

# Studying Surfactants Adsorption on Heterogeneous Substrates

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## Abstract

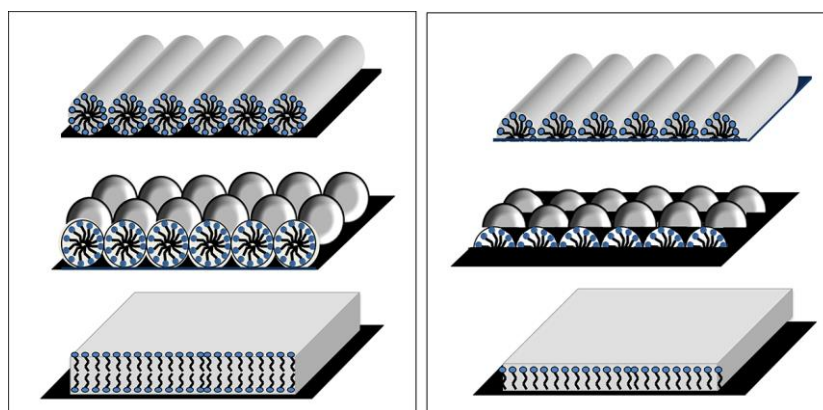
Surface active compounds are continually designed and formulated to advance a large number of modern applications. In the past, the key design principle was the amount of surfactants adsorbed on a surface, because most attention was on changing the substrate wettability. As technology progresses, this is no longer sufficient, and the community is interested in preparing uniform surfactant films on a variety of substrates, typically characterized by surface roughness, both geometric and chemical. Much of our understanding on surfactant films is due to advanced experimental techniques that function best on chemically homogeneous atomically smooth surfaces. Simulations studies have also been conducted on similar substrates, often achieving results in apparent agreement with experimental observations. However, mounting evidence suggests that surface heterogeneity strongly affects the properties of adsorbed surfactant aggregates. To probe using computational approaches systems relevant for experimental investigations, one requires a combination of atomistic and coarse-grained approaches, both implemented using advanced algorithms. We discuss here a few possible approaches that could be used to study surfactant films adsorbed on heterogeneous surfaces, and how they could be combined with experimental investigations. Some recent trends that attempt to predict surfactant performance are also briefly highlighted.

**Keywords:** Water, salt, AFM, surfactant aggregates

## Introduction

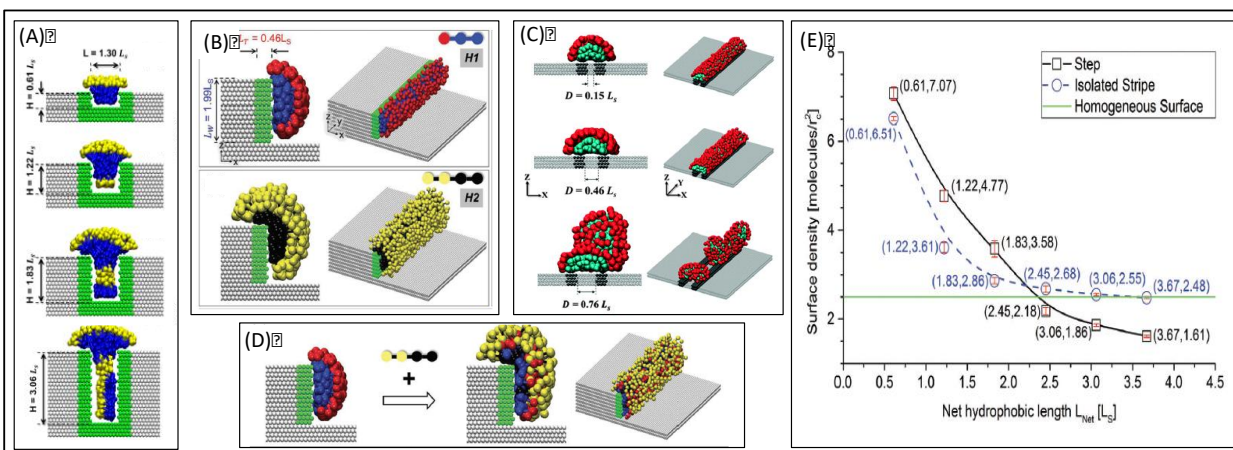
Surfactant adsorption is crucial for many global high-tech industrial challenges: they can provide resistance to corrosion,<sup>1</sup> disperse nanoparticles in aqueous systems,<sup>2</sup> support applications in food-stuff,<sup>3</sup> personal care products, etc. Surfactant design and formulation is supported by fundamental experimental and computational studies conducted, typically, on homogeneous flat substrates. Yet, it is well recognized that surface chemical heterogeneity and atomic-scale roughness are pervasive. Such atomic-scale features impact surfactant performance. It is likely that, by quantifying the effects of surface roughness and chemical heterogeneity on surfactant aggregates, it will be possible to enable breakthroughs in high-tech applications. We argue that simulations and experiments should be synergistically combined to further our understanding of surfactants adsorption. A few approaches are proposed.

