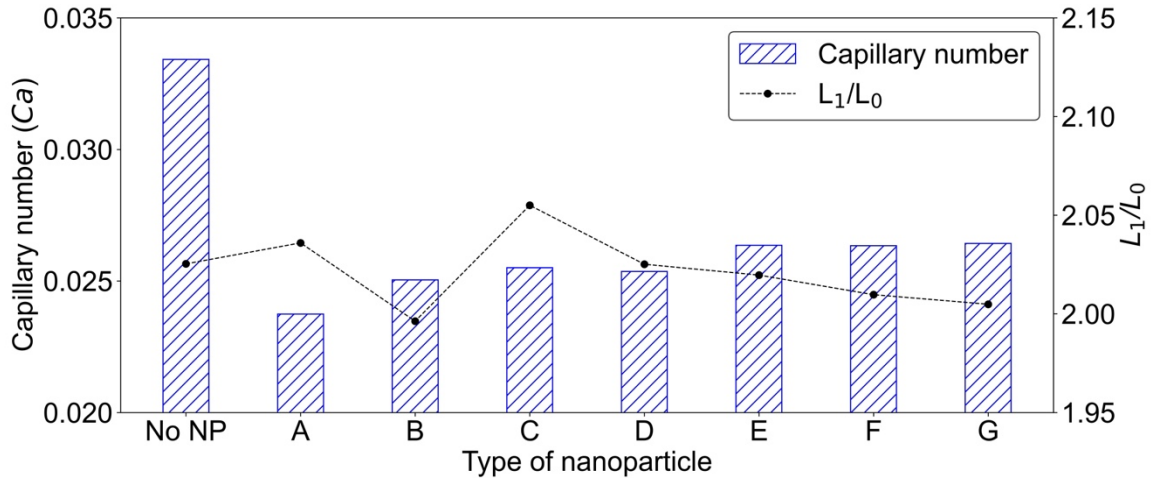


Figure 5.11. The Capillary number at which the finger length ratio is the same ($\frac{L_1}{L_0} \approx 2$) as a function of the NP wettability.

Detachment. As the water velocity increases, a second instability occurs. Water detaches from the walls, and a water droplet forms in the center region of the nanochannel. Hydrophobic solid walls were used in this study, causing the oil phase to attach to the walls, leading to the water droplet creation at the center of the channel. The values of the three-phase contact angle at which the detachment of the water phase from the solid wall occurs are provided in **Figure 5.12**. Despite the different types of NPs, there appears to be a critical three-phase contact angle that is consistent at $\theta_{CA} = 48.9 \pm 2.7^\circ$.

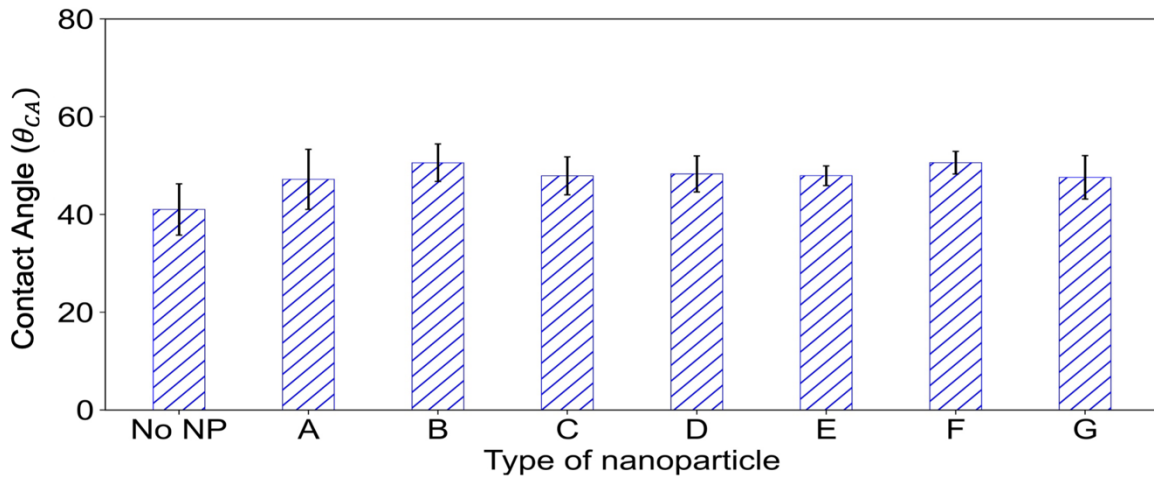


Figure 5.12. Three-phase contact angle (θ_{CA}) through the oil phase when the detachment of the water occurs. The same number of nanoparticles were located at the oil-water interface,

corresponding to 65% particle surface coverage. The error bars were calculated by the standard deviation of three contact angle measurements.

After the detachment occurs, the form of the water droplet resembles the formation of a Taylor bubble in classical two-phase flow cases. This elongated bubble remains slender and occupies nearly the entire cross-section of the channel as it moves through it. A Taylor bubble consists of four main components:¹⁵⁸ (1) a nose that resembles a hemisphere, (2) a central region encompassed by a developing film, (3) a developed film, and (4) a tail wake (see **Figure 5.13**). The value of the body force required to get to the critical contact angle for the detachment of water to create a droplet is shown in **Figure 5.13a**. The required critical body force does not display significant differences whether NPs are present or not (it is within 4%, with no systematic trend). The behavior of NPs once a drop is formed was examined in detail to gain a better understanding of how different types of NPs impacted the droplet shape in the channel. In principle, the water droplet tends to move forward, whereas the oil phase around the water droplet moves under the push of water, creating a slip velocity. Besides, as the water droplet moved to the center of the channel under the Poiseuille flow, NPs rearranged at the oil-water interface. It is seen that the NPs migrated to the rear side of droplets for all cases (**Figure 5.13b-e**). Similar observations have been reported for surface-active species (i.e., surfactants) by Luo et al.⁹⁷ It was shown that the surfactant exhibits a tendency to move across the surface of the droplet, traversing from the front to the rear. Distinct from the surfactants used in the study carried out by Luo et al., the surface-active species in our simulation are NPs, but those findings provide qualitative evidence to support the reliability of our results.

In the present computations, the formation of a second water droplet after detachment was not observed. Additional computations (not presented here) with a computational box twice as long, or twice as wide, did not reveal the formation of a second droplet. While droplet breakup has been observed in different situations with many-body DPD (MDPD),^{159, 160} the primary focus in the present work is to examine the behavior of a meniscus with the presence of NPs at the oil-water interface and the detachment of water droplets from the walls. The standard DPD technique serves well for investigating this issue.

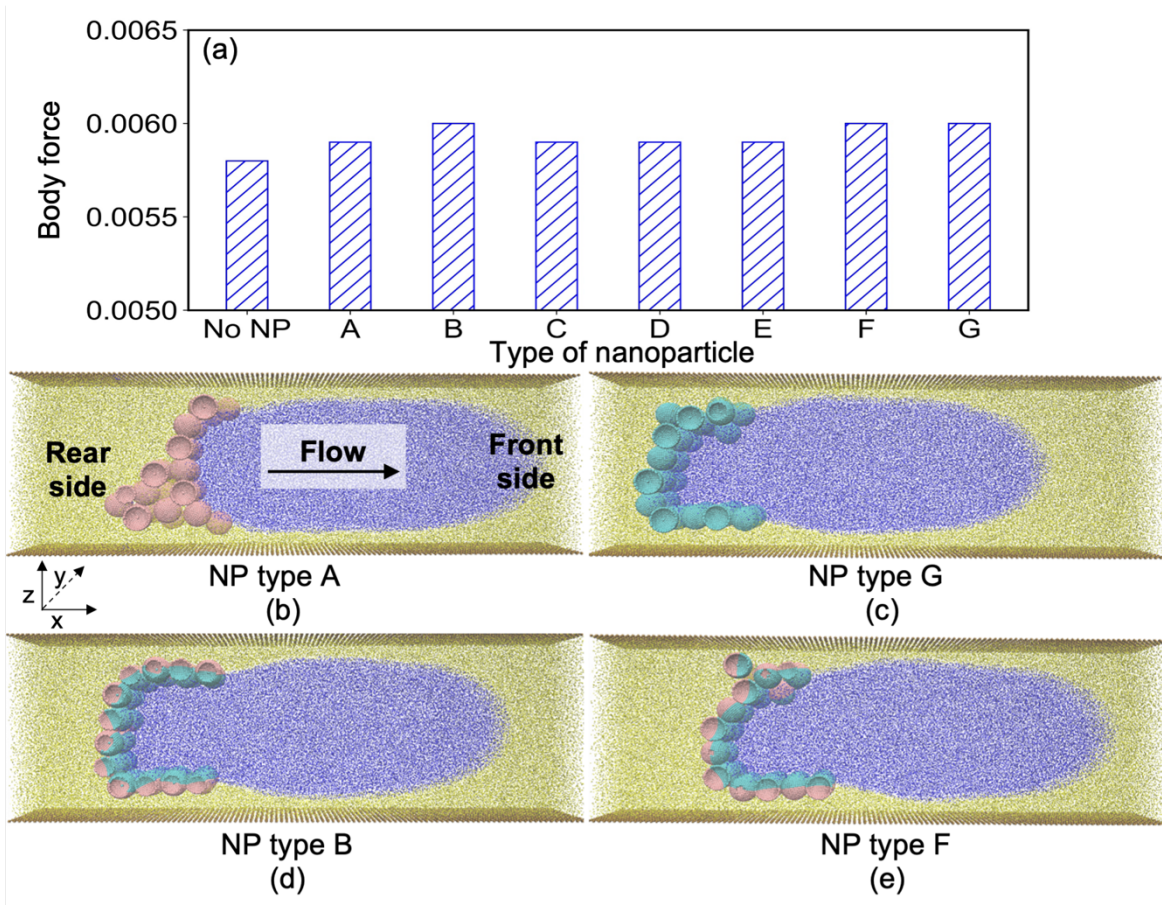


Figure 5.13. (a) Critical body force at which the water droplet detachment occurs. Simulation snapshot of a water droplet with nanoparticles located at the oil-water interface, including (b) hydrophobic nanoparticles, (c) hydrophilic nanoparticles, and Janus nanoparticles with (d) $\Delta\theta = 10.7^\circ$, and (e) $\Delta\theta = 47.8^\circ$. The color scheme reflects that of **Figure 5.1**.

Next, we examined how NPs were arranged when the droplet shape took its final form, since the NP arrangement can affect the final shape, size, and behavior of the resulting droplets. As seen in **Figure 5.13b-e**, the NPs mostly remained at the oil-water interface. In a few instances, some of the NPs migrated into one of the two fluid phases, depending on the particle wetting properties. To determine which phase might be preferred by the NPs when they were forced to partition into one of the fluids, the NP interaction energy between a single NP and either oil or water was calculated in a separate set of computations. The NPs were placed in the simulation box with only one fluid phase (only oil or only water), and the interaction energy was calculated starting from the 10,000th time step and then averaged over the next 1,000,000 time steps. As can be seen from **Figure 5.14**, each type of NP exhibits different interaction energies. This can be

explained as follows: A higher interaction energy when a NP is in the oil phase than when it is in the water phase indicates a stronger attraction between NPs and the oil phase. In other words, the NPs are more likely to partition into the oil phase than in the water phase. The cause of this behavior could be attributed to variations in the surface chemistry of the NPs, which are determined by the interaction parameters used in the simulations. **Table 5.6** presents the changes in the average interaction parameters between the hydrophilic or hydrophobic substrate of the NPs and the oil or water phase. The favored phase is also indicated in **Table 5.6**, where it is confirmed that the preferred phase is the one where the average repulsion is the lowest. Particles of type B, where the affinity for either fluid phase is similar, tend to remain at the interface as they modify the shape of the drop (see **Figure 5.14d**). In other cases, such as particles of type F seen in **Figure 5.14e**, a few particles migrate to the oil phase instead of modifying the drop shape.

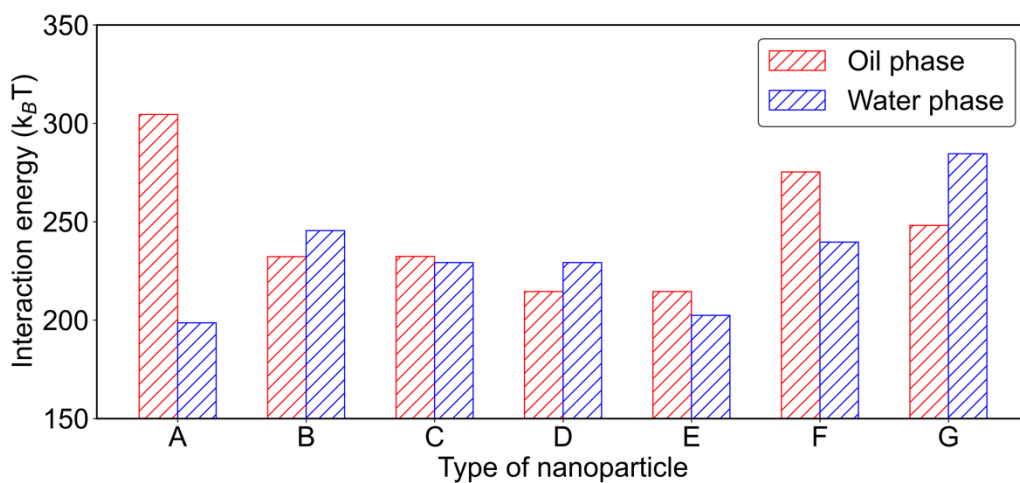


Figure 5.14. The interaction energy of one nanoparticle with oil or water is plotted as a function of the different NP amphiphilicity.

Table 5.6. Average interaction parameters for the oil phase and water phase applied for different types of NPs.

Particle Type	$\Delta\theta$	$\frac{a_{P-O} + a_{AP-O}}{2}$	$\frac{a_{P-W} + a_{AP-W}}{2}$	Favored Phase for partition
A (Hydrophobic nanoparticle)	0°	7.5	25	Oil
B (3528–2530)	10.7°	30	29	Oil-Water
C (3530–2540)	13.9°	30	35	Oil
Janus nanoparticle	D (5530–2540)	17.3°	40	Water
E (5530–2580)	31.0°	40	55	Oil
F (2520–1550)	47.8°	20	35	Oil
G (Hydrophilic nanoparticle)	0°	12.5	10	Water

5.4 Conclusions

In summary, we investigated the influence of different types of NPs on the meniscus of oil and water in the channel, including homogeneous nanoparticles (hydrophobic or hydrophilic) as well as amphiphilic Janus nanoparticles with or without flow using coarse-graining simulation methods. At equilibrium, the Janus particle's hydrophilic face reoriented to be in contact with the water phase, while its hydrophobic surface exhibited a tendency to face the oil, regardless of the JP's initial orientation at the interface. From the calculated oil-water IFT values for the case of NPs located at the oil-water interface, it can be concluded that NPs do not affect the IFT in any significant way, leading to minimal change in the equilibrium meniscus length, L_0 .

Under an applied Poiseuille flow, a linear relationship appears to apply between the finger length and the Capillary number. The wettability of the NPs affects meniscus stability, while the presence of hydrophobic particles increases finger-like protrusions of water in oil. In contrast, detachment of the water droplet occurs only when the three-phase contact angle reaches the critical value of $48.9^\circ \pm 2.7^\circ$, which is independent of the type of particles. Furthermore, the fluid velocity is also important. We have found that the pressure difference is more important for detachment from the wall and droplet formation, as low viscosity fluid displaces another fluid, than the properties of the particles, specifically when NPs are introduced into an oil and water mixture. Finally, once a drop is formed, the NPs do not distribute uniformly across the droplet surface but instead, they form more densely packed patches on the rear side of the drop. The NPs rearrange

themselves on the oil-water interface and they might even partition into the oil or water phases at the rear of the drop. The phase to which they might partition depends on their surface chemistry.

Chapter 6. Effect of Nanoparticles and Surfactants on The Interfacial Behavior of Immiscible Fluids under Non-Equilibrium Conditions

Abstract

The anticipation of fingering is crucial when addressing the displacement of immiscible fluids. This phenomenon occurs quite often when a low viscosity fluid (e.g., water) displaces a high viscosity fluid (e.g., oil) in porous media, but water moves more readily than oil, leading to instabilities and the development of water fingers. While viscous fingering phenomenon has been investigated for bare oil-water systems, the impacts of nanoparticles and surfactants presence at the oil-water interface have not been investigated in detail. The driving hypothesis is that the presence of interfacially active molecules in synergy with nanoparticles will have an effect on the development of fingering instabilities and that the wettability behavior of the particles will also play an important role in the resulting behavior. This study is a comprehensive comparison of the effects of two different types of nanoparticles (homogeneous and surface anisotropic particles) in conjunction with nonionic surfactants on the oil-water interface under Poiseuille flow conditions using dissipative particle dynamics (DPD) simulation methods. At equilibrium, a meniscus is formed at the oil-water interface, depending on the wetting properties of the channel walls. The oil phase would move when water was injected into the channel, causing finger-like instabilities, characterized by the critical driving force for the flow, the three-phase contact angle, and the deformation of the oil droplet. The full detachment of the oil drop from the solid walls of the channel, when the oil-water meniscus becomes unstable due to the water flow, was found to depend on the driving force for the flow. In presence of surfactants, the instability was found to develop at smaller pressure drops compared to the bare oil-water case. When both surfactants and nanoparticles were present, a larger driving force was required to detach the water or oil drop compared to either bare oil-water system or the surfactant-only case. A critical contact angle dictated the detachment of the oil droplet from the channel wall. These findings elucidate the mechanism of stabilizing the interface between oil and water using nanoparticles and surfactants, and have potential implications for tuning oil-water interfacial behavior.

6.1 Introduction

It is common in the industry to use immiscible fluid displacement,^{5, 139, 140} especially in secondary and tertiary oil recovery when chemicals and water displace viscous oils.^{8, 9} There is a tendency for water to move more readily than oil, which produces viscous fingers. The phenomenon is known as Saffman-Taylor instability.^{141, 142} In the work of Saffman and Taylor, they developed a theoretical analysis that examined how a finger of a low viscosity fluid evolves and grows as it displaces a more viscous fluid. They obtained a one-dimensional mathematical expression for the growth of the fingers.

More recently, Jamaloei et al.¹⁶¹ analyzed experimentally viscous fingers, their lengths, widths, and how the number of fingers grows with time and front position. A five-point injection scheme for hydrocarbon reservoirs was replicated at a lab scale by injecting water or polymer into a micro model, mimicking a commonly applied production scheme. For the case of high interfacial tension (IFT), i.e., when water displaced heavy oil, it was found that the flow rate did not affect the number of fingers. When polymer displaced the heavy oil, which is a case of low IFT, the number of fingers depended on the flow rate of the polymer. In addition to experiments, computational studies using the Lattice Boltzmann method have been applied to describe the viscous fingering phenomenon of two immiscible fluids.^{151, 162} Several factors that impacted the morphology of viscous fingers were considered, including the wettability of the walls, the capillary number, and the viscosity ratio between the two fluids. Results indicated that the viscosity ratio significantly impacts finger formation, but finger length does not increase monotonically with the viscosity ratio. The Capillary number (Ca) determined the degree of bending at the interface between two immiscible fluids; a large Ca caused the interface to form fingers. Furthermore, the Ca also affected the three-phase contact angle and the moving contact line.

However, most studies have focused on the simple case with only two immiscible fluids in the system; in practical applications, different types of chemicals are transported with oil and water, such as surfactants, polymers, and nanoparticles (NPs). There needs to be a careful examination of additives and impurities that could act as surface-active agents. Among the nonionic surfactants commonly used for EOR is octaethylene glycol monododecyl ether (C12E8)⁷² which is used in the present study. In addition, NPs have been noted to stimulate the oil recovery¹⁶³ when they are injected into the reservoir. The addition of NPs to oil-in-water emulsions can provide stabilization.¹⁰⁵ However, the presence of colloidal particles does not affect the IFT, which can be

reduced when surfactants are used.^{10, 11} In the energy and environmental sectors, synergies of surfactants and NPs, both present at the oil-water interface, have been studied.³²⁻³⁴ In our previous research, we sought to investigate the migration and adsorption behavior of surfactants on an oil droplet attached to a wall, and the displacement of this droplet immersed in water with or without surface anisotropic; i.e., JPs.¹⁵⁵ However, it has yet to be quantified what impact NPs and/or surfactants have on interfacial deformation in fluid displacement problems. Therefore, this work is focused on investigating the effect of surfactants, NPs, and the coexistence of surfactants and NPs on the oil and water displacement under flow.

The wettability of a solid surface is a key factor influencing the ultimate oil recovery.^{164, 165} In general, the more water-wet the solid surface, the less oil will adhere to it, and oil droplets will be more likely to be removed. Therefore, it is important to consider the wettability of surfaces in order to understand oil expulsion. This study involves two types of solid wall properties: water-wet (hydrophilic) and oil-wet (hydrophobic).

A controlled flow is simulated using the DPD coarse-graining computational approach. We present a comprehensive study to compare the effect of different types of NPs with or without surfactants on the oil-water interface under non-equilibrium conditions. Both homogeneous (hydrophilic or hydrophobic) particles and amphiphilic JPs are examined. Janus particles are anisotropic particles since their surface has areas of different wettability, where one particle side is hydrophilic and the other is hydrophobic. The displacement process consists of three phases: (1) the equilibrium phase before the flow is applied, (2) the stable phase after the flow is introduced, followed by (3) the formation of droplets.