In a classic contribution, Zhang and Somasundaran reviewed experimental techniques and results for pure and mixed surfactants adsorption on surfaces.<sup>4</sup> Traditionally, surfactant adsorption was measured via depletion measurements, which cannot quantify the structure of the adsorbed surfactant film. Neutron reflectivity,<sup>5</sup> neutron scattering<sup>6</sup> and ellipsometry<sup>7</sup> can probe the conformation of adsorbed surfactants. Ellipsometry and neutron reflectivity have been combined,<sup>8</sup> showing patchy or fully formed surfactant bilayers. Other techniques include NMR<sup>9</sup> and quartz crystal microbalance with dissipation (QCM-D).<sup>10</sup> Atomic force microscopy (AFM) is often used to assess the morphology of adsorbed surfactant aggregates, showing that, above the critical micelle concentration (CMC), surfactants yield spheres, cylinders and flat layers on different substrates.<sup>11</sup> The expected morphologies are sketched in **Figure 1**.<sup>4</sup> The fundamental question is whether we can predict how the aggregates of **Figure 1** change on surfaces that are heterogeneous. Surface heterogeneity could be a consequence of geometrical features (e.g., surface roughness), a distribution of chemical properties, or both.



**Figure 1.** Aqueous surfactant self-assembled aggregates expected on hydrophilic (left) and hydrophobic (right) flat and chemically homogeneous substrates. Left: cylinders, spheres, and flat bilayers from top to bottom. Right: hemi-cylinders, hemi-spheres, and flat mono-layers. Figure reproduced from Ref. [12].

Mounting evidence suggests that surface roughness affects surfactant aggregates.<sup>12</sup> For example, QCM-D shows that surfactants adsorption on rough surfaces is reduced compared to that on smooth ones.<sup>13</sup> Hamon et al. *probed experimentally surfactant aggregates on structured surfaces*.<sup>14</sup> This group used reactive ion etching to create silica pillars with upper-surface diameter ~15-35 nm. On top of the silica pillars the breakthrough distance changed systematically from the nearest edge, until a plateau was observed at distances ~ 50 nm from the edge, suggesting that the effect of surface roughness on the morphology of surfactant aggregates extends for lengths much longer than that of individual surfactant molecules. If this was the case for most surfactants and surfaces, then our understanding regarding surfactants adsorption on smooth chemically homogeneous substrates would be of little relevance for predicting surfactant aggregates morphology on realistic substrates.



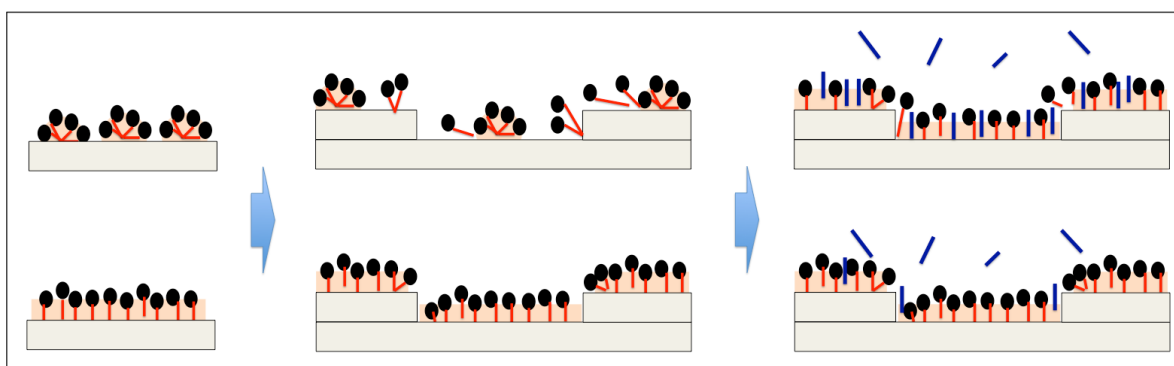
**Figure 2.** Simulation results for coarse-grained non-ionic surfactants on structured surfaces.<sup>20-22</sup> In panel (A), surfactants adsorb on narrow hydrophobic trenches. Blue and yellow are tail- and head-groups, respectively. The simulation results show that the aggregates change dramatically as trench depth increases. In panel (B), surfactants adsorb on edges. Depending on the surfactant morphology, the whole hydrophobic surface (green) can be covered, or *not*. Panel (C) is for surfactants adsorbed on thin hydrophobic stripes approaching each other. Although isolated stripes are too narrow to support a surfactant aggregate, close to each other they can support hemi-cylinders. At intermediate distances, metastable structures form (bottom). Panel (D) shows that mixing surfactants with different head-groups (red and yellow) leads to complete coverage of a hydrophobic step. Panel (E) is an example in which the amount of surfactants adsorbed on steps is compared to that adsorbed on flat surfaces. Depending on the morphology of the surface, the amount of surfactant adsorbed can be larger or smaller than that predicted based on a flat homogeneous surface. Figure adapted from Refs. [20-22].

To understand these experimental observations, one could conduct molecular simulations. Atomistic molecular dynamics (MD) simulations have been conducted for several surfactants on flat surfaces.<sup>2,15-17</sup> Some atomistic simulations have been used to quantify the effect of surface roughness. For example, Sammalkorpi et al.<sup>18</sup> showed the preferential adsorption of surfactants on surface defects found on graphite. However, the time scales accessible to atomistic MD simulations are much shorter than those relevant to experiments, requiring coarse-grained (CG) approaches. Lin et al.<sup>19</sup> demonstrated how to use atomistic simulation results to inform CG approaches, which can yield adsorption isotherms for surfactants on various materials.

The results of selected CG simulations for model non-ionic surfactants are pictorially summarised in **Figure 2**.<sup>20-22</sup> The results suggest that surface heterogeneity has a strong effect up to length scales comparable to the length of one surfactant molecule, which seems to be at odds with recent experiments.<sup>14</sup> Although many approximations are intrinsic to these simulations (e.g., electrostatic interactions are not included), the model surfactants yield flat mono-layers on

a homogeneous flat surface. It is possible that longer-ranged effects manifest when surfactants yield, e.g., hemicylinders.

It should also be recognised that surfactant aggregates can change morphology in the presence of chemical additives. Shi et al. measured hexaethylene glycol monododecyl ether ( $C_{12}E_6$ ) and cetyl trimethyl ammonium bromide (CTAB) adsorption from aqueous solutions containing toluene, phenol, and 1-hexanol.<sup>23</sup> In the case of CTAB, which yields adsorbed cylinders, the co-adsorbents almost doubled the amount adsorbed, suggesting a morphological change to flat layers. In the case of  $C_{12}E_6$ , which yields flat layers by itself, no large differences were observed in the measured adsorbed amount due to co-adsorbents. These results suggest that, perhaps, co-adsorbents could be designed to achieve uniform films on structured substrates. This concept is summarised schematically in **Figure 3**.