6.2 Simulation details

The schematic configuration of all species used in the DPD simulations is shown **Figure 6.1**, while the conversion of time and length scales from DPD units to physical units is seen in **Table 5.1**. As designated in **Figure 6.1**, six water molecules were combined into each water bead (W), and dodecane molecules ($C_{12}H_{26}$) represented the oil phase with each dodecane molecule divided into two oil beads (O). The surfactant chosen is C12E8, which were represented by two hydrophobic tail beads (T) and four hydrophilic head beads (H). For the Janus nanoparticle, amidine polystyrene latex and gold domains were used as the hydrophobic and hydrophilic sides, respectively. The DPD model for this type of JP has been developed and validated previously.¹⁰³

Water beads were randomly distributed between two parallel solid plates that created a nanochannel. Next to the water, oil beads were also distributed from one side of the nanochannel to the other, while surfactants and/or NPs were added at the oil-water interface depending on the experiment to be run. As seen in **Figure 6.1b-i**, a meniscus was formed at the oil-water interface. To reach equilibrium without flow, the system runs for 10,000 computational steps. During the computations, an NVE ensemble (constant volume, constant energy) was used with temperature rescaling every 200 time steps. The simulation time step was set to $\Delta t = 0.02$ in DPD units, and the total number of steps after equilibration was 1,000,000.

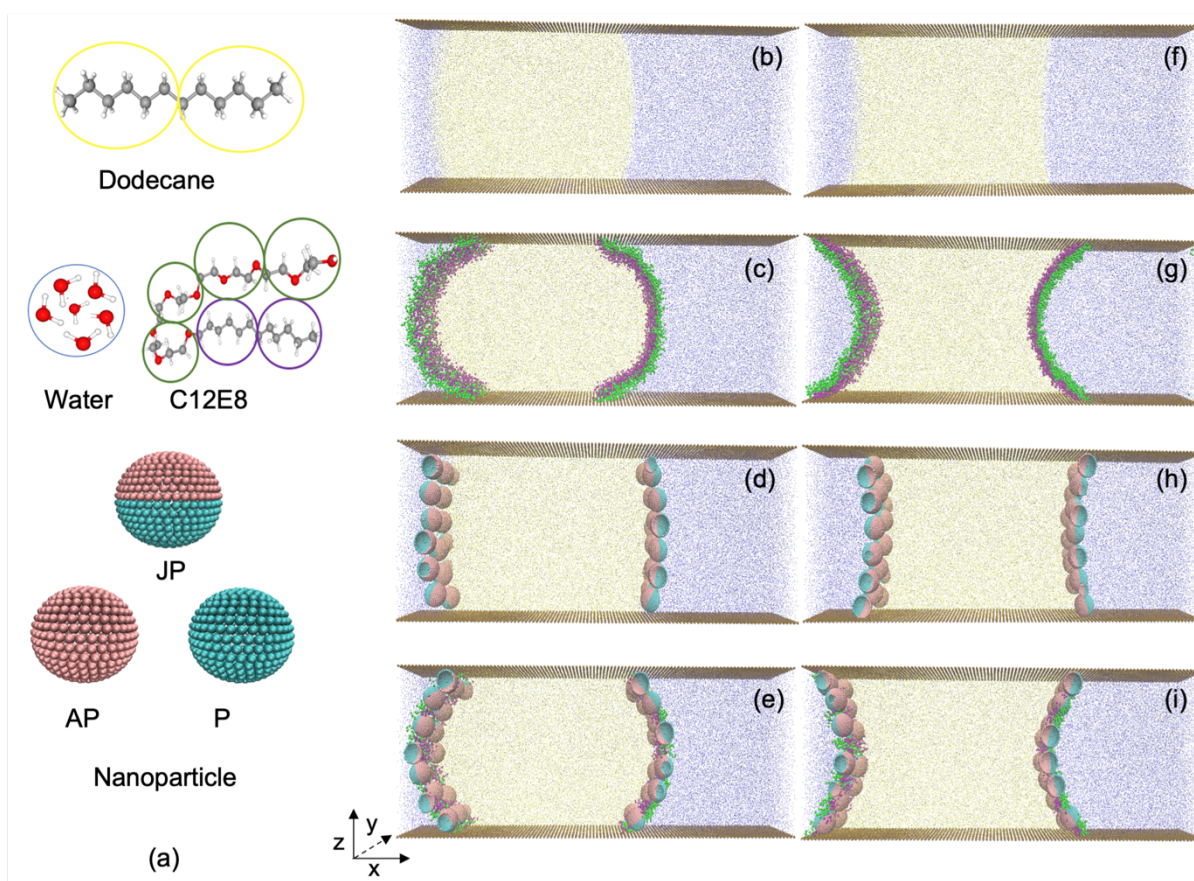


Figure 6.1. (a) A schematic representation of the beads employed by DPD simulations with water, dodecane, Janus particle (JP), homogeneous particles (hydrophobic-AP and hydrophilic-P nanoparticle), and C12E8 surfactant molecules. Red, white, and gray spheres represent oxygen, hydrogen, and carbon, respectively. Modeling the oil layer in the hydrophilic channel (b-e) and hydrophobic channel (f-i) for various systems studied: (b, f) oil, water; (c, g) oil, water, and surfactant; (d, h) oil, water, and JPs; (e, i) oil, water, surfactants, and JPs system. The wall,

water, and oil beads are shown as ochre, blue, and yellow, respectively. Cyan color represents the hydrophilic part, while pink is used for the hydrophobic face of the NPs. Purple and green represent the tail and head beads of the surfactant, respectively.

After equilibrium was established, a constant body force was applied to the water beads to generate a Poiseuille flow. In this way, we simulated a lower viscosity fluid that was continuously moving along the x -direction of the channel. The channel dimensions were established as $90 \times 10 \times 31 r_c^3$, (dimensionless DPD units in the x, y, z directions). There were 2,938 wall beads and 138,600 fluid beads within the computational domain, and the fluid density in DPD units was set as 5 (i.e., 1 DPD bead per unit volume of the simulation) ⁴⁴. Additional computations were conducted with a bigger simulation box $120 \times 10 \times 31 r_c^3$ in order to verify the position of fully detached oil drops in the presence of NPs and surfactants at the Critical Micelle Concentration (CMC). There were 3,900 wall beads, 72,2000 oil beads, and 104,261 water beads used in those simulations. No-slip boundary conditions had to be enforced at the channel walls, while periodic boundaries were applied in the two other directions. To prevent the formation of micelles, the surfactant concentration was carefully controlled. If the concentration of surfactant molecules at the interface exceeded the CMC, surfactants would partition out to the water and create micelles.¹¹⁹ Thus, for this study, the maximum surfactant concentration is set at the CMC. The repulsion parameters for the case of C12E8 and/or NPs at the oil-water interface with two types of wall properties (hydrophilic and hydrophobic walls) are listed in **Table 6.1** and **Table 6.2**, respectively.

Table 6.1. Details of the repulsion parameters (a_{ij}) used in the simulations for the channel with hydrophilic walls*

	H	T	W	O	AP	P	Wall
H	15	25	14	25	25	15	25
T		15	30	14.5	15	25	35
W			15	129	50	20	15
O				15	15	25	20
AP					15	25	35
P						15	15.5
Wall							15

Table 6.2. Details of the repulsion parameters (a_{ij}) used in the simulations for the channel with hydrophobic walls*

	H	T	W	O	AP	P	Wall
H	15	25	14	25	25	15	35
T		15	30	14.5	15	25	25
W			15	129	50	20	30
O				15	15	25	20
AP					15	25	15.5
P						15	35
Wall							15

* H and T represent the head and tail of C12E8 surfactant, while W and O symbolize water and oil, respectively. The NPs include hydrophobic (AP) and hydrophilic (P) beads.

6.3 Results and Discussion

The immiscible viscous fingering process can be divided into three different stages. The first stage is the equilibrium phase, which occurs before introducing any flow. During this stage, the fluids are in equilibrium, and no flow conditions are imposed. The second stage includes two scenarios: the stable phase, which occurs after applying the Poiseuille flow, and the finger formation process until the breakthrough. During this stage, the fluids start to move as the external body force increases. The meniscus starts to deform and looks like a finger that grows and propagates. Finally, the last stage is the formation of droplets, which occurs when one liquid phase detaches from the wall and droplets of one phase are dispersed in the other.

6.3.1 The case of equilibrium and no flow

To verify the integrity of the computations, the dodecane-water IFT was calculated for a flat oil-water interface at equilibrium, following the procedure outlined in the ref³⁶ for heptadecane and water. The oil and water beads were distributed initially in three continuous regions as water-oil-water. Because of the periodic boundary conditions in all directions, there were two oil-water interfaces. Following the start-up period for each of these simulations, the IFT values were determined every 100 time steps of the simulation and then averaged for 1,000,000 steps. The number of surfactant molecules added to the oil-water interface was determined as follows: The

interfacial concentration of C12E8 on the dodecane-water interface, corresponding to the critical micelle concentration (CMC), is $2.67 \times 10^{-10} \text{ mol/cm}^2$.¹²¹ In DPD units, this translates to 1.49 molecules per $1 r_c^2$ of interfacial area for the system of C12E8 at the oil-water interface. Thus, the surface concentration of C12E8 at CMC was calculated as $N_{CMC} = 1.49 \times S_0$, where S_0 is the interfacial area between oil and water. The IFT of the oil-water interface is plotted in **Figure 6.2** using the flat interface. In **Figure 6.2a** there were no NPs, and the IFT is plotted as a function of the surfactant concentration ranging from zero to beyond the CMC. In **Figure 6.2b** there are only NPs present, and in **Figure 6.2c** there are both surfactants and NPs present at the interface. The NP coverage of the interface was calculated as $c = n\pi \frac{R^2}{S_0}$, where n is the total number of NPs at the interface and R is the NP radius. The experimental data for dodecane-water interfacial tension (IFT) with the presence of C12E8 at CMC was found to be $IFT \approx 3.10 \text{ mN/m}$,¹²¹ which was close to our simulation result for dodecane-water $IFT \approx 2.03 \text{ mN/m}$ (see **Figure 6.2a**). In addition, it is seen that the value of IFT decreased significantly with the concentration of surfactant on the oil-water interface. Whereas, the NPs do not have a noticeable impact on the interface tension (see **Figure 6.2b**), as already shown in previous studies.^{36, 156, 157, 166, 167} However, the presence of NPs reduces the effective interfacial area, causing an increase in surfactant concentration when compared to the case when only surfactants were in the system. Consequently, the IFT between oil and water decreases when the number of NPs increases with the same number of surfactant molecules. The most significant observation is that Janus and hydrophilic (P) nanoparticles display similar behaviors, while hydrophobic (AP) nanoparticles demonstrate a decrease in the IFT. This effect is demonstrated in **Figure 6.2c**. The difference in the IFT for the same coverage can be attributed to the fact that the hydrophobic NPs used in this study occupy a smaller surface area of the oil-water interface in comparison to other NPs. The hydrophobic particles are mostly in the oil phase, so the interfacial area available to the surfactants is higher and the IFT is also higher.

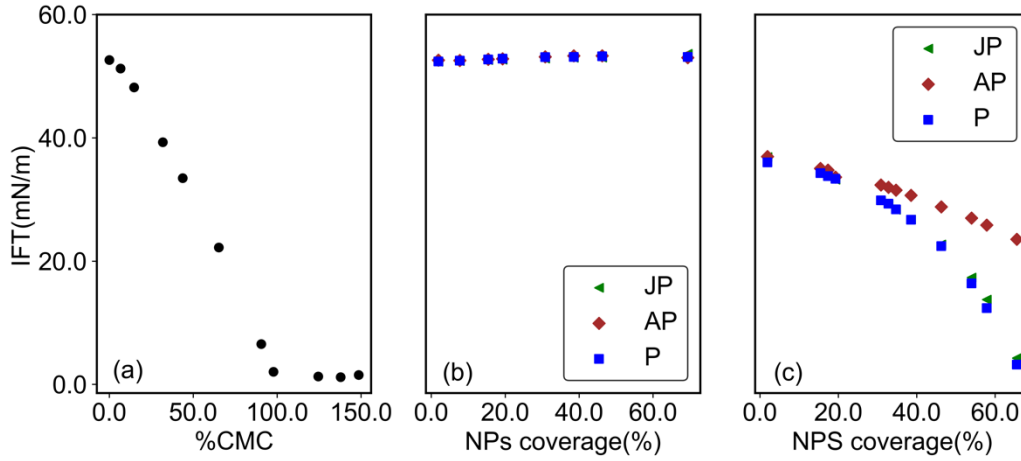


Figure 6.2. The IFT of oil and water with (a) the nonionic surfactant C12E8, (b) NPs (Janus, hydrophilic (P) and hydrophobic (AP) nanoparticles) without surfactant, and (c) surfactant with $C_{C12E8} = 35\% \text{ CMC}$ and different types of NPs located at the interface.

When the oil-water interface took the shape of a meniscus, the arc length of the meniscus and the width of the channel were used to calculate the interfacial area. In **Figure 6.4a-b**, a sketch of the finger in the channel is shown, in which the arc length L_0 can be found during a static calculation, i.e., when no flow is present. θ_{CA} indicates the three-phase contact angle of oil surrounded by water and the solid walls, and it was determined after the system reached equilibrium at 10,000 steps after the total energy reached a plateau (see **Figure 6.3**). The arc length changed as the contact angle changed, depending on the wettability of the channel solid walls. If the surface is hydrophobic, the contact angle for the oil and the solid will be $\theta_{CA} < 90^\circ$; otherwise, if the surface is hydrophilic, the contact angle will be greater than 90° . As a result, the three-phase contact angles for the hydrophilic wall and the hydrophobic wall are $\theta_{CA} \approx 116.6 \pm 1.0^\circ$ and $\theta_{CA} \approx 63.9 \pm 0.3^\circ$, respectively. Then the calculated surface areas for hydrophilic and hydrophobic surfaces are found to be $S_0 \approx 319.6 r_c^2$ for the hydrophilic surface and $S_0 \approx 319.2 r_c^2$ for the hydrophobic surface.

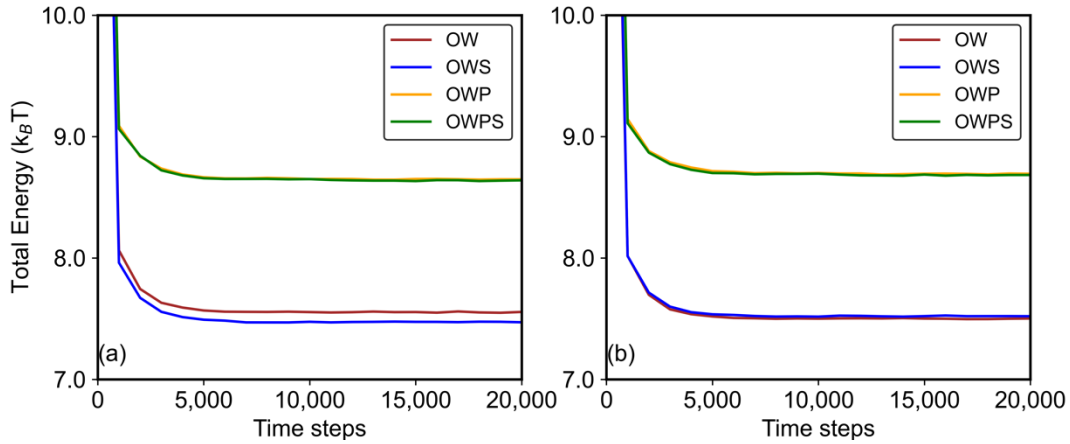


Figure 6.3. The total energy of various systems during the first 20,000 DPD simulation time steps for (a) hydrophilic wall and (b) hydrophobic wall. OW: Oil-Water; OWS: Oil-Water-C12E8; OWP: Oil-Water-NPs and OWPS: Oil-Water-NPs-C12E8.

As can be seen in **Figure 6.4c**, when nonionic surfactants were added to the oil-water interface, the effect of the surfactant concentration on the three-phase contact angle can depend on the properties of the solid wall. C12E8 nonionic surfactant has a relatively small hydrophobic tail, making the solid surface more hydrophilic. The contact angle of the oil phase with the wall increases for hydrophilic walls ($\theta_{CA} \approx 189.6 \pm 0.8^\circ$) and decreases for hydrophobic walls ($\theta_{CA} \approx 15.9 \pm 2.2^\circ$) at the critical micelle concentration of the surfactant. A larger contact angle indicates more wetting, indicating that the water has a greater affinity for the surface. This results in the water spreading out more extensively over the surface, leading to a longer meniscus arc length in the channel. Conversely, a smaller contact angle indicates weaker attraction between the water and the surface, resulting in reduced spreading of the water and a shorter arc length of the meniscus for hydrophilic walls. Whereas, the hydrophobic wall exhibits a longer meniscus arc length when the three-phase contact angle becomes smaller as the surfactant concentration reaches the CMC value.

The three-phase contact angle for the case of NPs present at the oil-water meniscus interface is shown in **Figure 6.4d**. The effect of NP coverage is shown. The contact angle remained constant at $\theta_{CA} \approx 118.3 \pm 2.3^\circ$ for the case of the hydrophilic wall. The NPs can adsorb at the oil-water interface instead of interacting with the solid walls. It is already discussed that the NPs themselves did not remarkably affect the IFT. Furthermore, for the case of the hydrophobic wall,

θ_{CA} remained constant at around $61.0 \pm 3.2^\circ$, and this is the same values measured for the pure system (no particles, no surfactant). This result is in good agreement with our previous research findings¹⁶⁸. In conclusion, the number of NPs considered in this study does not affect the value of the three-phase contact angle.

As surfactants were added to the system with NPs at a concentration of 35% of the CMC, they caused a significant effect in the three-phase contact angle (see **Figure 6.4e**). The surfactant concentration value of 35% of the CMC was selected because this corresponds to the critical micelle concentration when 65% of the interface is covered by JPs. In **Figure 6.4e**, for hydrophilic walls, when the number of NPs goes up, the three-phase contact angle increases dramatically, especially in the case of 65% of NPs located at the oil-water interface. The contact angle changes from $\theta_{CA} \approx 116.6 \pm 1.0^\circ$ (oil-water) to $\theta_{CA} \approx 152.2 \pm 2.3^\circ$ (oil-water-JP 65%), $\theta_{CA} \approx 146.6 \pm 2.6^\circ$ (oil-water-P 65%), and $\theta_{CA} \approx 148.5 \pm 4.1^\circ$ (oil-water-AP 65%). As discussed earlier, the role of surfactants in reducing the contact angle is related to their ability to lower the surface tension at the interface between oil and water. However, NPs do not significantly affect the three-phase contact angle but decrease the effective interfacial area, reducing the IFT between oil and water, as illustrated in **Figure 6.2**. The CMC will be created with 65% coverage of NPs in the system, generating the lowest IFT and the highest three-phase contact angle. Also, for hydrophobic walls, an increase in hydrophobicity was observed as more NPs were added to the oil-water-surfactant system. The three-phase contact angle went down dramatically between $\theta_{CA} \approx 63.9 \pm 0.3^\circ$ (oil-water) and $\theta_{CA} \approx 37.9 \pm 2.8^\circ$ (oil-water-JP 65%), and $\theta_{CA} \approx 41.8 \pm 1.0^\circ$ (oil-water-P 65%), and $\theta_{CA} \approx 45.1 \pm 1.5^\circ$ (oil-water-AP 65%).

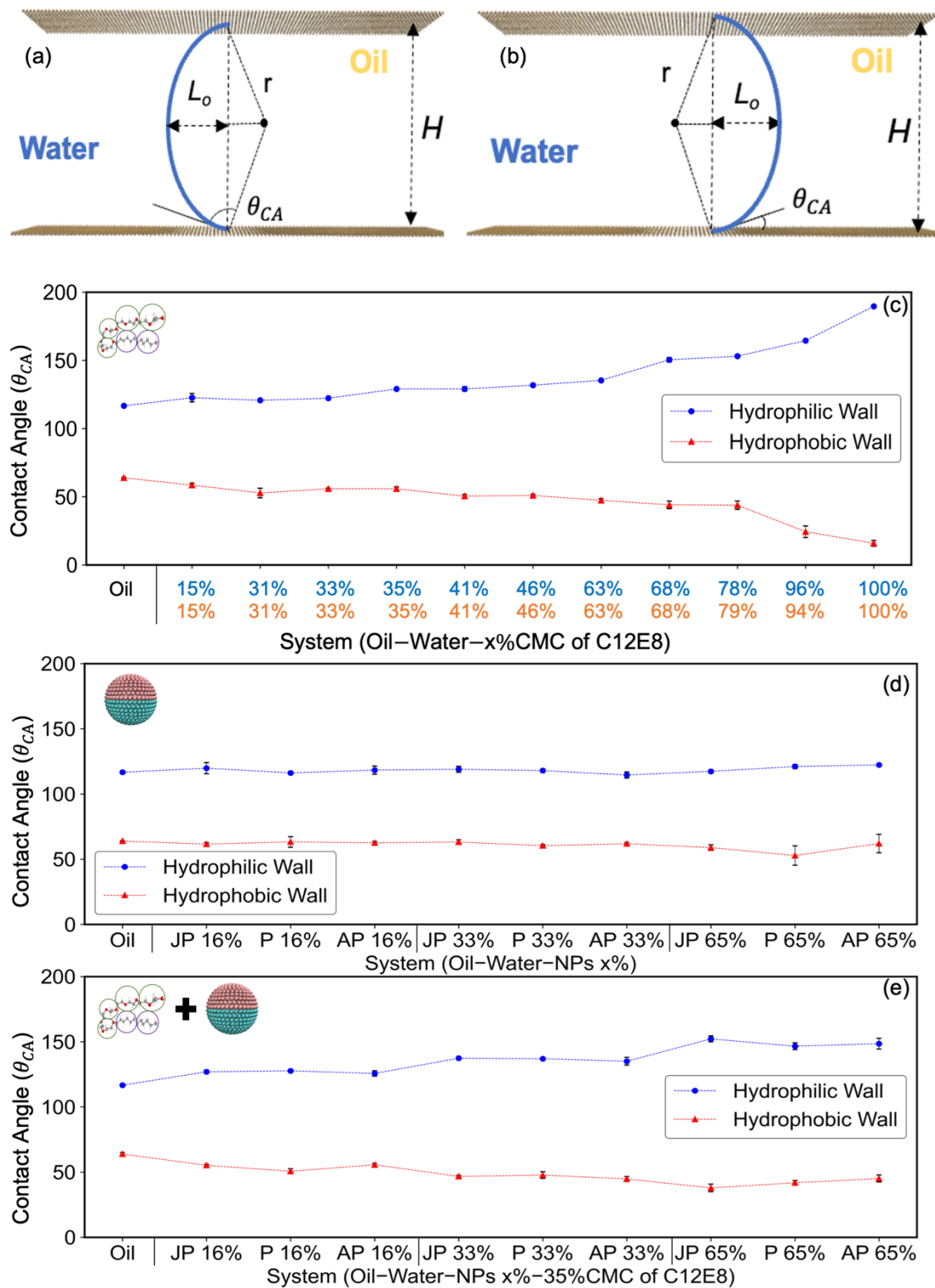


Figure 6.4. Schematic illustration of simulation geometry for (a) hydrophilic wall and (b) hydrophobic wall. The arc length, represented as L_o , is specified. Effect of (c) different

surfactant concentrations, (d) different types and percentage cover areas of NPs, and (e) coexistence of surfactant and NPs on the three-phase contact angle for hydrophilic and hydrophobic solid walls. The error bars were calculated by the standard deviation of three contact angle measurements.

The presence of surface-active species can impact the wetting behavior of the fluids on the channel walls, which can, in turn, affect the three-phase contact angle. From the contact angle, the length of the finger can be determined by a mathematical formula and validated with the computation results that are reported and shown in **Figure 6.5**. Our simulation model agrees well with these equations, which shows only an average relative deviation of 6.7% and 8.0% for hydrophilic and hydrophobic walls, respectively. The arc length of the meniscus depended on the three-phase contact angle for the oil drop, which can be described by equation (6.1) and (6.2), as follows:

Hydrophilic walls

$$\theta_{CA} = \frac{\pi}{2} + \arctan\left(\frac{H/2}{r - L_0}\right) \quad (6.1)$$

Hydrophobic walls

$$\theta_{CA} = \frac{\pi}{2} - \arctan\left(\frac{H/2}{r - L_0}\right) \quad (6.2)$$

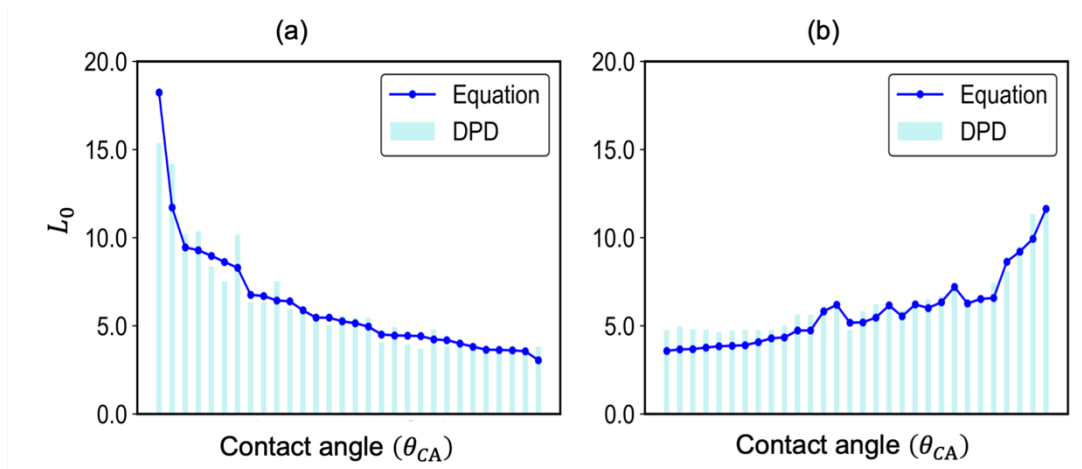


Figure 6.5. Comparison of the simulation and mathematical results regarding L_0 as a function of the three-phase contact angle, θ_{CA} , in the case of a channel with (a) hydrophilic walls and (b) hydrophobic walls.

6.3.2 The stable phase after the flow is introduced

To better understand how surfactants and NPs affect the shape of an oil-water interface, a Poiseuille flow is applied to create non-equilibrium conditions. In the context of the oil and water system, Ca is used to consider how the finger length will be affected. The dimensionless Ca is calculated using the viscosity of the displacing fluid (water) and the maximum fluid velocity at the channel center. Simulation results are generated by changing the initial velocity of water as the displacing fluid and IFT to generate different Ca . As illustrated in **Figure 6.6a-b** and **Figure 6.7a-b**, a finger of length L_1 can be observed during flow; the difference $\Delta L = L_1 - L_0$ shows how the finger length changes over time. This difference, denoted as ΔL , signifies the deformation of the finger shape and is calculated based on the distance between the head and the tail of the finger (from the farthest point of the interface to the nearest point to the water drop center).

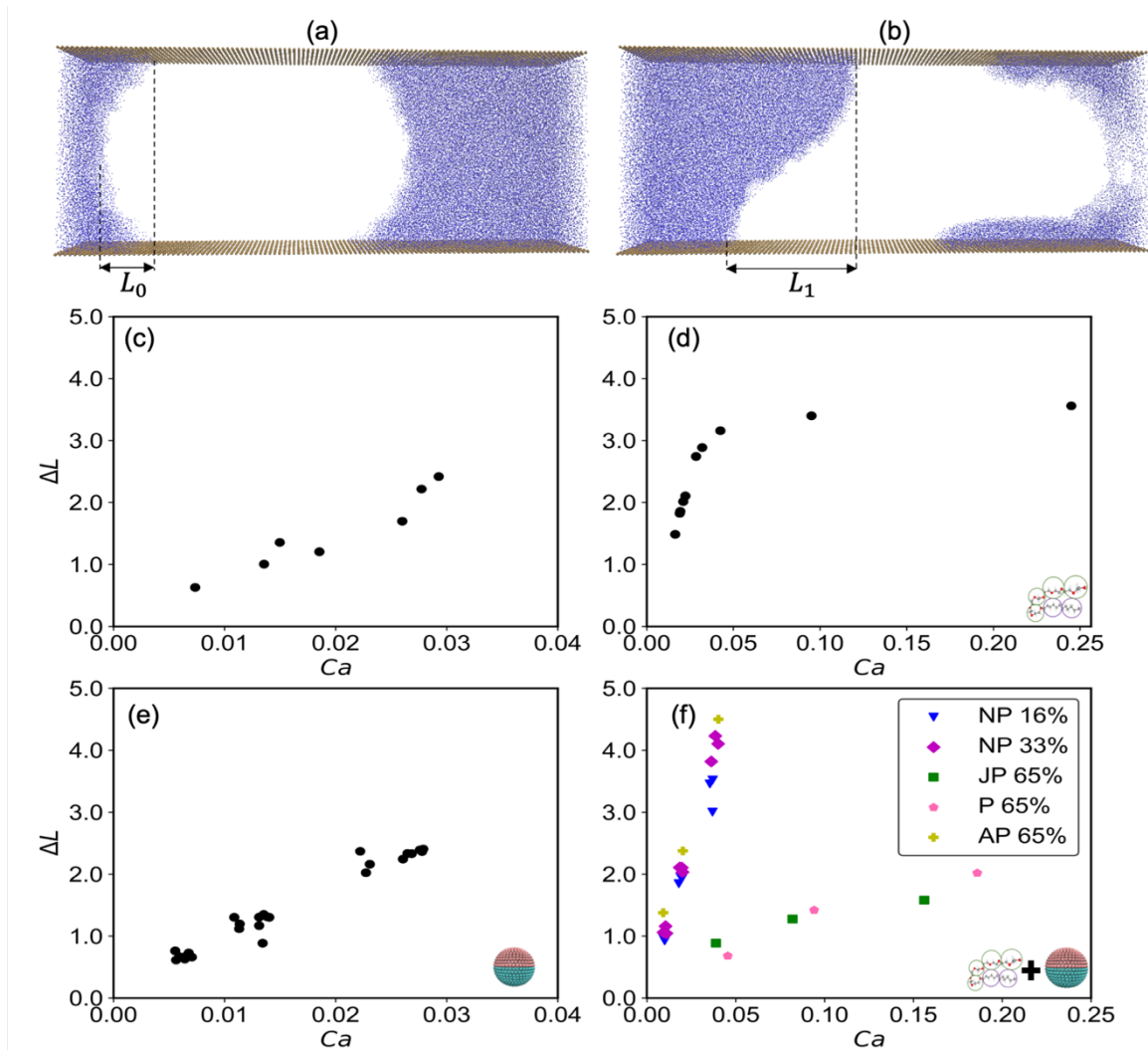


Figure 6.6 This schematic diagram displays the hydrophilic walls under two circumstances: (a) no water flow and (b) water flow applied. Capillary number as a function of the ratio of finger's length for the system includes (c) oil and water; (d) oil, water, and surfactants; (e) oil, water, and NPs; and (f) oil, water, NPs, and surfactants. In (f), the surfactant concentration is 35% of the CMC, while the JP, P and AP cases for 16% NP coverage are plotted with the same color, as are the 33% NP coverage cases.

The change in finger length is plotted as a function of Ca in **Figure 6.6c-f**. In general, ΔL increased with increasing Ca , but it reached a plateau in the case of the presence of surfactants at the interface (as seen in **Figure 6.6d**). In **Figure 6.6c** and **Figure 6.6e**, the IFT remains unchanged but there is an increase in the velocity of water and the length of the finger. With increasing Ca , the curvature of the meniscus increases. Thus, a finger is formed. While experimental data for the conditions of the current simulations are not available, there are observations of similar finger patterns observed in Lattice Boltzmann simulations for a bare oil and water system.¹⁶² Distinct from the bare oil-water study carried out by Kang et al.,¹⁶² we include surface-active species in our simulation (NPs and surfactants), but those findings provide qualitative evidence to support the reliability of our results, as follows: The physical parameters applied in our simulation differ from those in their works (for example, the viscosity ratio between the displaced and displacing fluids was $M = 1$, $M = 3$, and $M = 10$ while in our current simulation, a viscosity ratio of $M \approx 1.5$ is used) the qualitative behavior is similar for the curvature of the meniscus. They showed that fingers are observed for all viscosity ratios examined, given that the fluid velocity was higher than a threshold value. In **Figure 6.6d**, the finger length jumped sharply at low Ca ($Ca < 0.05$) in the presence of only surfactant in the system. However, at high Ca , the finger length gradually increased and rose slowly with increasing surfactant concentration. This is because when the water flow was applied, the interface area of the oil-water expanded, causing the surfactant to dilute and gather at the tip of the forming finger. Thus, IFT at that point of high surfactant concentration decreased, which could cause the finger to grow longer. When higher surfactant concentration was used under the same conditions for water flow, the IFT between the oil and water phases still decreased, but surfactant molecules spread out on the interface at higher surfactant concentrations instead of gathering at the tip of the finger, which tended to reduce the meniscus curvature.

Therefore, the finger length still increased with an increase in the Ca , despite the fact that the growth rate was slower.

Finally, when both NPs and surfactants were present at the oil-water interface, the same trend was observed. The finger length increased with the increase in the Ca , as illustrated in **Figure 6.6f**. When the coverage of NPs was low ($c \leq 33\%$), the surfactant concentration was below the critical micelle concentration (CMC), resulting in a significant increase in the growth rate of the finger length. At 65% NP coverage, hydrophobic NPs followed a trend comparable to that observed with smaller coverage areas of NPs, but Janus and hydrophilic NPs showed a slower increase. This was due to the addition of surfactants in the system, coupled with the presence of NPs, which significantly reduced the IFT in the case of Janus and hydrophilic NP presence. The IFT changed to $IFT_{JP} \approx 6.18 \text{ mN/m}$ and $IFT_P \approx 5.14 \text{ mN/m}$, respectively, but the coexistence of surfactant and NPs had a minimal impact on the IFT when hydrophobic NPs was used, which remained at $IFT_{AP} \approx 24.53 \text{ mN/m}$. This happened because the hydrophobic NPs occupied a smaller area of the interface as discussed earlier in Section 6.3.1.

A similar trend was noticed in the case of hydrophobic channel walls, where the length of fingers grew as the value of Ca rose for all combinations of fluids (see **Figure 6.7c, e**). In **Figure 6.7d**, when the surfactant was added into the system in the presence of water flow, the reduced surface tension allowed water to penetrate deeper into the channel and push through the oil phase, and the meniscus deformed more, as described above. Hence, surfactants play a vital role in significantly extending the length of the finger with a higher Ca , as compared to situations where only bare oil or only NPs are present in the system. Additionally, when both surfactant and NPs are present in the system, the rate of finger length increase is higher for low coverage of NPs. This linear relationship between ΔL and Ca can be observed in **Figure 6.7f**. Specifically with the same number of surfactant molecules and NPs, only for the 65% Janus and hydrophilic NPs coverage, the value of Ca exceeds 0.04, and the growth rate is less compared to other cases where both surfactant and NPs were present in the system. These findings agree well with the case of the hydrophilic walls; the main reason is the IFT. At high NP coverage (65% NP coverage), hydrophobic NPs demonstrate a similar trend to other scenarios with a lower percentage of NP coverage, where both surfactant and NPs were present in the system. Moreover, longer fingers were observed in the presence of hydrophobic walls compared to the case of hydrophilic walls under the same Ca for all scenarios, including those with no NPs and surfactants, only surfactants

or NPs, and the coexistence of NPs and surfactants. An example of this phenomenon can be seen when considering a system of oil and water with surfactants (see **Figure 6.6d** and **Figure 6.7d**). ΔL increases up to 7.39 in the presence of hydrophobic walls ($Ca \approx 0.043$), whereas it only reaches 3.16 in the presence of hydrophilic walls when the number of surfactant molecules is the same.

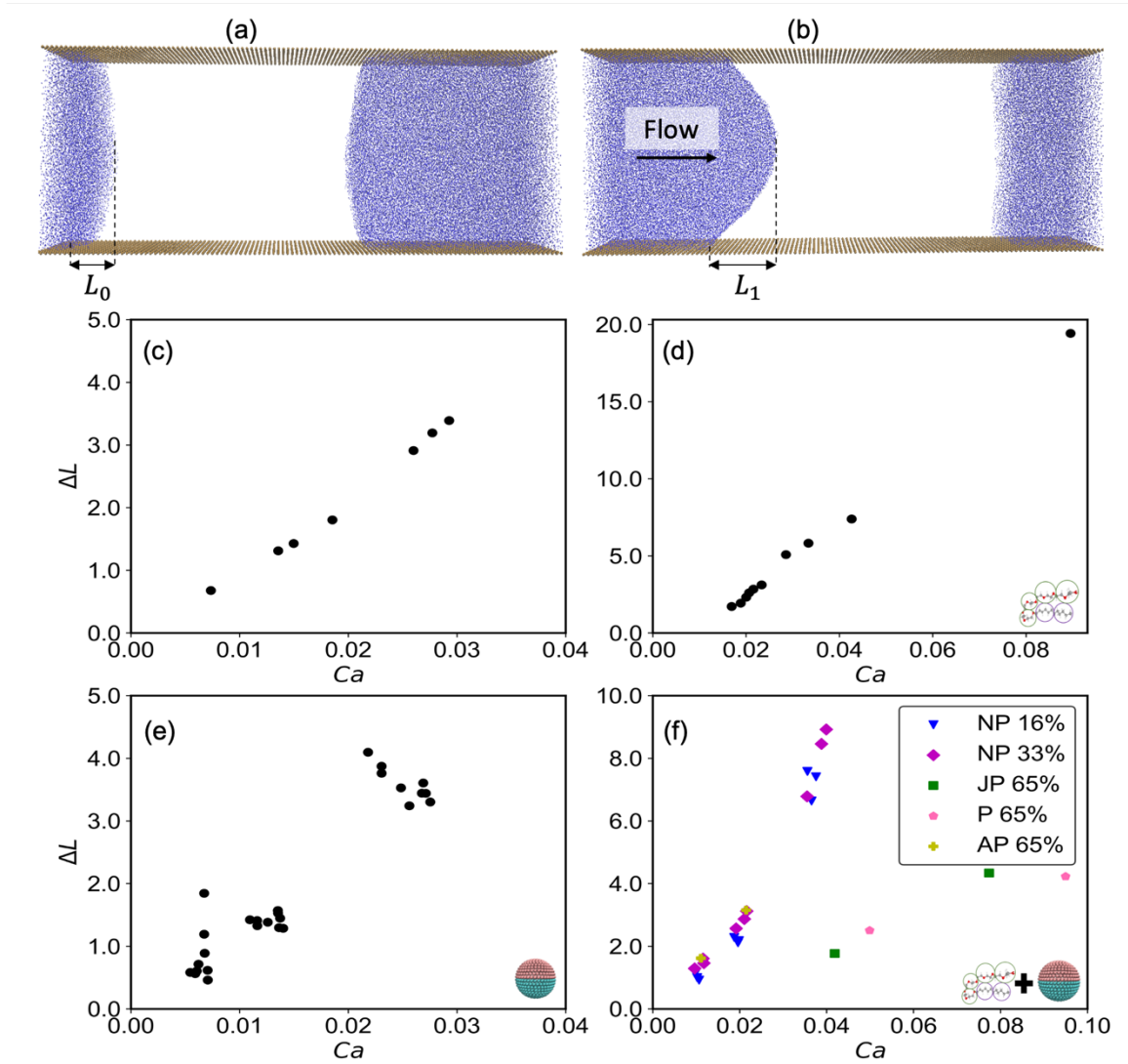


Figure 6.7 A schematic diagram of hydrophobic walls (a) without water flow and (b) with water flow was applied. The correlation between the capillary number and the ratio of finger length for the system includes (c) oil and water; (d) oil, water, and surfactants; (e) oil, water, and NPs; and (f) oil, water, NPs, and surfactants. In (f), the surfactant concentration is 35% of the CMC, while

the JP, P and AP cases for 16% NP coverage are plotted with the same color, as are the 33% NP coverage cases.

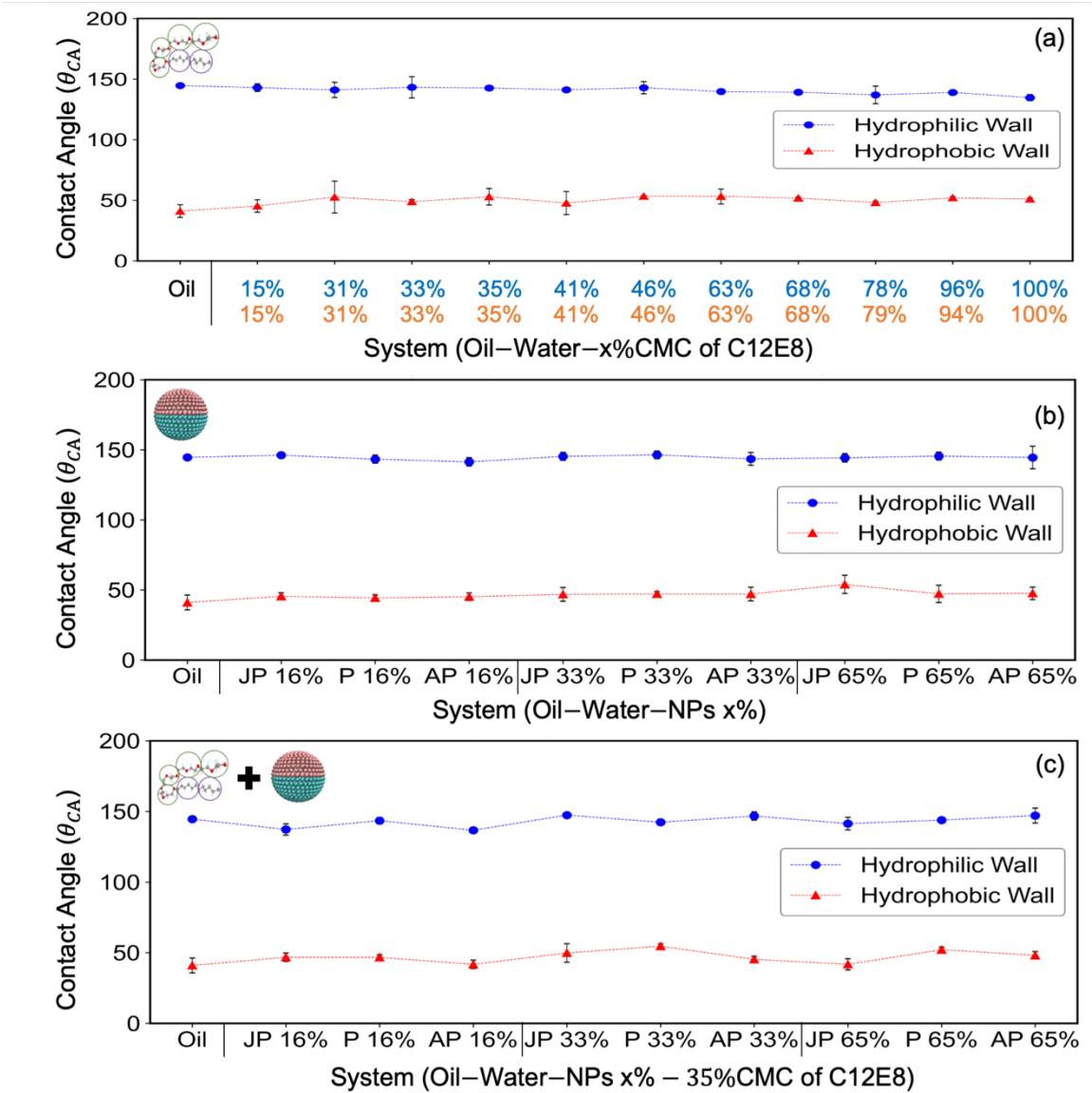


Figure 6.8. Three-phase contact angle at the interface of hydrophilic and hydrophobic solid walls at detachment for (a) varying amounts of surfactant concentration, (b) different types and surface coverage of NPs, and (c) 35% of the CMC of surfactant and different NP coverage. The error bars correspond to the standard deviation for three contact angle measurements.

At high enough water velocity, the fluid-fluid interface can be severely distorted to the point of detachment from the wall, leading to the formation of drops. We investigate the critical

three-phase contact angle and the fluid velocity at which this detachment from the wall occurs. As illustrated in **Figure 6.8**, the three-phase contact angle is important for the formation of droplets. For all cases considered, including a hydrophilic channel wall or a hydrophobic channel wall, the mechanism of detachment from the wall is quite consistent. When hydrophilic walls are involved, the critical three-phase contact angle for fluid detachment was calculated as $142.5 \pm 3.3^\circ$, while for hydrophobic walls, the angle was $48.3 \pm 3.8^\circ$. In conclusion, the detachment occurred when the three-phase contact angle was equal to a critical value, regardless of the number of particles, the properties of the particles, and the concentration of surfactants.

Our results showed that the detachment of fluid from the wall occurred when the driving force for the flow (i.e., the body force propelling the flow in the simulation, which is proportional to the pressure drop for the flow) increased beyond a critical value. There were two possible outcomes at the point of detachment: either partial detachment, where fluid is detached from one wall of the channel while remaining attached to the other, or full detachment, which refers to the elongation into a slag extending from one wall to the other and eventually breaking off to form a drop in the middle of the channel. In most cases, a partial detachment can appear at small body force (see **Figure 6.9a-d**), while a full detachment is observable under higher body force conditions instead of the partial detachment. The full detachment requires a higher driving force than partial detachment because partial detachment involves the creation of a new interface within the water and does not necessarily require breaking the contact between the oil droplet and both solid walls of the channel. Partial detachment is displayed in **Figure 6.9a-d** for the case of JPs 65% – 35% CMC of C12E8 with hydrophilic walls and a body force $g_x = 0.0052$. This process is observed starting from equilibrium (time step $t = 10,000$), with the development of fingering becoming evident at time steps $t = 24,000$ and $t = 49,000$. Subsequently, the partial detachment appears until the end of the simulation. However, with an increase in body force to $g_x = 0.0053$, the full detachment is recorded (shown in **Figure 6.9h**), while the remaining steps, including the equilibrium (**Figure 6.9e**) and fingering formation stages (**Figure 6.9f-g**), remain unchanged. Regarding channels with hydrophilic walls, the case with surfactant concentration at 35% of the CMC was selected as an example (**Figure 6.9i-l**). A full detachment is observed at $g_x = 0.0071$. the presence of oil droplets is observed in the case of hydrophilic walls, whereas in the case of hydrophobic walls, a water droplet is created. More information about partial detachment can be found in **Figure 6.10** and **Figure 6.11**.

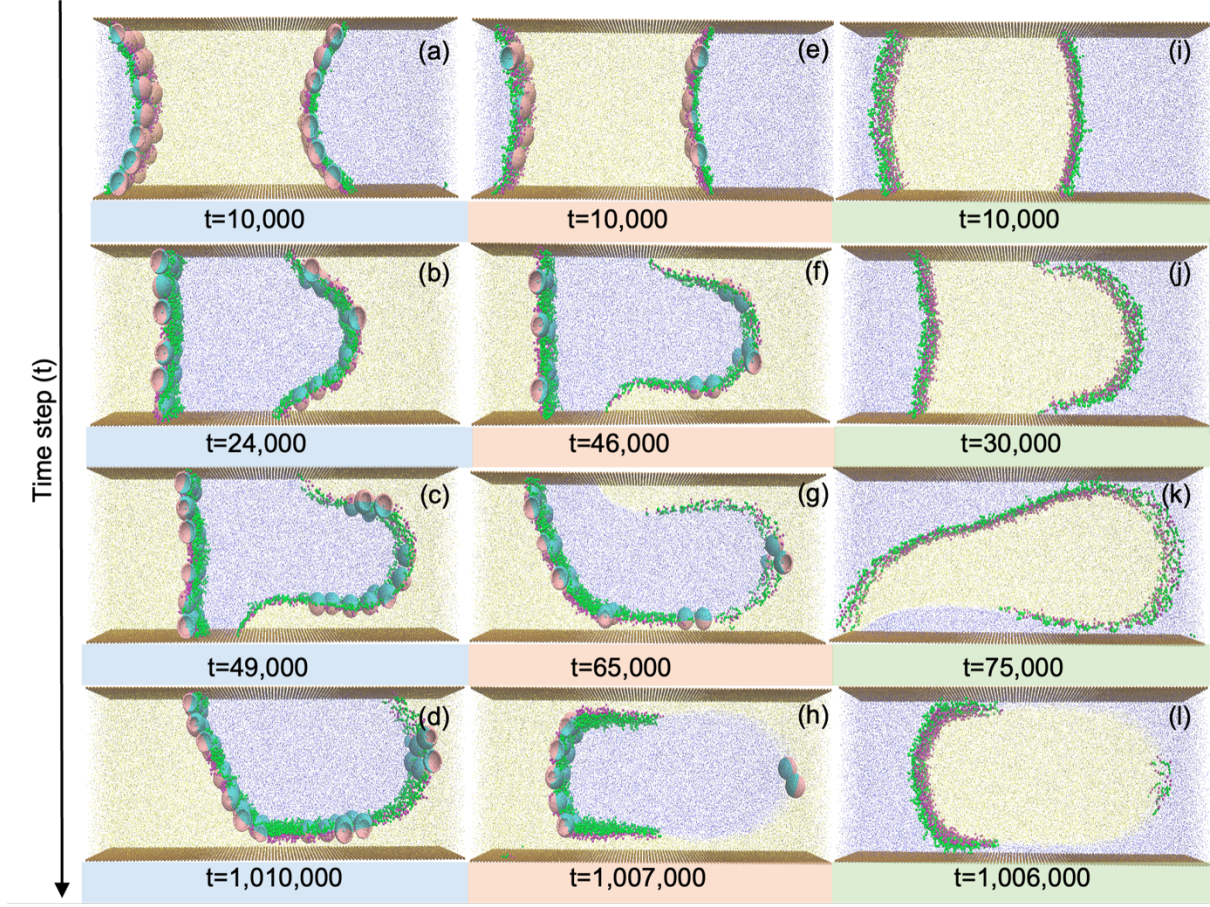


Figure 6.9. The illustration of droplet deformation within the channel in the designated scenario of (a-d) JP 65% – 35% of the CMC of surfactant with hydrophobic walls and the body force $g_x = 0.0052$; (e-h) JP 65% – 35% of the CMC of surfactant with hydrophobic walls and the body force $g_x = 0.0053$; (i-l) 35% of the CMC of surfactant with hydrophilic walls and the body force $g_x = 0.0071$. The arrow indicates the progression of the simulation over increasing time steps. The color scheme is consistent with the one in **Figure 6.1**.

The process to create the partial detachment in the case of NPs 65% – 35% CMC of C12E8 with hydrophilic walls is illustrated in **Figure 6.10a-e**. JPs 65% – 35% CMC of C12E8 at the body force $g_x = 0.0069$ is utilized as a case in point for this particular phenomenon. In this case, the length of the meniscus is extended significantly (time step $t = 609,000$ and $t = 777,000$) because of the existence of surfactant in the system. The top of the oil droplet can interact with the tail of the oil droplet, resulting in the generation of a small water droplet that adheres to

the wall (time step $t = 998,000$). The occurrence can be attributed to the limitations in the simulation box size. More precisely, the length of the simulation box, which exhibits periodicity along the x -direction, may not provide enough space for the movement of the droplet, thereby facilitating the merging of the oil droplet's components and subsequent creation of the attached water droplet on the channel wall. To verify this point, a simulation with an extended simulation box was conducted, with $L_x = 120 r_c$ (DPD units). As shown in **Figure 6.11**, the oil droplet was generated by detaching from the walls ($L_x = 120 r_c$) with the same body force $g_x = 0.0069$ as for the case of a small simulation box $L_x = 90 r_c$. In this scenario, the front part of the oil droplet is unable to connect with the rear section, preventing the formation of smaller droplets (time step $t = 42,000$). As can be seen in **Figure 6.10f**, the partial detachment occurs as high NP coverage, which requires a smaller driving force compared to the cases shown in **Figure 6.12c** (the simulation box is $L_x \times L_y \times L_z = 90 \times 10 \times 31 r_c^3$). The critical body force was reduced when the NP coverage reached the 65% mark when the effective surfactant concentration approached the CMC value.

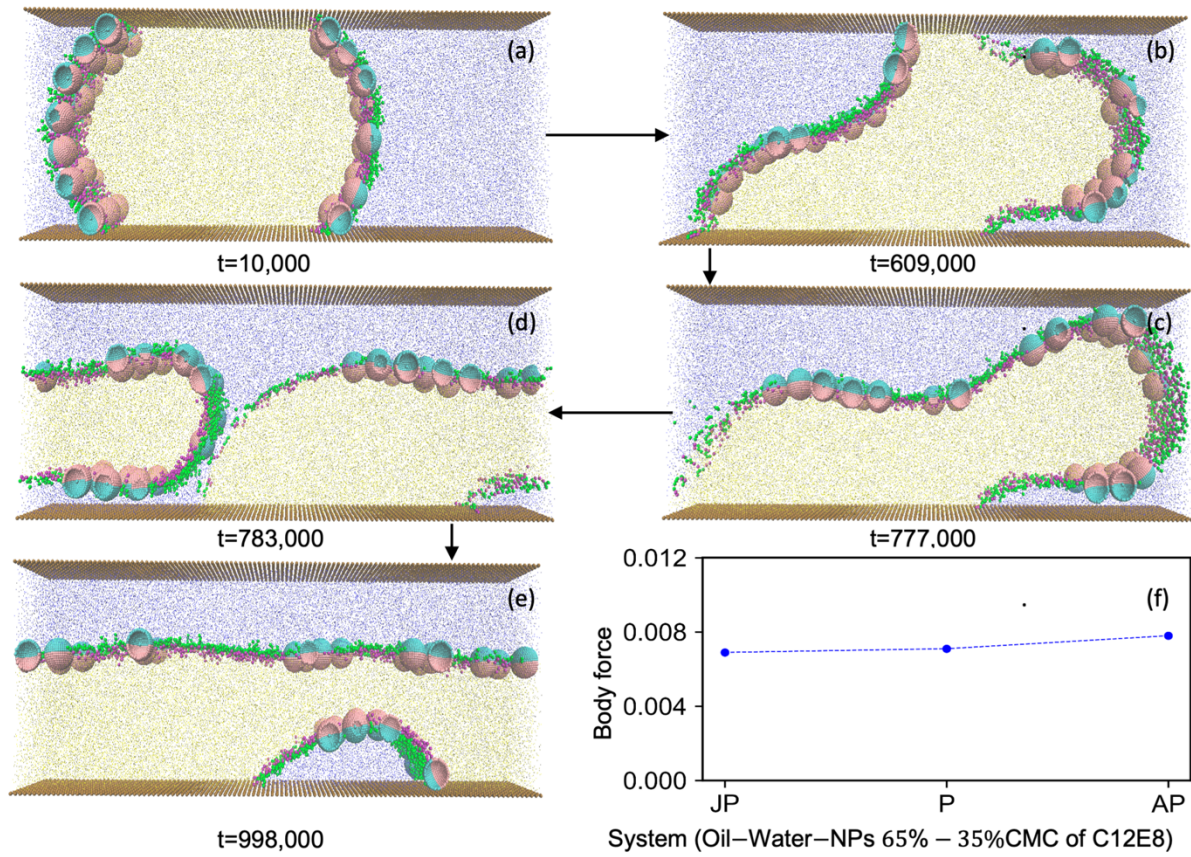


Figure 6.10. (a-e) The visual depiction of the droplet deformation at $g_x = 0.0069$ within the channel in the specified instance of JP 65% – 35% of the CMC of surfactant, and (f) the body

force needed to create the partial detachment with different types of NPs. The arrows indicate the direction of the developmental process over increasing time steps. The color scheme is consistent with **Figure 6.1**.

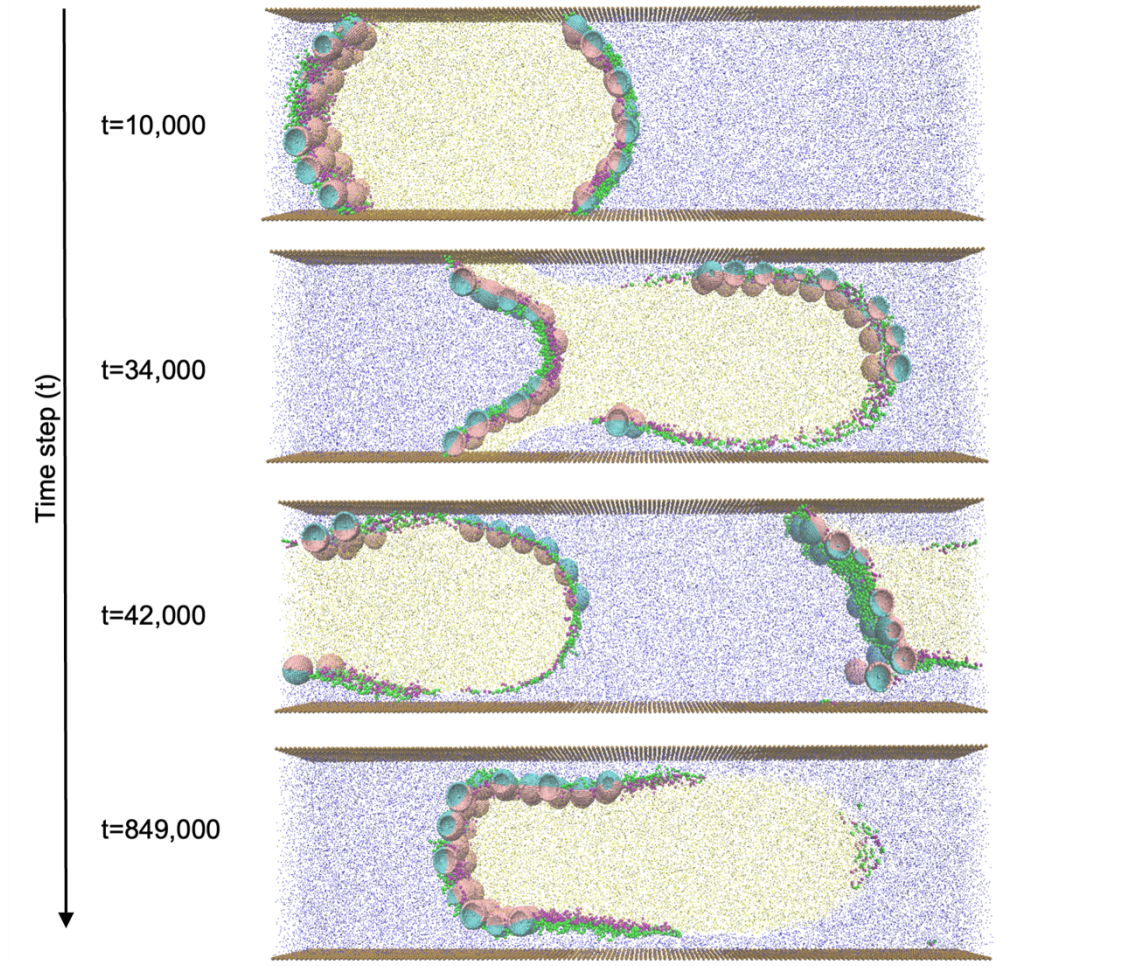


Figure 6.11. The visual depiction of the droplet deformation at $g_x = 0.0069$ within the length of channel $L_x = 120 r_c$ in the specified instance of NPs 65% – 35% of the CMC of surfactant. The direction of the developmental process over increasing time steps is highlighted by the arrow.

The color scheme is consistent with **Figure 6.1**.

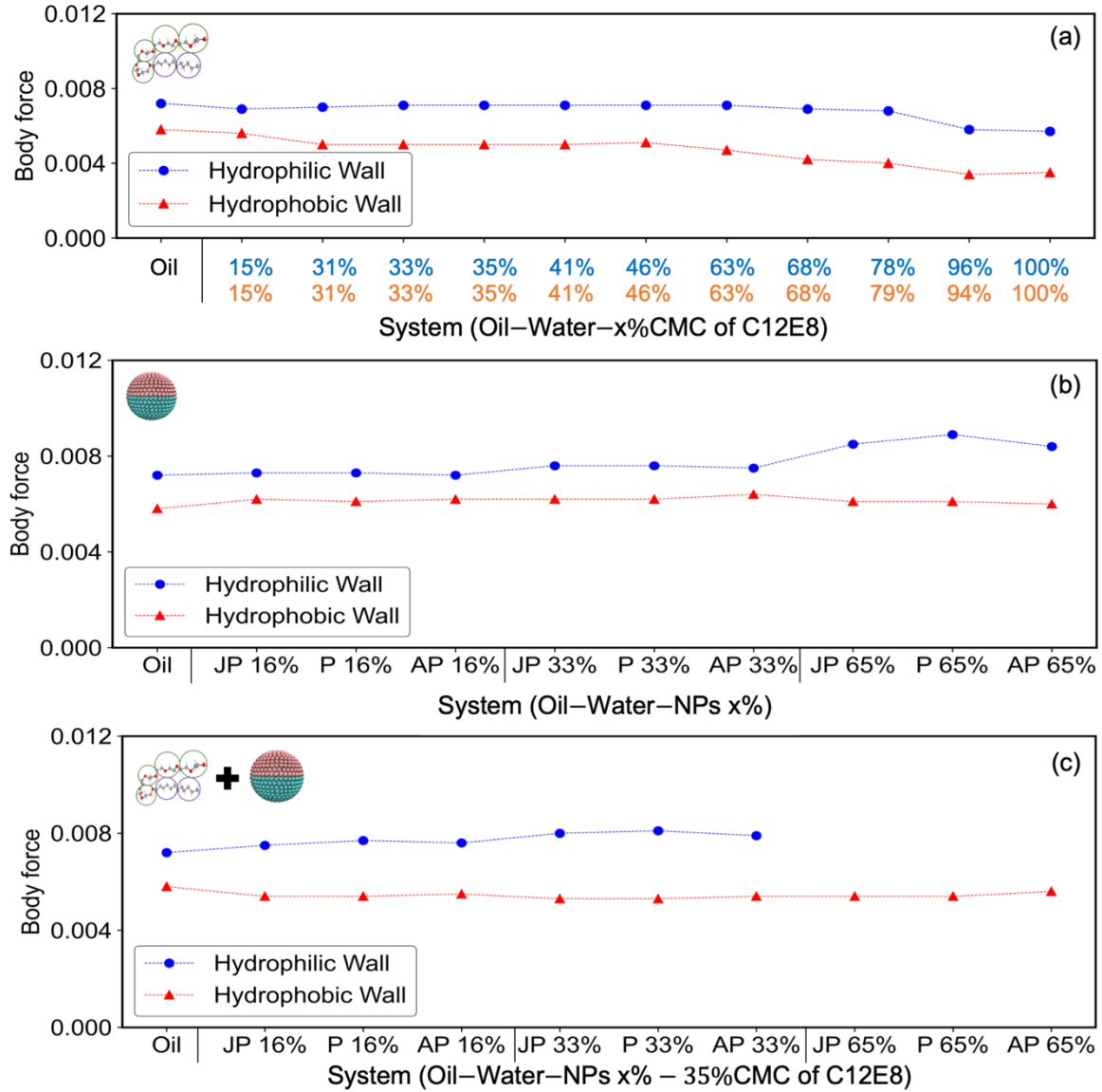


Figure 6.12. The critical body force that led to a full detachment from the wall for different cases simulated. (a) Oil-water with only surfactant at the interface, (b) only NPs at the oil-water interface, and (c) both surfactants and NPs at the interface. Values for channel walls with different wetting behavior are shown.

The point at which the driving body force became strong enough to cause detachment was defined as the critical threshold value, shown in **Figure 6.12**. In **Figure 6.12a**, the case of a system with surfactant only is displayed. The critical body force was roughly constant $g_x = 0.007$ up to surfactant concentration at 78% of the CMC, when the critical driving force started to decrease in channels with hydrophilic walls. When the surfactant concentration reached approximately the

CMC value, a significant decrease was observed to $g_x = 0.0057$ compared to $g_x = 0.0072$ for the bare oil case (this is about 26% reduction in the driving force needed to detach the oil from the hydrophilic wall). Hydrophilic walls have a high affinity for water, which can result in the formation of stable water layers on the surface of the walls, whereas the surfactant molecules can create a layer of molecules at the oil-water interface, reducing the surface tension between the oil and water. Thus, adding surfactant molecules to the oil-water interface could lead to droplet formation. At the point of detachment, an oil droplet is formed in the middle of the channel by breaking the contact between the oil and the surface of the channel (see **Figure 6.9I**). In addition, full detachment appears for hydrophobic walls when the surfactant concentration is increased, and the effect of reduced IFT to detachment becomes more noticeable. At low IFT, the three-phase contact angle grows, leading to a reduced interaction of the oil and the wall and a reduction of the pressure difference required to overcome the surface tension and initiate the detachment of droplets compared to the case of bare oil with no surfactants. Moreover, the reduction in IFT can make the drop of oil elongate in the water phase rather than in the case of bare oil. The droplet behavior and the effect of surfactants in the case of hydrophobic walls can be different than in hydrophilic walls. A noticeable reduction in critical body force was observed (from 0.0058 to 0.0035, about 40% reduction in needed driving force) when the surfactant concentration reached the CMC value, compared to the system of bare oil with no surfactant present. A full detachment occurs with hydrophobic walls regardless of the concentration of surfactants.

The case of oil-water and NPs only is examined in **Figure 6.12b**. In comparison to bare oil without NPs, when NPs were present in the system, the critical external body force increased by 24% (from $g_x = 0.0072$ to $g_x = 0.0089$) for hydrophilic walls but did not change much for hydrophobic walls (ranging from $g_x = 0.0058$ to $g_x = 0.0061$). The NPs at the oil-water interface tend to accumulate at the interface when the drop moves and this accumulation alters drop deformation compared to the case with bare oil-water (see **Figure 6.13**). At low concentrations of NPs, NPs do not fully cover the oil-water interface, leading to a reduced impact on fingering. As a result, the critical body force remains similar to the scenario without NPs.

Figure 6.12c illustrates the synergisms between the surfactant and the NPs on the oil-water interface. For the scenario involving hydrophilic walls, the critical body force required to create the detachment increased with 35% CMC of C12E8 molecules added to the system. While surfactants have the potential to decrease the body force required for full detachment, the surfactant

concentration, in this case, remains below the CMC. The key factor contributing to the slight increase in body force is the coverage of NPs. This implies that with an increased quantity of NPs introduced into the system, the body force necessary for full detachment would be further enhanced in comparison to the case of bare oil.

When hydrophobic solid walls were introduced, adding surfactants reduced the stabilizing impact of NPs, as seen when one compares **Figure 6.12b** and c. The critical force appears to be the same irrespective of particle coverage (**Figure 6.12c**). This behavior is similar to the situation where only NPs were introduced into the system with hydrophobic walls (**Figure 6.12b**). Essentially when surfactants are present, the effect of NPs is weakened, reducing the critical body force needed for the phase separation. This is supported by measurements showing $g_x = 0.0054$, $g_x = 0.0054$, and $g_x = 0.0056$ for the coexistence of surfactants with Janus, hydrophilic, and hydrophobic NPs, respectively, compared to $g_x = 0.0061$, $g_x = 0.0061$, $g_x = 0.006$ for systems containing only Janus, hydrophilic, and hydrophobic NPs, respectively, with an NP coverage area of 65%. Therefore, it can be inferred that there are competing effects when surfactants and NPs are present at the interface. In particular, surfactants can act as stabilizing agents for NP dispersions, effectively preventing agglomeration. This stabilization effect not only improves the dispersibility and uniformity of NPs within the system but also has the potential to alter their interactions with other NPs present.

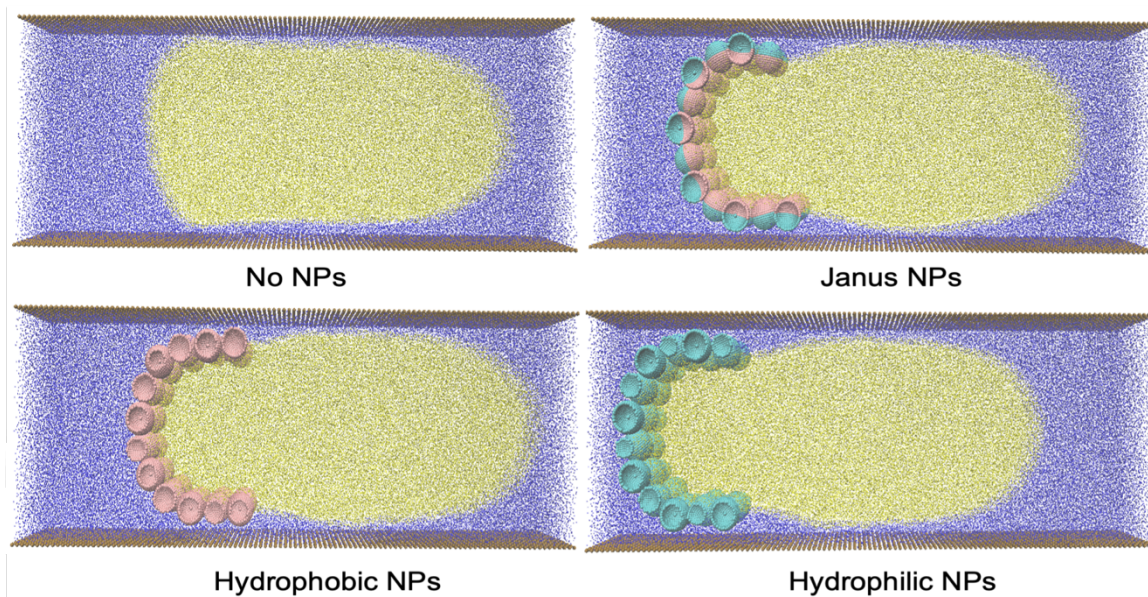


Figure 6.13. The visual representation of NPs accumulated at the oil-water interface. The number of NPs coverage is 65%. The color scheme is similar to that in **Figure 6.1**.

6.3.3 Phase separation and formation of droplets

This section focuses on surfactant and NP transport on a drop surface under an applied Poiseuille flow. **Figure 6.14** is a presentation of two possible cases: an oil droplet was created by detachment from the hydrophilic walls (seen in **Figure 6.14a**), and a water drop might form flowing in the center of the channel when the solid wall is hydrophobic (seen in **Figure 6.14b**). The aim here is to gain further insight into the physical mechanisms that affect the arrangement of surfactants and NPs at the drop surface in hydrophilic and hydrophobic channels. Therefore, we created contour plots of the different velocities of surfactants, NPs, and oil relative to the velocity of the center of mass of the oil or water droplet.

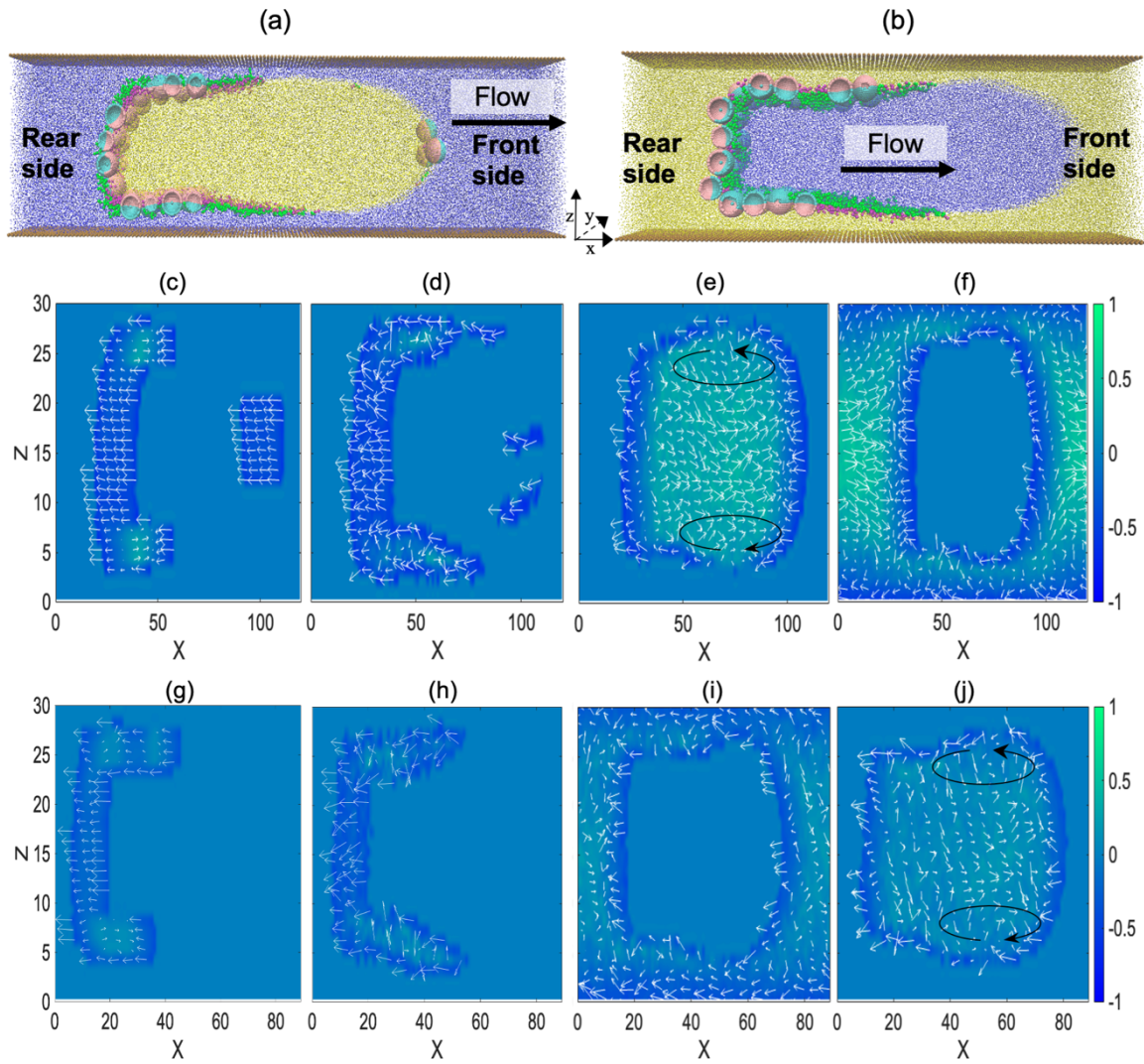


Figure 6.14. The fully detached drop is illustrated in these simulation snapshots of (a) the hydrophilic walls and (b) the hydrophobic walls, demonstrating the simulation geometry. The

color scheme is consistent with **Figure 6.1**. The contour of slip velocity of (c) JPs ($\Delta V_{NP,Philic\ Walls}$), (d) C12E8 ($\Delta V_{C12E8,Philic\ Walls}$), (e) Oil ($\Delta V_{O,Philic\ Walls}$), (f) Water ($\Delta V_{W,Philic\ Walls}$) in hydrophilic solid walls with $L_x = 120r_c$, $g_x = 0.0069$; (g) JPs ($\Delta V_{NP,Phobic\ Walls}$), (h) C12E8 ($\Delta V_{C12E8,Phobic\ Walls}$), (i) Oil ($\Delta V_{O,Phobic\ Walls}$), and (j) Water ($\Delta V_{W,Phobic\ Walls}$) for Oil-Water-NPs 65%- 35% CMC of C12E8 system with hydrophobic walls ($L_x = 90r_c$). The body force $g_x = 0.0054$.

The case of NPs and surfactants coexisting on the oil-water interface is presented in **Figure 6.14c-j**. The case when only NPs are present in the system is presented in **Figure 6.15**, and the case of surfactants only is presented in **Figure 6.16**. These plots were constructed by dividing the computational domain into 180×62 bins in the xz plane. The total surfactant molecules in each bin were counted and averaged over 1,000,000 time steps. The oil or water droplet migration velocity, V_{COM-O} or V_{COM-W} respectively, was calculated based on the velocity at the center of mass of the droplet at a specific time step. The velocities designated as V_W , V_O , V_{NP} , and V_{C12E8} represent the carrier fluid (water), oil phase, NPs, and surfactants, respectively. For the case of hydrophilic walls, the differences between two velocities are designated as follows: $\Delta V_{W,Philic\ Walls} = V_W - V_{COM-O}$; $\Delta V_{O,Philic\ Walls} = V_O - V_{COM-O}$; $\Delta V_{NP,Philic\ Walls} = V_{NP} - V_{COM-O}$; and $\Delta V_{C12E8,Philic\ Walls} = V_{C12E8} - V_{COM-O}$. For hydrophobic walls, the subscript $COM - O$ is substituted with $COM - W$.

As seen in **Figure 6.14c**, several NPs migrated to the rear side of the oil drop, where the oil-water interface is rather flat. The NPs exhibit movement toward the left, as the $\Delta V_{NP,Philic\ Walls}$ velocity arrows depict. In **Figure 6.14d**, the surfactant concentration was higher at the rear side of an oil droplet than on the front side when only the surfactant was present in the oil-water system. This observation was made during the oil droplet formation at the center of the channel in the case of hydrophilic solid walls. Only a very small number of NPs and surfactant molecules adhere to the front cap of the oil droplet. The reason for this observation was explained by the existence of a stagnation ring near the edge of the front cap, coupled with a quite weak surface flow on the front cap directed from the stagnation ring to the front cap center.^{99, 169} The velocity vectors for the oil phase, $\Delta V_{O,Philic\ Walls}$, are shown in **Figure 6.14e**, where a circulation pattern inside the oil drop is noted. A clockwise circulation is observed at the lower half of the drop, near the bottom wall, and an anticlockwise pattern is seen close to the top wall, showing that the oil phase moves

outward from the center to the border of the oil droplet. Consequently, surfactant molecules are anticipated to move to the rear side of the droplet instead of the front side. Notably, the relative velocity of the water next to the drop interface, $\Delta V_{W,Philic\ Walls}$, was also contributing to the migration of surfactants to the rear of the drop, as depicted in **Figure 6.14f**. Moreover, $\Delta V_{W,Philic\ Walls}$ close to the solid walls shows a small counterflow in the negative x -direction. As mentioned above, a drop of water was created when the walls were hydrophobic. In this scenario (see **Figure 6.14g-j**), both surfactant and NPs generally migrated toward the rear of the droplet's entire surface, assembling into densely packed surface structures. As a result, the strong interactions among nanoparticles could reduce the local surface tension. The relative velocity arrows display the direction of NPs movement (**Figure 6.14g**) and surfactant motion (**Figure 6.14h**), which tends to shift right to the left, opposing the direction of the water droplet. The presence of two circulation patterns within the drop is seen **Figure 6.14j**. The water movement inside the droplet occurs from the center to the outside, indicating that the water beads at the periphery move in the opposite direction to those at the center. Consequently, the water flow can drag the oil layer in a direction opposite to the direction of the water drop motion, toward the left, as illustrated in **Figure 6.14i**. The interfacial jamming of the closely packed surfactant and NPs caused by their specific distribution at the rear side of the oil or water droplet leads to a difference in the drop shape between the front and the rear part, as shown in **Figure 6.14a-b**. This phenomenon could lead to the surface becoming immobilized and deforming into a bulletlike shape. Our findings demonstrated droplet deformation similar to findings reported within a microchannel.^{97, 170, 171}

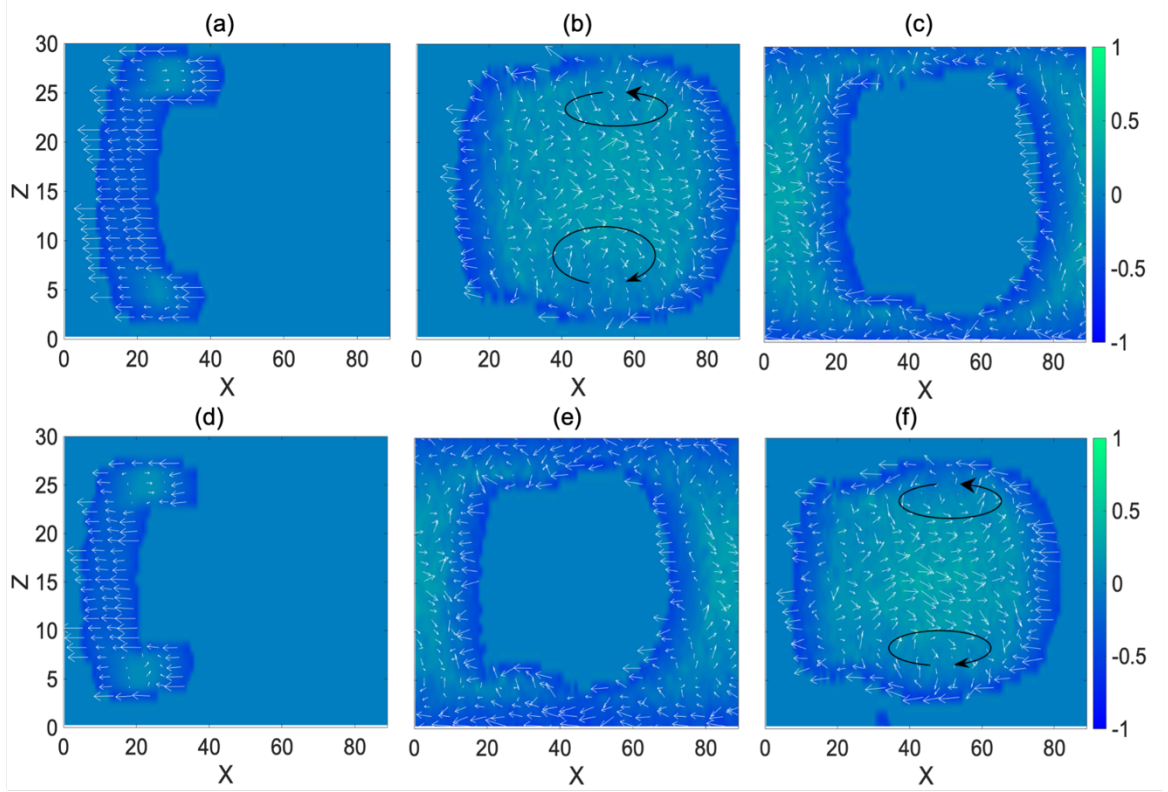


Figure 6.15. The contour of slip velocity of (a) JPs ($\Delta V_{NP,Philic\ Walls}$), (b) Oil ($\Delta V_{O,Philic\ Walls}$), (c) Water ($\Delta V_{W,Philic\ Walls}$) in hydrophilic solid walls, $g_x = 0.0085$; (d) JPs ($\Delta V_{NP,Phobic\ Walls}$), (e) Oil ($\Delta V_{O,Phobic\ Walls}$), and (f) Water ($\Delta V_{W,Phobic\ Walls}$), for Oil-Water-NPs 65% system in the hydrophobic walls, $g_x = 0.0061$.

The trend observed in **Figure 6.14c-j** is replicated in **Figure 6.15** and **Figure 6.16**, where the presence of NPs or surfactants at the oil-water interface follows the same pattern. For different wettability of solid walls, NPs or surfactants settle at the droplet's rear. There are two circulation patterns created within the oil droplet for hydrophilic walls, and within the water droplet for hydrophobic walls. These circulation patterns indicate the movement direction of surface active agents under the influence of Poiseuille flow.

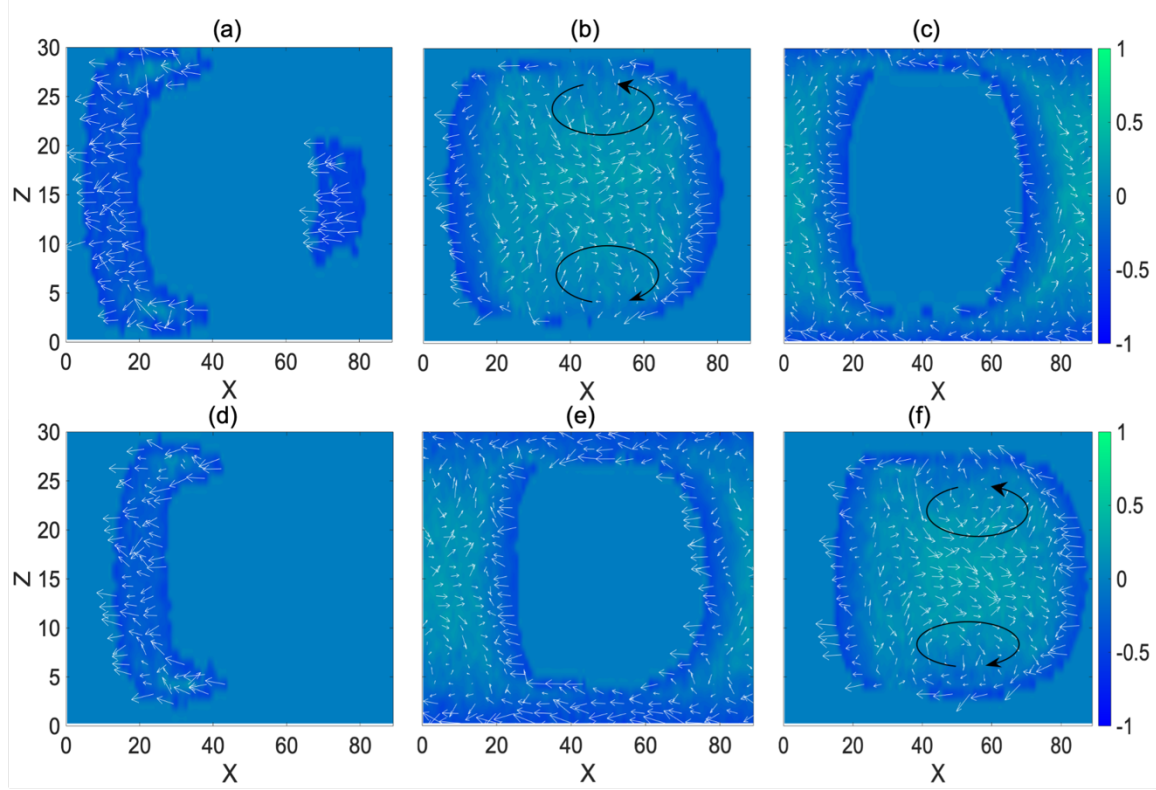


Figure 6.16. Contours of the relative velocity of (a) C12E8 ($\Delta V_{C12E8, Philic Walls}$), (b) Oil ($\Delta V_{O, Philic Walls}$) (c) Water ($\Delta V_{W, Philic Walls}$) in hydrophilic solid walls with the body force $g_x = 0.0071$; (d) C12E8 ($\Delta V_{C12E8, Phobic Walls}$), (e) Oil ($\Delta V_{O, Phobic Walls}$), and (f) Water ($\Delta V_{W, Phobic Walls}$), for Oil-Water-35% CMC of C12E8 system in the presence of hydrophobic walls. The body force $g_x = 0.005$.

6.4 Conclusions

In this study, we have numerically investigated the motion of an oil droplet with and without the presence of surfactant and Janus particles under non-equilibrium conditions by using the DPD simulation method. NPs covered the oil-water interface at 0 – 65% and contained surfactants at 0 – 100% of the interfacial surfactant concentration corresponding to the CMC. At equilibrium, the surfactant made an outstanding contribution to the three-phase contact angle formed between the oil droplet and the walls, while the wettability of solid walls significantly influenced this interaction. Additionally, the IFT was reduced by the presence of surfactants in the system, either when only surfactants were present or when a combination of surfactants and NPs was present. However, NPs alone did not have an effect on the IFT. For hydrophilic walls, the

introduction of surfactants resulted in a larger contact angle and a longer curve length within the channel as the surfactant concentration reached the CMC value. On the other hand, a longer curve length was exhibited with hydrophobic walls, significantly reducing the three-phase contact angle.

When the fingering phenomenon appeared, the fingering length increased with an increase in the Capillary number, but the growth rate depended on the type of surface active species added to the system, affecting the stability of the oil-water interface. The presence of NPs enhanced the stability of the oil-water interface by creating additional barriers to deformation and interacting with the surfactant layer at the interface. The fluid-fluid interface can undergo significant instability leading to droplet formation when exposed to a sufficiently high driving force. It is demonstrated that the oil or water droplet could detach from the walls, depending on the Poiseuille flow's driving force and the solid walls' wettability. The occurrence of deformation was independent of the number and properties of NPs and occurred at a critical three-phase contact angle. As the pressure drop increased, droplets were formed in the center of the channel – water droplets for hydrophonic walls and oil droplets for hydrophilic walls. In the presence of surfactants, the NPs demonstrated a more uniform distribution at the interface, and as a result, a higher driving force was needed to generate the drops relative to the case of bare oil and water and the case of surfactant present in the system alone.

Finally, the relative velocity of surfactant molecules and NPs against the droplet center of mass was shown to explain the transport of surfactant and/or NPs on the surface of a droplet, as well as their arrangement at the drop surface within hydrophilic and hydrophobic channels.

Chapter 7. Influence of Surface-Active Agents on The Transport Behavior of Nanoparticles Between Fluid Interfaces

Abstract

The energy required for the migration of single nanoparticles (including homogeneous and amphiphilic NPs) between the oil and water phases was investigated using Dissipative Particle Dynamics (DPD) simulation methods, considering the presence of only nanoparticles (NPs), surfactants, or their coexistence. Our simulations determined the free energy of the system as NPs transitioned between the immiscible liquids, with surfactants reducing the energy requirement for desorption. However, the formation of an NP layer presented challenges for individual NP movements. NPs exhibited lower desorption energy in the water phase compared to the significantly higher energy required in the oil phase. Furthermore, the combined presence of surfactants and NPs at the interface was analyzed to assess their impact on the desorption energy necessary for NP transport to the bulk phase.

The insights gained from this research enhance our understanding of the adsorption and desorption processes at the oil-water interface, particularly in the presence of surface-active agents, which has implications for applications in enhanced oil recovery and other fluid interface engineering fields.

7.1 Introduction

In recent years, there has been an increasing interest in the behavior of nanoparticles (NPs) and surfactants adsorbed at the fluid interfaces. The behavior of colloidal particles near interfaces is important in a host of industrial and environmental applications¹⁷² such as emulsion stabilization¹⁷³ and oil recovery processes.¹⁷⁴

As evidenced extensively in studies by Binks et al.,^{138, 175} solid nanoparticles have the potential to stabilize emulsions. Particularly, Janus nanoparticles (JPs), characterized by two distinct surface regions with different wettabilities, have emerged as superior emulsion stabilizers. This characteristic is credited to the increased desorption energy needed to detach JPs from the interface, compared to homogeneous nanoparticles. Despite advancements in recent experimental techniques,^{23, 176, 177} studying the properties of nanoparticles (NPs) at oil-water interfaces through experiments remains challenging. To complement experimental approaches, simulation methods are increasingly utilized to explore the free energy associated with NPs positioned near the interface of two immiscible liquids. A computational approach offers valuable insights into the

behavior and interactions of NPs at complex interfaces, enhancing our understanding of their fundamental properties and applications. Using Molecular Dynamics simulation, Fan et al.¹⁷⁸ found that the energy required to remove JPs from the interface typically exceeds that needed for the corresponding homogeneous nanoparticles. For most NPs considered, desorption into the aqueous phase is favored over desorption into the organic phase. Furthermore, Razavi et al.¹⁷⁹ compared simulation findings with experimental results to investigate the force exerted on the particle, and the free energy of the system as a function of the particle's distance from the interface. However, the dynamics of NP adsorption to an interface, particularly in the context of complex interfaces containing surface active agents, have not been sufficiently addressed. Most studies have focused on the case with only two immiscible fluids in a system with no surface agent, therefore, the understanding of the interaction between NPs and surfactants at interfaces remains limited. This underscores the necessity for further research and attention in this area.

It is common knowledge that surfactants and NPs can stabilize oil-water interfaces,^{1, 36, 105, 110-115}. In this study, nonionic surfactant octaethylene glycol monododecyl ether (C12E8) and different types of NPs including homogeneous and amphiphilic nanoparticles were used to represent the surface-active agents commonly found in oil recovery processes. The nonionic C12E8 is employed in enhanced oil recovery (EOR) operations to displace residual oil from hydrocarbon reservoirs through chemical flooding.⁷² Often, NPs in suspension can stimulate oil recovery through modification of the contact angle at the substrate,^{106, 107} increasing the oil recovery rate.¹⁰⁸

Our research aims to gain insights into the energy required for individual NPs as they transition between two immiscible liquids, employing Dissipative Particle Dynamics (DPD) simulation methods. The properties of the interface will be modified by added surfactants, NPs, or the concurrent presence of both surfactants and NPs.

7.2 Simulation details

The schematic configuration of all species used in the DPD simulations is shown in **Figure 7.1a**, while the conversion of time and length scales from DPD units to physical units is seen in **Table 5.1**.

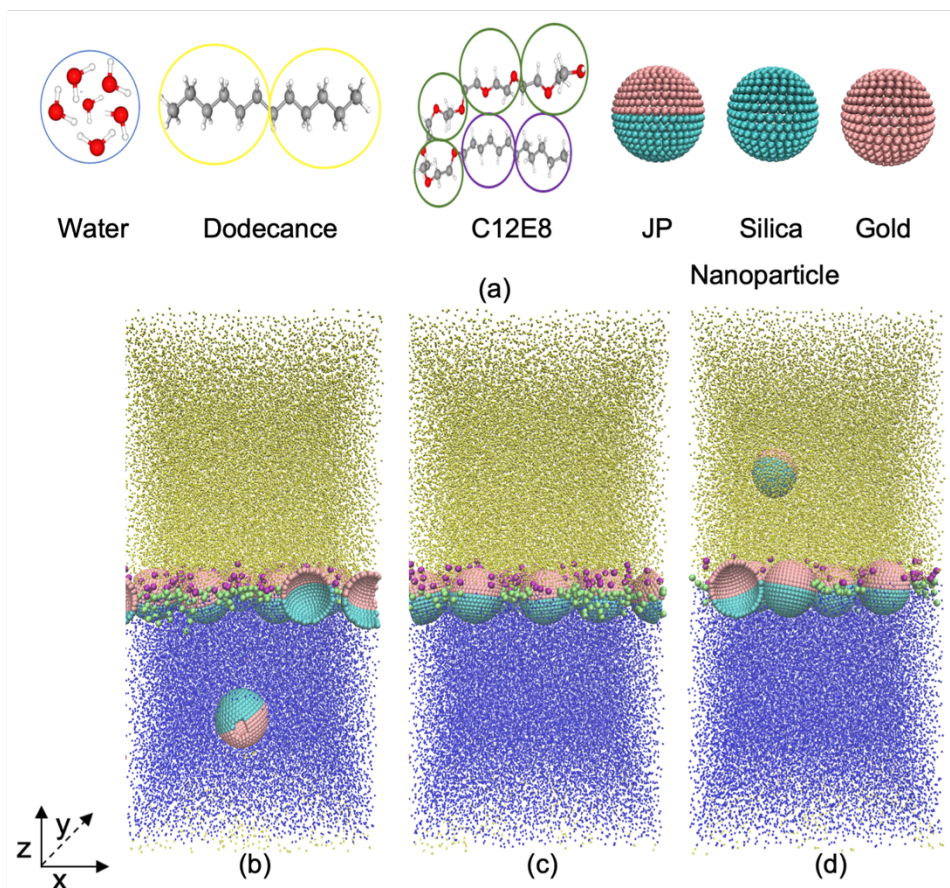


Figure 7.1 (a) A schematic representation of the beads generated by DPD simulations with water, dodecane, C12E8 surfactant molecules, a Janus particle (JP), and homogeneous particles (silica and gold nanoparticle). Red, white, and gray spheres represent oxygen, hydrogen, and carbon, respectively. A nanoparticle bead's silica surface is cyan, while its gold surface is pink. (b-d) The process of JP transfer from the water phase to the oil phase with the coexistence of surfactant and JPs at the oil-water interface.

Six water molecules were lumped into each water bead (W), while the oil phase was represented by dodecane molecules ($C_{12}H_{26}$) with each dodecane molecule represented by two oil beads (O). The selected nonionic surfactant, C12E8, was previously employed in our research,^{36, 104, 155, 168} which was represented by two hydrophobic tail beads (T) and four hydrophilic head

beads (H). The maximum surfactant concentration used in this research is set at the critical micelle concentration (CMC) or below, to prevent the formation of micelles.¹¹⁹ About the NPs, the radius of each NP was set to $2 r_c$ (DPD unit) with $1 r_c = 9.66 \times 10^{-10} \text{m}$, as presented in **Table 5.1**. The NP was crafted to possess hollow structures, with vacant spaces inside. The hydrophilic and hydrophobic sides of the JP used in this study are silica (SiO_2) and gold (Au), respectively. In a previous study, Vu et al.¹⁰³ illustrated the validation of the wetting behavior of the two faces of the Janus particles, characterized by one hydrophobic hemisphere and the other hemisphere as hydrophilic, using amidine polystyrene latex and gold. The computations were verified against experimentally measured contact angles.¹⁸⁰ In this study, we employ identical interaction parameters for the gold surface of NPs as employed by Vu et al. The DPD parameters for the silica surface of JPs were adjusted to match experimental results as shown in **Figure S 1** in the **Supporting Information**. A single silica NP (S) was placed at the oil-water interface. The interaction parameters for a silica surface with oil and water (a_{O-S} and a_{W-S}) were adjusted to align with the experiment findings¹⁸¹ based on the measured three-phase contact angle values. The determination of the value of the contact angle within the water phase was found to be dependent on the distance between the center of the NP and the position of the oil-water interface, $\theta_S = 67.8 \pm 3.6^\circ$. Moreover, the contact angles for the gold NPs (G) and JPs were $\theta_G = 81.4 \pm 3.4^\circ$ and $\theta_{JP} = 79.9 \pm 3.3^\circ$, respectively. The interaction parameters for the surfactant head with the silica surface (a_{H-S}) and surfactant tail with silica surface of JP (a_{T-S}) were determined based on experimentally obtained adsorption isotherms for C12E8 in an aqueous solution onto silica¹⁸² (see **Figure S 2b**). The amount of surfactants adsorbed on the silica surface was determined by measuring the distance between the surfactant molecule and the surface in the computational results. If the distance was less than $5r_c$, the surfactant molecule would be considered adsorbed (see **Figure S 2a**). The repulsion parameters for the case of C12E8 and/or NPs at the oil-water interface are listed in **Table 7.1**.

Table 7.1. Details of the repulsion parameters (a_{ij}) used in the simulations

	H	T	W	O	G	S
H	15	25	15	25	15	28
T		15	38	14.5	25	15
W			15	129	20	20
O				15	25	55
G					15	25
S						15

* H and T represent the head and tail of C12E8 surfactant, while W and O symbolize water and oil, respectively. The NPs include gold (G) and silica (S) beads.

The computational box was established as $20 \times 20 \times 40 r_c^3$, (dimensionless DPD units in the x , y , z directions). Periodic boundary conditions were applied in all three dimensions. There were 80,000 fluid beads within the computational domain to keep the fluid density in DPD units at 5 (i.e., 5 DPD bead per unit volume of the simulation).⁴⁴ More specifically, 39,916 oil beads were randomly arranged in layers of $20 r_c$ thickness along the z -direction. The number of water beads varied depending on the quantity of NPs and/or surfactant molecules introduced into the system. The NP coverage at the interface was kept between 0 – 0.77. Consistent with earlier reports,^{183, 184} surfactants, and NPs were positioned at the oil-water interface to reduce computational time. Furthermore, one targeted NP, chosen for movement analysis, was inserted at the oil-water interface at the beginning of the simulation. To reach equilibrium, the system was set to run 200,000 computational steps. The NVT ensemble (constant number of beads, volume, and temperature) was used during the computations. The temperature remained constant at $T = 1$, with periodic relaxation of the temperature every 100 time steps, employing the DPD units of temperature.

The process of NP transfer from the bulk of phase 1 (water) to phase 2 (oil) was employed using the steered molecular dynamics (SMD) algorithm to display the adsorption and desorption process in addition to calculating the free energy differences. Upon achieving equilibrium, the center of mass of the targeted NP was moved into the water phase, as shown in **Figure 7.1b**, and then allowed to equilibrate for an additional 100,000 time steps. A fictitious spring with a force

constant of $500 k_B T / r_c$ was used to pull the NP from the water phase to the interface (**Figure 7.1c**) and then the oil phase (**Figure 7.1d**) at a constant relative velocity of $0.0005 r_c$ per timestep. At the same time, other NPs and surfactants were free to move across the oil-water interface. The simulation time step was set to $\Delta t = 0.02$ in DPD units, and the total number of steps required for the pulling process was 2,000,000. The data of the potential of mean force (PMF) for the system can be determined using SMD through the application of Jarzynski's equality $\langle e^{-W/k_B T} \rangle = e^{-\Delta F/k_B T}$.¹⁸⁵ In this study, the potential of mean force (PMF) provides valuable insights into the energetics and barriers encountered by a targeted NP as it goes through various stages, such as adsorption, desorption, and migration at the interface, in the presence of surface-active agents such as surfactants and NPs, given that the PMF reflects the free energy difference between two states during a non-equilibrium process.

7.3 Results and Discussion

7.3.1 NP movement across the oil-water interface

In **Table 7.2**, the difference in energy, expressed in $k_B T$, for absorbing single homogeneous or Janus NP into the oil-water interface, as determined by equation (1.7) and equation (1.8), is presented. The energy difference was also obtained directly from simulations, as illustrated in **Figure 7.2**.

Table 7.2. The energy required when NP comes into the water, ΔE_{water} or oil, ΔE_{oil} calculated from the three-phase contact angle, θ_E using equation (1.7) and equation (1.8).

	JP	S	G
θ_E	$79.9 \pm 3.3^\circ$	$67.8 \pm 3.6^\circ$	$81.4 \pm 3.4^\circ$
$\Delta E_{water} (k_B T)$	107.5 ± 15.4	57.8 ± 11.5	107.5 ± 15.4
$\Delta E_{oil} (k_B T)$	264.2 ± 20.3	282.2 ± 24.1	196.4 ± 20.4

In **Figure 7.2**, the necessary energy for the translation process is shown as a function of distance from the interface for both phases and the center of the NP. State (I), illustrates the single NP completely immersed in Fluid 1 (water), positioned far from the interface. This state was chosen as the reference state for all three particle types due to the absence of any interaction between the NP and the interface. As the particle approaches the interface, the free energy remains

constant, denoted as state (I-II). As the particle approaches the oil-water interface, there is a decrease in energy, reaching its minimum at the interface (III) when the nanoparticle finds its preferred position. Finally, the energy experiences a sharp increase (III-IV) denoting the desorption energy, reaching a plateau as the NP transports away from the interface and enters deeper into Fluid 2 (oil phase) (IV-V). The potential of mean forces collected along the coordinate is shown in **Table 7.3**.

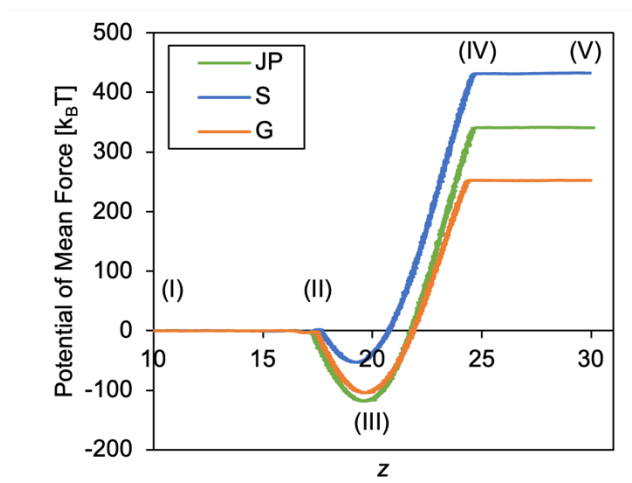


Figure 7.2. The energy required for different types of NP to transition from the water phase to the oil phase.

The behavior of NPs at oil-water interfaces involves intricate dynamics, as evidenced by observed phenomena upon NP contact with the interface. Variations in the energy required to pull different types of NPs from the aqueous phase to the interface suggest distinct interactions dictated by NP properties. As can be seen from **Figure 7.2**, JP requires the highest energy to approach the oil-water interface from the water phase compared to the homogeneous NPs. Moreover, a protective water shell around the NP upon interface approach is shown in **Figure 7.3b**, resulting in a bulged interface due to water molecule accumulation. Subsequently, an oil bridge was observed when NP moved continuously close to the interface (**Figure 7.3c**), attributed to the stronger interaction of NPs with the oil phase at this point.

Furthermore, silica NPs require the most energy for transitioning from the interface into the oil phase, whereas gold NPs display the lowest energy difference, with Janus particles occupying an intermediate position. In all cases, the energy required to remove one NP from the interface into the water phase is observed to be lesser than that required to displace it into the oil

phase. The reason for this is that both silica and gold used in this study tend to favor the water phase over the oil phase ($\theta_P < \theta_{AP} < 90^\circ$). However, silica NPs still demand higher additional energy to transition into the oil phase because of the larger surface area coverage of silica NPs in water compared to gold NPs.

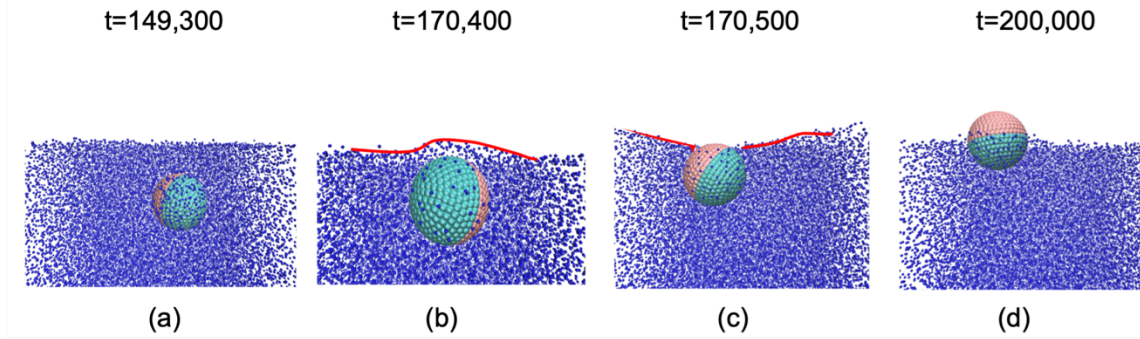


Figure 7.3. Snapshots of the oil-water when JP approach the interface during the simulation time steps from $t = 149,300$ to $t = 200,000$. The color code is similar to **Figure 7.1**.

Table 7.3. Difference energy when NP entered the water, ΔE_{water} or oil, ΔE_{oil} determined from the simulation results.

	JP	S	G
$\Delta E_{water} (k_B T)$	113.9	52.3	95.7
$\Delta E_{oil} (k_B T)$	426.7	477.6	351.6

When comparing the energy difference values (ΔE_{oil}) obtained from the simulations (**Table 7.3**) with the desorption energy calculated using the equations provided in **Table 7.2**, a disparity is observed. The discrepancy might originate from differences in the equilibrium three-phase contact angle used in the energy calculation equation. The position of the center of mass of the NP changes as the NP moves at the interface, which in turn leads to fluctuations in the contact angle values during the simulation. Although the deviation in the three-phase contact angle is small, even slight variations can result in significant fluctuations in the desorption energy (shown in **Table 7.2**). Another possibility is from hydrodynamic dissipation effects, which are not included in the calculation of desorption energy calculations by applying theoretical models.¹⁷⁸ The position

of the three-phase contact line was assumed to align with the liquid-liquid interface and ignore the small meniscus that may form near the NP. In addition, the capillary bridge (with the oil-water interface, and the oil bridge (**Figure 7.3**) or water bridge (**Figure 7.4**) that appeared when NP approached or detached the interface) is considered a contributing factor to these observed differences. Observation of simulation snapshots illustrates the formation of a capillary bridge during the desorption of NPs into the oil phase, notably forming a water bridge as shown in **Figure 7.4**. This phenomenon occurs because even in the oil phase, water molecules may still be attracted to the silica part of NPs, forming a thin layer of water behind them. At this point, the water bridge extends farther into the oil phase, leading to surface deformation and a non-flat oil-water interface. These findings are consistent with previous studies.^{178, 179} This differs from the assumption of a flat interface in the desorption energy equation used to measure the contact angle, leading to variations in the values of the free energy. In general, despite these differences, both methods agree that all NPs, exhibit a preference for approach into the aqueous phase from the interface rather than desorption into the oil phase. The corresponding free energy differences for the translation process are also calculated by the Umbrella Sampling method. The comparison between the Steered Molecular Dynamics and Umbrella Sampling method is shown in **Figure 7.5**. The two methods are consistent, indicating that the SMD model with the calculation of the PMF is reliable.

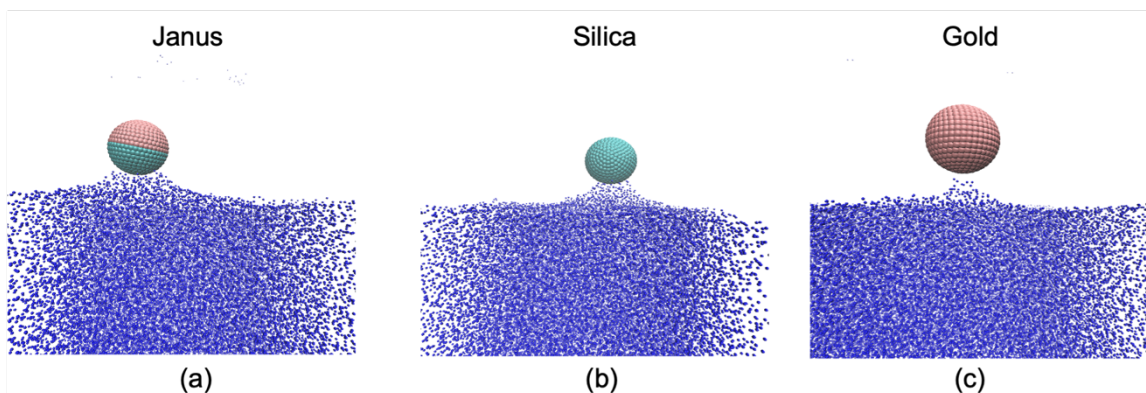


Figure 7.4. Snapshot depicting the formation of a capillary bridge between (a) Janus NP, (b) Silica NP, (c) Gold NP, and the oil-water interface. The color scheme is similar to that used in **Figure 7.1**. The oil phase is omitted for clarity.

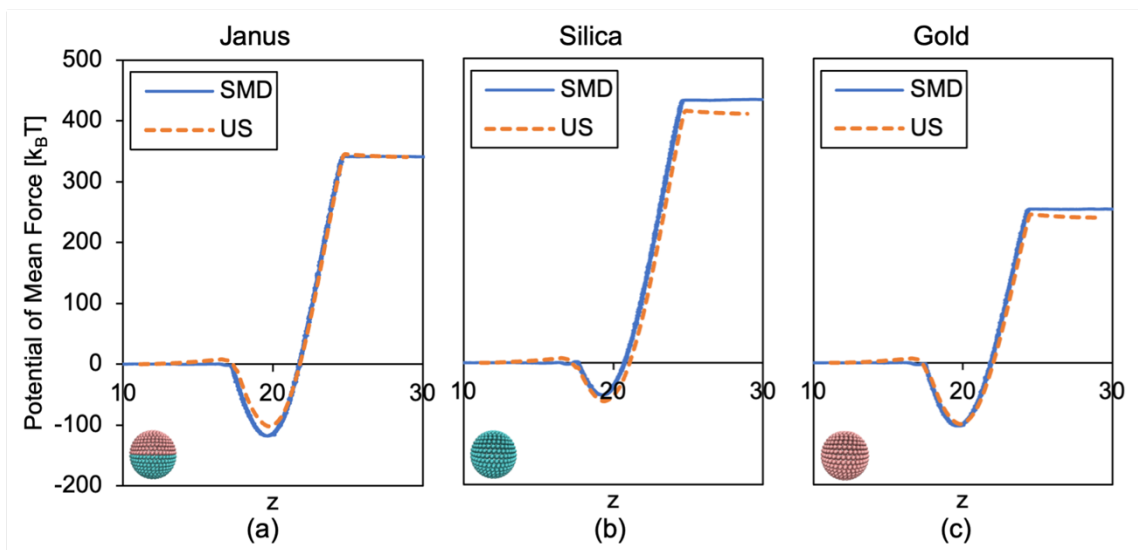


Figure 7.5. Umbrella sampling method to compute the free energy (compared with SMD method) for single nanoparticles of varying surface properties: (a) Janus nanoparticles, (b) silica nanoparticles, and (c) gold nanoparticles. The range of the reaction coordinate was divided into 180 windows with the harmonic force constant set to 500 $k_B T$.

7.3.2 NP movement across the oil-water interface in the presence of surfactants

The addition of nonionic surfactants to the oil-water interface serves as a crucial aspect in exploring the dynamics of single NP movement between two immiscible fluids. This section discusses the energy requirements associated with the motion of a single NP across the interface between oil and water, as well as the influence of surfactant concentration on the necessary energy.

The energy demands for different types of single NP transitioning between two immiscible fluids, comparing scenarios with and without surfactants at the interface are shown in **Figure 7.6**. The presence of surfactants alters the interfacial properties, potentially lowering the energy barrier for NP movement by reducing the interfacial tension significantly at the CMC value ($IFT_{C12E8} \approx 4.7 \text{ mN/m}$). This reduction in interfacial tension facilitates the movement of NPs across the interface by minimizing the energy barrier they encounter. Therefore, the value of energy required to remove the NP from the interface decreases rapidly upon the addition of surfactants, regardless of the NP type, in contrast to scenarios where no surfactants are present. A silica NP still needs the most energy to migrate to the oil phase, then Janus NP, and finally gold NP.

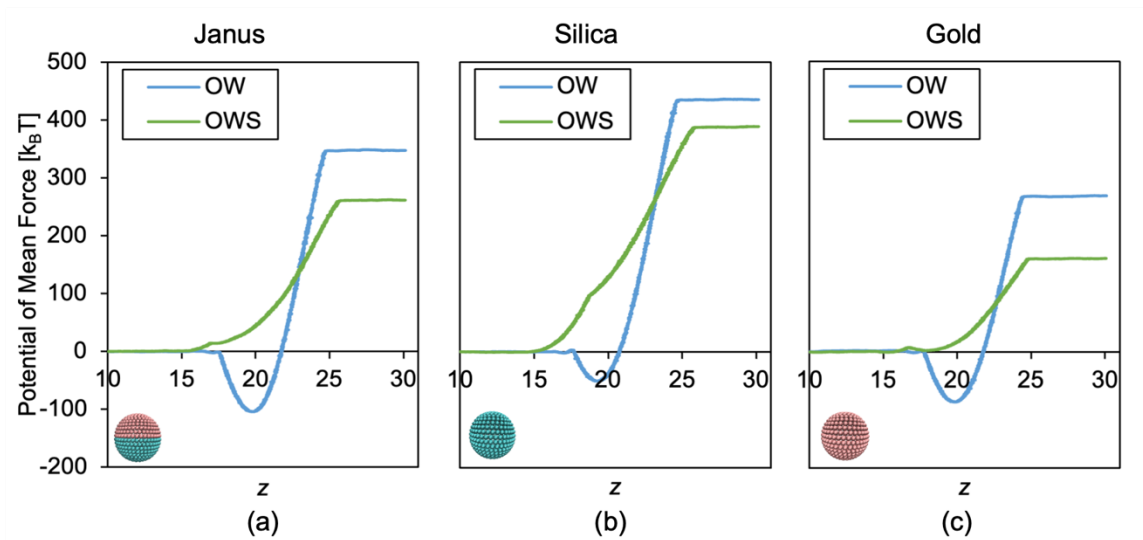


Figure 7.6. The potential of mean force (PMF) profile of the system when (a) Janu, (b) Silica, (c) Gold NPs moving toward oil and water phases, with and without the presence of surfactants.

OW: bare oil-water interface, OWS: oil-water interface with surfactants.

When surfactants are present, NPs demand more energy for absorption to the interface compared to being situated in the water phase; however, in the absence of surfactants, they still exhibit a preference for remaining at the oil-water interface. Notably, silica NPs exhibit a higher energy demand in this context (see **Figure 7.6b**). This is due to the silica NP displaying a preference for being situated deeper within the water phase rather than at the interface (see **Figure 7.7c-d**). Regarding Janus and gold NPs, they tend to remain at the interface, although mostly submerged in the water due to their stronger interaction properties with the oil phase compared to silica NP.

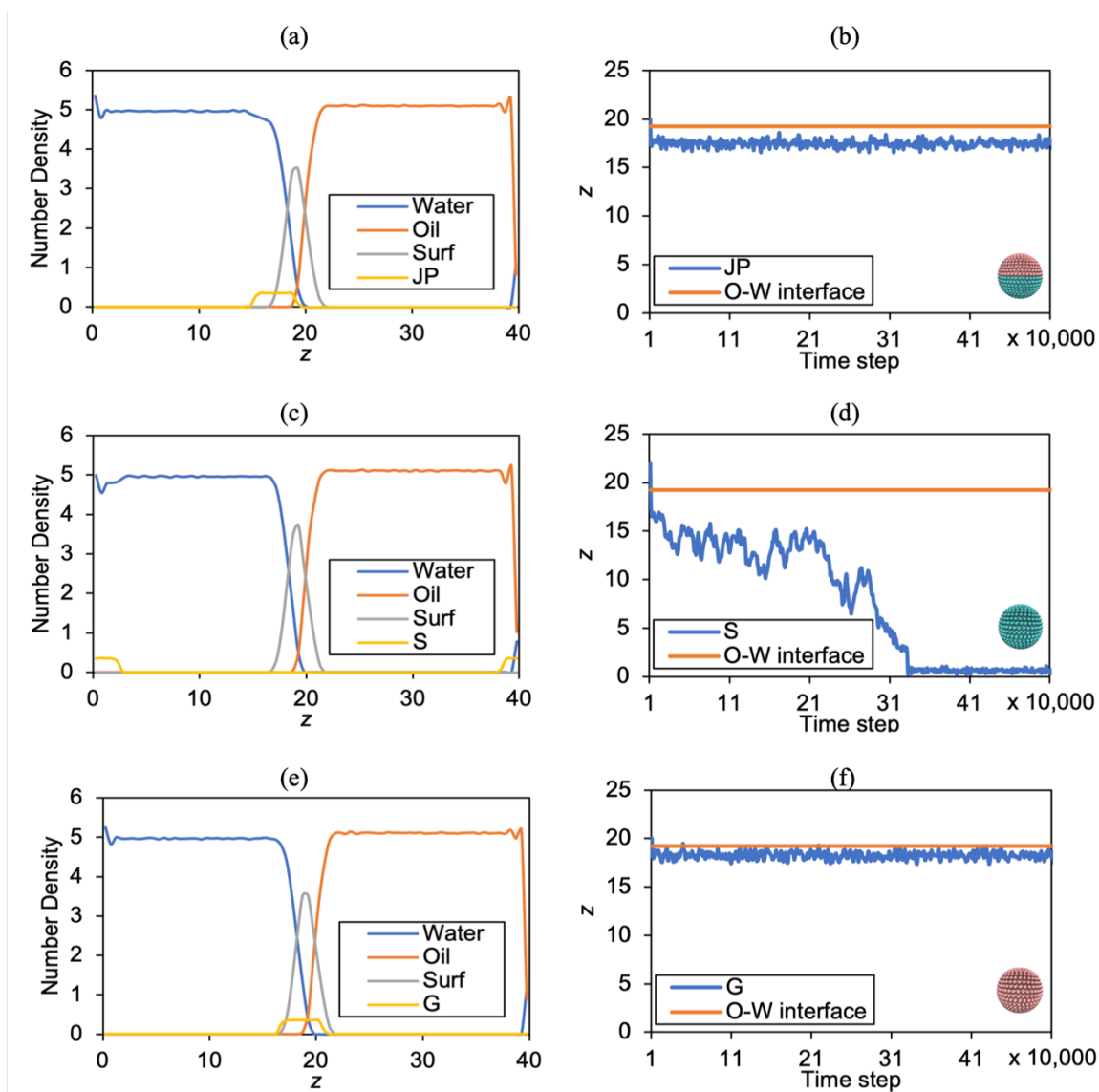


Figure 7.7. Density profiles when a single NP and surfactants are located at the oil-water interface (a, c, e); the position between the center of the NP and the oil-water interface (b, d, f) as a function of simulation time. The NP is (a-b) a Janus NP; (c-d) a silica NP, (e-f) a gold NP.

The effect of surfactant concentration on the energy necessary to displace a single NP from the water phase to the interface and into the oil phase is demonstrated in **Figure 7.8**. The concentration of surfactants was increased from 0 CMC (no surfactant) to the CMC value and JP was selected as the subject of investigation. As can be seen from **Figure 7.8a**, at lower concentrations of surfactant, the desorption energy from the interface to the oil phase remains comparatively elevated but decreases notably as the interfacial surfactant concentration

approaches the CMC. This reduction can be attributed to the decrease in interfacial tension as shown in **Figure 7.8b**.

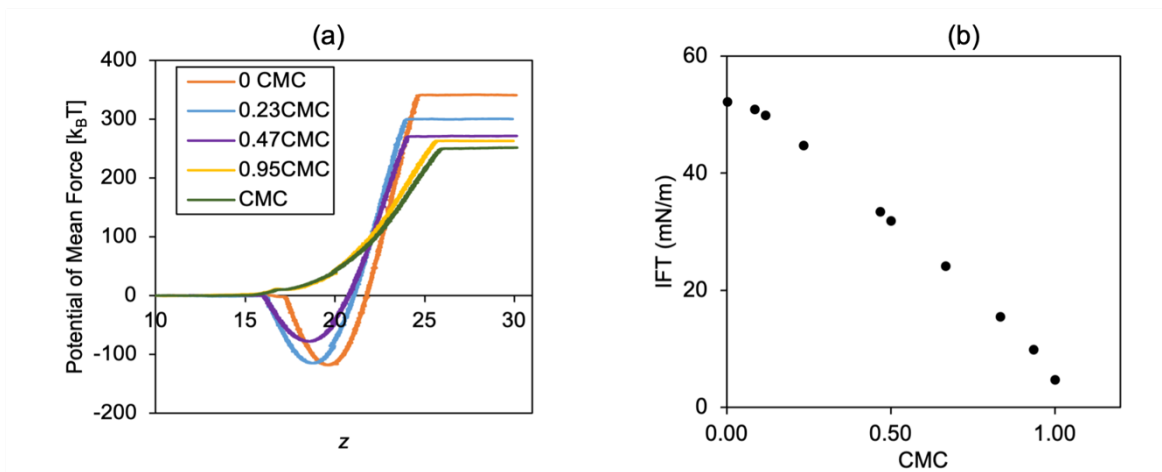


Figure 7.8. (a) Potential energy differences as a function of the NP position when a JP transports from the water phase to the oil phase within the presence of surfactants at the interface. (b) The interfacial tension between oil and water at varying concentrations of surfactants.

The presence of the capillary bridge is also noted during the desorption of the NP particle from the interface to the oil phase, but in this case, it seems that a surfactant bridge is formed. The surfactant bridge can influence the release kinetics of NPs from the interface by increasing the necessary energy.

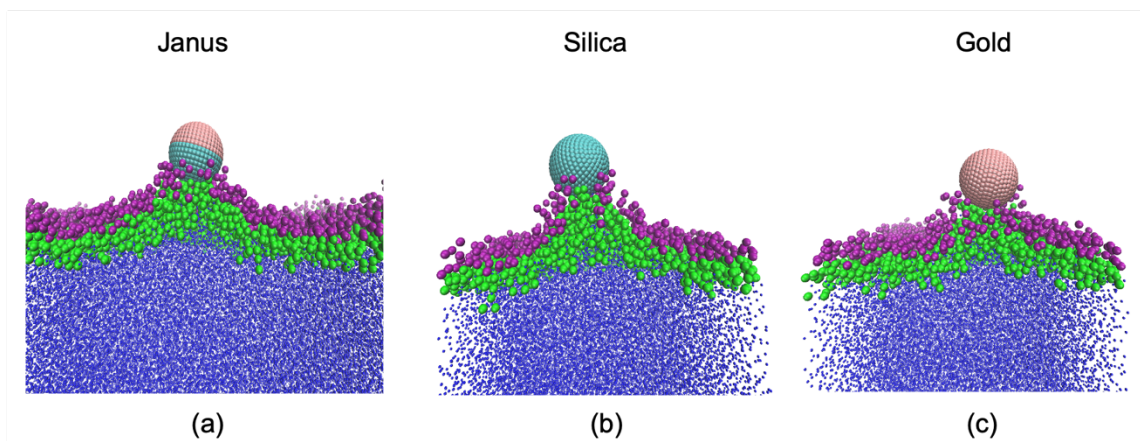


Figure 7.9. Snapshots illustrating the formation of a surfactant bridge between (a) Janus, (b) Silica, (c) Gold NP, and the oil-water with surfactant interface. The color scheme aligns with that utilized in **Figure 7.1**. The oil phase is omitted for clarity.

7.3.3 NP movement across the oil-water interface in the presence of NPs

Because the NPs do not have a noticeable impact on the interface tension, as evidenced by prior research,^{36, 156, 157, 166, 167} the absorption energy needed for the single NPs absorbed on the interface closely resembles the scenario in which no NPs are present at the interface, as illustrated in **Figure 7.10**, except in the instance of JP transport (or silica NPs), where a 0.77 coverage area of JP or silica NPs is observed at the oil-water interface.

While IFT remains unchanged, the presence of NPs at the interface still creates a barrier that impedes the transport of one other NP from the water phase to the oil phase. Consequently, the energy required for desorption from the interface to the oil phase is higher than the case without NPs located at the oil-water interface. The NPs at the interface form a layer that needs to be penetrated by the moving NP. The more the surface cover area increased (from 0.36 to 0.77) by the presence of NPs, the more the desorption energy increased from the interface. When comparing various types of NPs, the silica NP demands the highest energy for transportation to the interface (**Figure 7.10a**), whereas the gold NP exhibits the lowest energy requirement (**Figure 7.10c**).

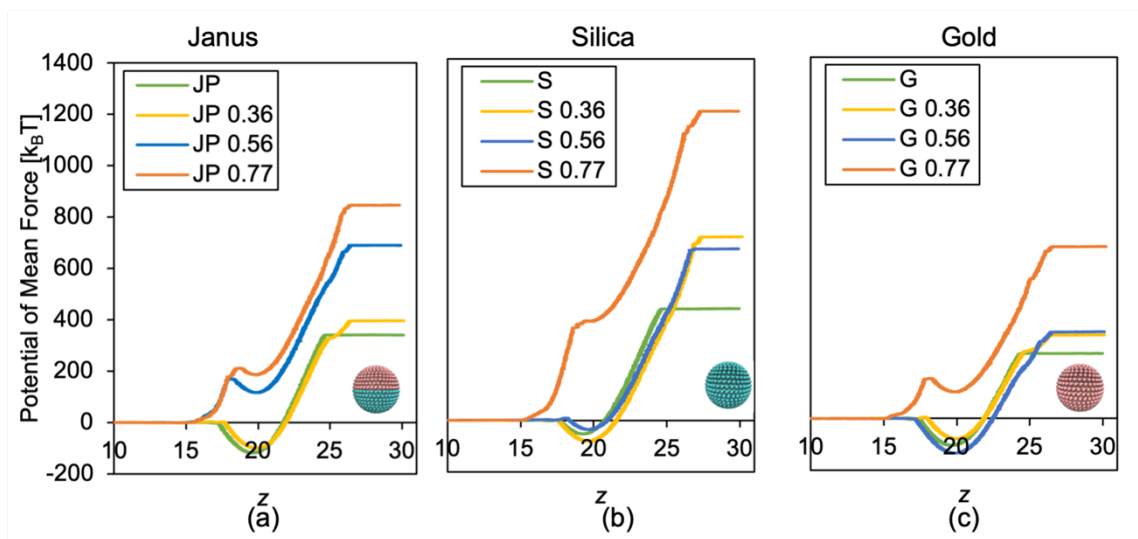


Figure 7.10. Potential energy variations for the distance of the NP as it transitions from the water phase to the oil phase within the layer of similar NP types at the interface, different types of NPs including (a) Janus, (b) Silica, (c) Gold NP. The percentage of NP coverage changed from 0 (no NP at the oil-water interface), to 0.36, 0.56, and 0.77 coverage of interface area.

There are some abnormal cases observed in **Figure 7.10a** and **Figure 7.10b**, where a large number of NPs are distributed on the surface (0.77 coverage area of the oil-water interface by NPs

or 0.56 coverage area of JP). Although we expected that when the number of NPs increased, the movement of the target NP became difficult as mentioned above, the shape of the increment should be the same when the distribution of NPs rose from 0.56 to 0.77. But this significant high PMF value can come from something that happens at the interface when NPs approach the interface. To validate these results, snapshots of the simulation process were collected and shown in **Figure 7.11**.

In **Figure 7.11a**, the absorption process of JP to the oil-water interface is depicted step-by-step, with a JP coverage of 0.77 in the oil-water interface area. A notable increase in energy requirement was observed as the JP approached the oil-water interface, particularly when attempting to locate a vacant space within the clustered JPs. This high energy demand is due to the requirement of moving through the interaction zone of neighboring NPs (highlighted by the red circle). At this point, additional energy was required to break the interaction between NPs, resulting in the observation of heightened energy levels. Once the preferred position is determined, the target NP can establish interactions with neighboring NPs, thereby maintaining stability at the interface, with energy levels remaining unchanged. The residual desorption process from the interface to the oil phase follows the same pattern as in other scenarios, demanding significant energy. Compared with **Figure 7.11b**, this phenomenon did not appear. In this case, the gold NP found the vacant space without the clustered JPs when it came closer to the interface, eliminating the need for additional energy to overcome the NP barrier.

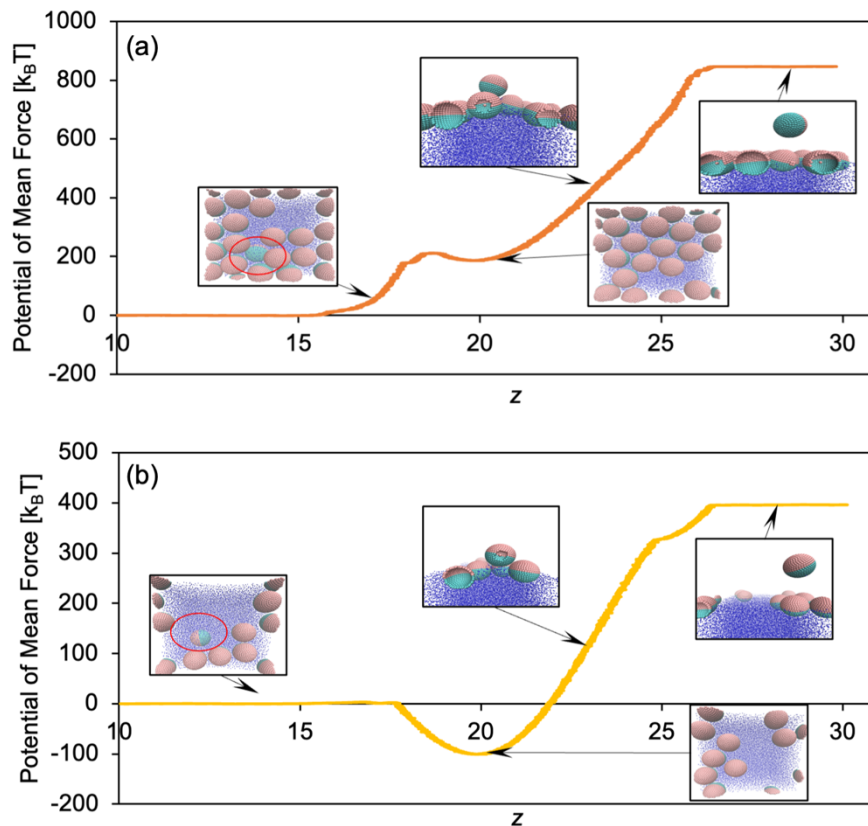


Figure 7.11. The process of NP transfer from the water phase to the oil phase, includes (a) a single JP occupying 0.77 of the interface area and (b) a single JP with 0.36 coverage surface area. The color scheme is similar to that used in **Figure 7.1**. The oil phase is omitted for clarity.

The snapshots of NP distribution on the oil-water interface are shown in **Figure 7.12a-c** and the final simulation steps before the detachment of a single NP from the NP layer to the oil phase are depicted in **Figure 7.12d-f**. No capillary bridge was observed due to the NP layer, instead, the reason causing the growth of desorption energy to the oil phase is the interaction between NP-NP. When a single NP attempted to transition to the oil phase, extra energy was needed to distract its interaction with neighboring NPs and force it to leave its favorite position.

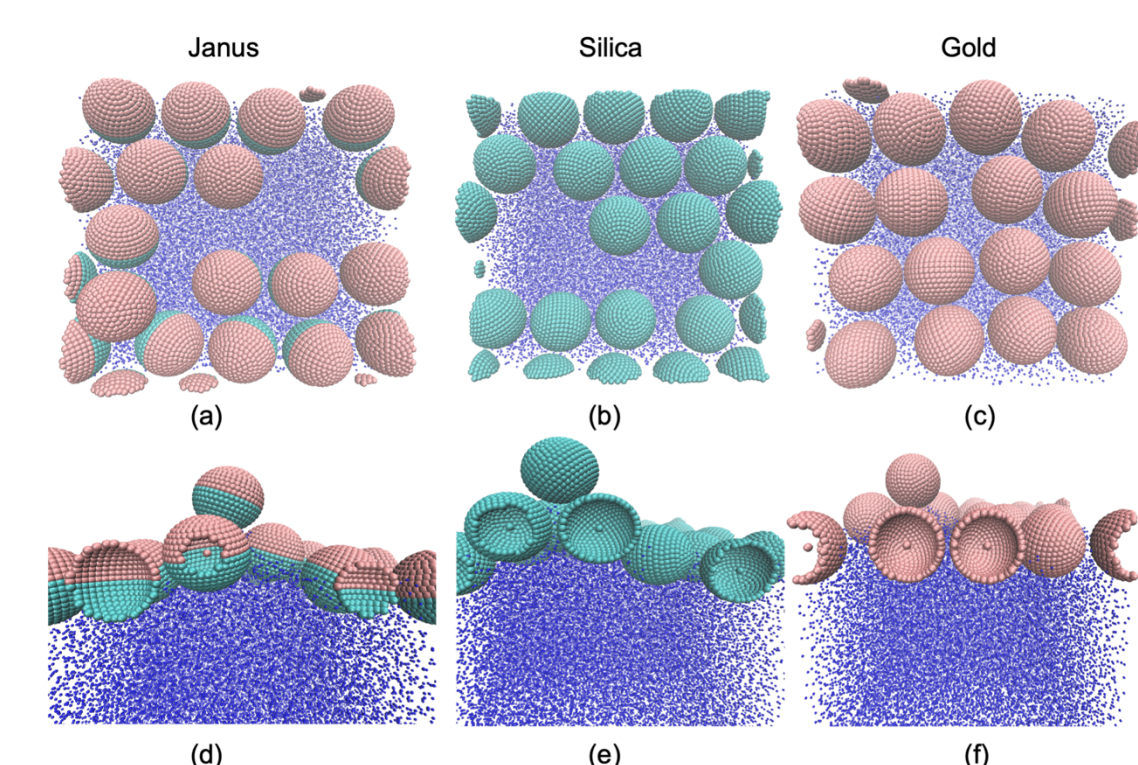


Figure 7.12. The distribution of (a) Janus NP, (b) Silica NP, and (c) Gold NP covers 0.77 the area of the oil-water interface. Snapshots before detachment of (d) Janus, (e) Silic, and (f) Gold NP from the NP layer. The color scheme is similar to that used in **Figure 7.1**. The oil phase is omitted for clarity.

7.3.4 NP movement across the oil-water interface with the coexistence of NPs and surfactants

To explore the impact of the coexistence of NPs and a surfactant layer on the absorption or desorption energy required for NP transport, a single NP was introduced to transition between two immiscible liquids. The interface comprised 0.4 CMC surface concentration, with NP coverage of 0.56 (see **Figure 7.13**). The presence of NPs reduces the effective interfacial area, leading to a higher concentration of surfactants compared to scenarios where only surfactants are present. Consequently, the active concentration of C12E8 in this case matches the CMC value observed in systems without NPs.

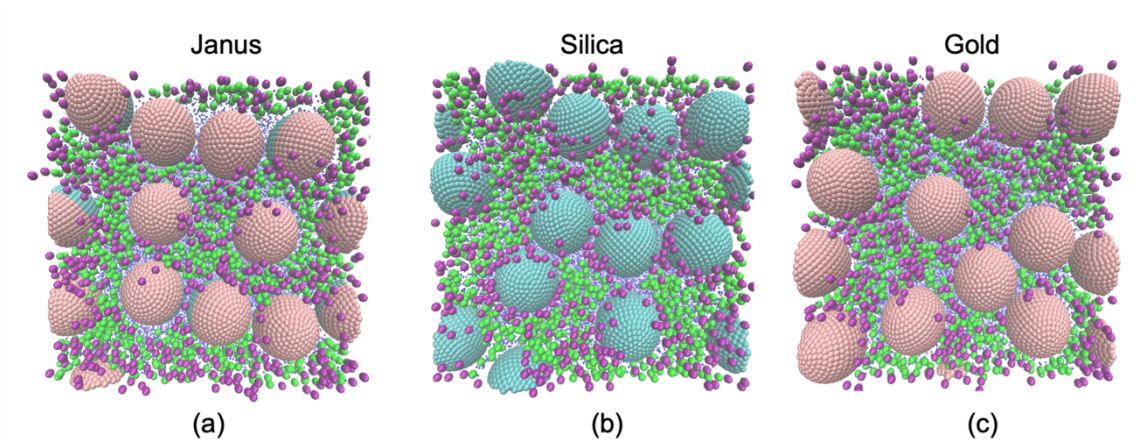


Figure 7.13. The interface comprised 0.4 CMC surface concentration and 0.56 coverage of (a) Janus, (b) Silica, and (c) Gold NP coverage of 0.56. The color scheme is similar to that used in **Figure 7.1**. The oil phase has been left out for clarity.

The plot of the potential of mean force as a function of the distance of NP movement, shown in **Figure 7.14** was utilized to compare the effects of the presence and absence of surfactant at the interface on NP movement. During the absorption process from the aqueous phase to the interface, wherein NPs and surfactants coexist, NP-NP interactions persist as individual NPs approach the interface. This leads to a higher energy requirement for absorption compared to scenarios where only surfactants are present at the interface. Once a single NP enters the interface, it prefers to remain there due to the attractive NP-NP interactions. Detaching a single NP from the interface into the water phase is more difficult when only surfactants are present at the interface relative to only surfactants present at the interface. Furthermore, compared to the scenario where only NPs occupy the interface, the presence of both NPs and surfactants at the interface lowers the absorption energy required at the interface. This reduction can be attributed to the decrease in IFT when surfactants were added to the system. **Figure 7.13** illustrates the distribution of the NPs at the interface, indicating that surfactants can disperse NP clusters. This action decreases the NP-NP interactions, consequently lowering the absorption energy when a single NP absorbs into the interface. The same trend was noted when NPs detached from the interface and migrated to the oil phase. The desorption energy was smaller when NPs and surfactants coexisted at the interface compared to scenarios where only NPs occupied the interface, but higher than when only surfactants were present at the interface.

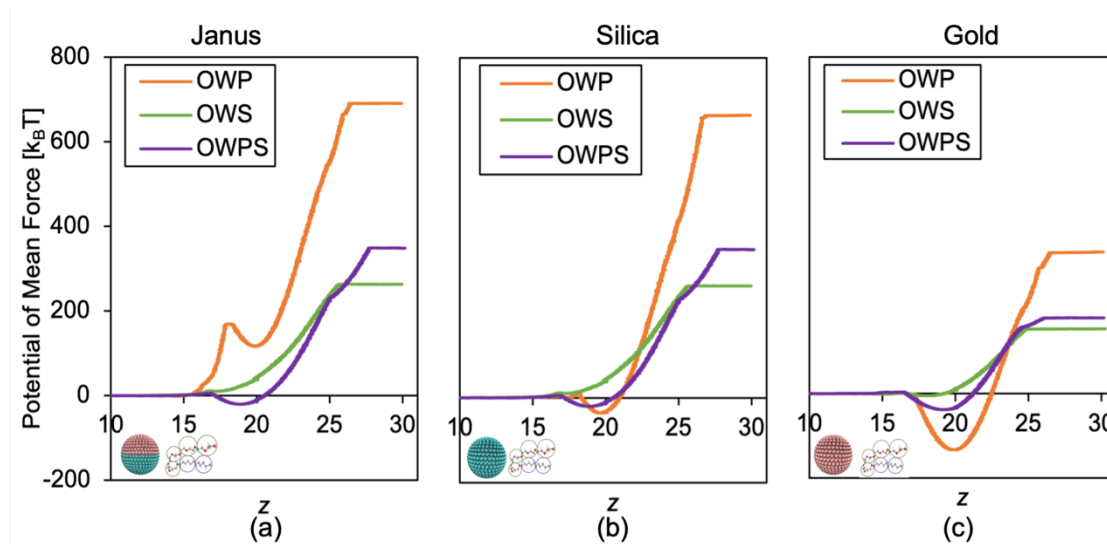


Figure 7.14. The potential of mean force (PMF) profile of the system when (a) Janus, (b) Silica, and (c) Gold NP migration from the oil phase to the water phase considering the presence or absence of surfactants and the coexistence of NPs and surfactants.

7.4 Conclusions

In this study, we have numerically investigated the process of particle translation through an interface of two immiscible liquids with and without the presence of surfactant and Janus particles at the interface. NPs covered the oil and water interface at 0 – 0.77 coverage interface area and contained surfactants up to the critical micelle concentration of C12E8. We find that when required to detach from the interface, all NPs tend to prefer the water phase rather than the oil phase. The formation of a capillary bridge is initiated by the NP desorption into the oil phase, significantly increasing the energy demand due to the challenging task of disrupting the interactions between the NPs and the surrounding water or surfactant molecules. In addition, in the scenario where only NPs cover the oil-water interface, an increase in desorption energy is observed compared to when only oil and water are present. Additional energy is required to disrupt the interactions between neighboring NPs and force the single NP to leave its preferred position when transitioning to the oil phase. Finally, the desorption energy was lower when NPs and surfactants coexisted at the interface compared to only NPs occupying the interface, but higher than when only surfactants were present at the interface.

Chapter 8. Summary and Future Works

8.1 Summary

This thesis focuses on exploring how surface-active agents including surfactants and nanoparticles influence the properties of two immiscible fluids under non-equilibrium conditions. The primary conclusions can be outlined as follows:

- We focused on investigating the dynamic behavior of immiscible fluids in Poiseuille or Couette flow and the interaction of surfactants with the oil-water interface using DPD simulations. The no-slip boundary conditions with frozen wall particles and bounce-back conditions to prevent penetration of fluid beads into the wall was implemented. Additionally, adjusting the dissipative parameter for each fluid accurately models differences in fluid viscosity in multiphase flow simulations. Under shear flow conditions, the presence of surfactants at the oil-water interface significantly influenced fluid dynamics by modifying the velocity profile and the effective viscosities of both phases. The observed desorption of surfactants at higher shear rates highlighted the dynamic nature of these interfaces, particularly in unstable Poiseuille flow where local surfactant concentrations varied due to wave formation. Micelle formation below the CMC was only observed in the Poiseuille flow. The effects of viscosity and shear rate induced by surfactants were further substantiated through robust calculations in a simulation box of increased width, affirming the importance of these factors in understanding and predicting complex fluid behaviors. These findings contribute valuable insights into the interplay between dissipation parameters, surfactant behavior, and fluid dynamics, with implications for diverse applications.
- Regarding the movement of oil droplets, it is significantly influenced by the presence of surfactants and Janus particles in Couette flow. Surfactants at the oil droplet surface enhance migration velocity by affecting interfacial tension, which improves momentum transfer from water to oil and reduces oil-water slip. There is a linear relationship between slip velocity and interfacial tension. However, Marangoni stresses can counter this motion by generating oil movement opposite to the shear flow direction, slowing overall drop motion. Furthermore, JPs gather at the drop-solid contact line, boosting friction between the drop and the wall, and thereby decelerating drop migration. When comparing

displacement, oil droplets with the coexistence of JPs and surfactants displace more than bare oil droplets.

- Concerning the behavior of NPs at the oil-water meniscus, our analysis of oil-water IFT values with NPs positioned at the oil-water interface revealed that NPs had minimal impact on IFT, resulting in a negligible change in the equilibrium meniscus length (L_0). Under Poiseuille flow, we observed a linear relationship between finger length and Capillary number. The wettability of NPs influenced meniscus stability, with hydrophobic particles promoting finger-like water protrusions in oil. Droplet detachment occurred when the three-phase contact angle reached a critical value, independent of NP type. Fluid velocity was crucial, as pressure differences played a more significant role in detachment and droplet formation than particle properties, especially in oil-water mixtures containing NPs. After droplet formation, NPs did not distribute uniformly on the droplet surface; instead, they tended to form densely packed patches on the rear side of the droplet. NPs rearranged themselves at the oil-water interface and could even partition into the oil or water phases at the droplet's rear, depending on their surface chemistry.
- Added surfactants to the system reduced the oil-water IFT, leading to a significant difference in the movement of two immiscible fluids compared to the case of only NPs located at the meniscus. Firstly, at equilibrium, the surfactant played a crucial role in determining the three-phase contact angle between the oil droplet and the walls, with the wettability of the solid walls exerting a notable influence on this interaction. When the walls were hydrophilic, the presence of surfactants led to a larger contact angle and increased curve length within the channel, particularly as the surfactant concentration approached the CMC. Conversely, on hydrophobic walls, the introduction of surfactants resulted in a longer curve length but significantly reduced the three-phase contact angle. Secondly, when observing the fingering phenomenon, the length of fingering increased with a higher Capillary number, with the growth rate influenced by the type of surface-active species present, affecting the stability of the oil-water interface. NPs contributed to enhancing interface stability by impeding deformation and interacting with the surfactant layer at the interface. Under sufficient driving force, the fluid-fluid interface became unstable, leading to droplet formation. In the presence of surfactants, NPs distributed more uniformly at the interface, requiring a higher driving force for drop generation compared

to scenarios with bare oil/water or surfactants alone. Lastly, the relative velocity between surfactant molecules/NPs and the droplet's center of mass explains their transport and arrangement on droplet surfaces within hydrophilic or hydrophobic channels.

- Regarding the energy required for the migration of single nanoparticles (including homogeneous and amphiphilic NPs) between the oil and water phases, based on our findings, the formation of a capillary bridge is created by the desorption of NPs into the bulk phase, resulting in a significant increase in energy demand. When considering scenarios where NPs exclusively cover the oil-water interface, the desorption energy increases compared to situations involving only oil and water. This increase is attributed to the additional energy required to disrupt interactions between neighboring NPs and to displace a single NP from its preferred position during the transition to the oil phase. Furthermore, when NPs coexist with surfactants at the interface, the desorption energy is lower than that observed when only NPs occupy the interface, but higher than when only surfactants are present. This indicates a complex interplay of interactions at the interface, affecting the energy required for NP absorption/desorption into the interface of two immiscible fluids.

8.2 Suggestions for Future Research

Expanding on the methodology and discoveries of this thesis, several areas for future research can be developed:

- Effect of hydrodynamic dissipations on various aspects of NP behavior, including their motion, stability, and interactions with other particles or surfaces.
- Effect of NPs shape and size on the movement of two immiscible fluids when used separately or combined with surfactants.
- Calculate the parameters G' (storage modulus) and G'' (loss modulus) for bulk phase since they are key components in the characterization of viscoelastic materials, including polymer solutions, and complex fluids like colloidal suspensions.
- Apply the many-body Dissipative Particle Dynamics (DPD) to study the behavior of NPs and surfactants. This method required higher-order interactions, enabling a more detailed representation of complex systems, leading to improved accuracy in predicting behaviors of surface-active agents.

Supporting Information

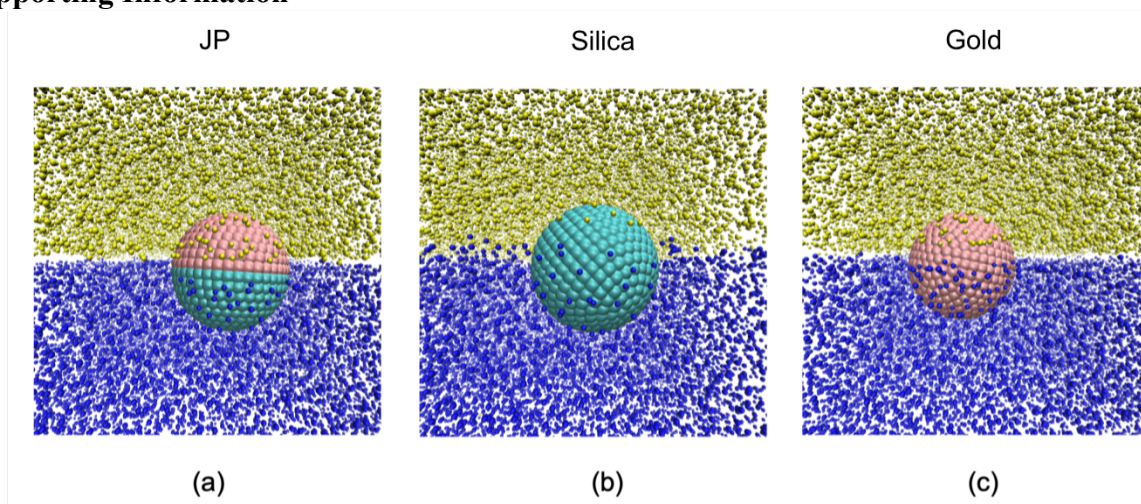


Figure S 1. The single (a) Janus NP, (b) Silica NP, and (c) Gold NP located at the oil-water interface. The color scheme is similar to that used in **Figure 7.1**.

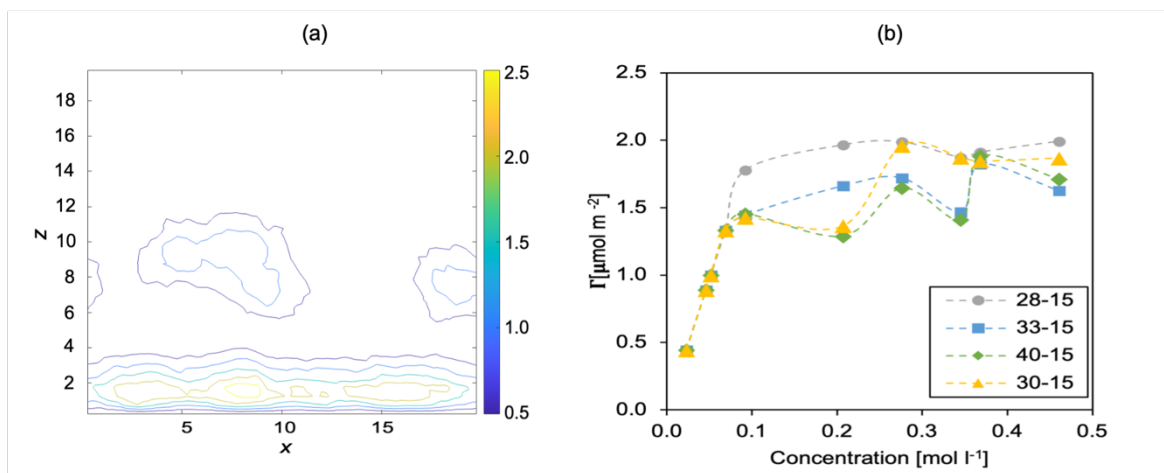


Figure S 2. (a) Contour of surfactant's density adsorb at the silica interface. (b) Adsorption isotherm for C12E8 on the silica surface with different values of interaction parameter of a_{H-P} and a_{T-P} , respectively.

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