**Figure 3.** Conceptual description of the effect of surface heterogeneity, combined with that of chemical additives, on the features of adsorbed surfactant aggregates. Top and bottom represent surfactants yielding hemi-cylinders and flat monolayers, respectively (left panels). Surface roughness is expected to disrupt the surfactant aggregates (middle panels). Black dots, red and blue lines represent surfactant hydrophilic heads, hydrophobic tails and co-adsorbents, respectively. Co-adsorbents could affect the ability of the surfactants to cover the surface (right panels).

In this representation, surfactants yield either hemi-cylinders or mono-layers on flat homogeneous substrates (left). On structured surfaces these surfactants could yield a variety of aggregate morphologies (middle). Many surfactants have been studied extensively:  $C_{12}E_5$  are non-ionic surfactants that form a flat mono-layer on hydrophobic surfaces: surface features such as roughness are expected to have short-range effects. CTAB is a hemi-cylinder – forming ionic surfactant: salt effects will be pronounced, and its adsorption on rough surfaces could be very different compared to that on flat homogeneous surfaces because amplified by changes in the aggregate morphology. Adding co-adsorbents has been shown to change CTAB aggregates,<sup>23</sup> potentially into uniform films. SDS yields hemi-cylinders as CTAB, but it is negatively rather than positively charged. The aerosol OT surfactant AOT (dioctyl sulfosuccinate sodium salt) has two tails. As SDS, it is anionic, but because of the large tail group, it yields flat, molecularly disordered layers. On the contrary, di-decyl dimethyl ammonium chloride (dDAC) is a dual-tailed positively charged surfactant used

commercially as a corrosion inhibitor. This surfactant's behavior could be compared to that of AOT, which also has two tails, but is negatively charged. It is possible that adding co-adsorbents yields uniform surfactant films on heterogeneous substrates (right in **Figure 3**). One should design the chemical additives depending on the surface features and on the surfactants' molecular properties, as it is possible that co-adsorbents (blue in right panel) could be more effective for hemi-cylinders than for mono-layer surfactants.

To relate the surfactant-additive films formed on various substrates to their performance in advanced applications, the fourth step in the conceptual development of **Figure 3** could be the quantification of molecular traffic across the surfactant-laden interface. For example, recent simulation studies show that the molecular packing of surfactants and co-adsorbents at interfaces controls methane transport across the interface,<sup>24</sup> which could affect the formation of gas hydrates in oil and gas pipelines. In what follows we suggest possible protocols to quantify the structure of surfactant aggregates on heterogeneous substrates. We also suggest possible validation protocols. While some of the proposed approaches have not yet been attempted, they are within grasp of modern computational and experimental protocols.

### **Possible Simulation Approaches to Study Surfactants Adsorption**

Given the typical small size of surfactant molecules, the possibility of using molecular simulations to understand, predict and ultimately control surfactants adsorption is attractive. However, any simulation faces three challenges: (1) **Physical models** – the tradeoff between computer power and temporal resolution requires a choice of model, atomistic or coarse-grained (CG). To study surfactant adsorption on heterogeneous substrates, consistent models will have to be implemented for solvent, surfactants, chemical additives, as well as solid substrates. (2) **Time scales** – it is not uncommon to use weeks of computer time to obtain  $\mu$ s-long simulations. Studying surfactants assemblies is affected by the time scales accessible to the simulations. Paredes et al.<sup>25</sup> showed that to predict the interfacial tension for the water-tetradecane interface in the presence of sodium hexadecane benzene sulfonate surfactants, it is necessary to conduct simulations for several  $\mu$ s. This length scale far exceeds that of most MD simulation studies reported to quantify the properties of surfactant aggregates, including those from our group. (3) **Validation** – It is always good practice to validate simulation results against available experimental data. One strategy is to adjust simulation parameters until selected experimental observations are reproduced. When doing so, it should be remembered that the force fields may not be transferable to predicting properties different than those used to derive the force fields in the first place.

In what follows a few suggestions are proposed to address the three challenges:

**Physical Models.** It is expected that surfactants simulations should be conducted in aqueous systems. Although the scientific community has investigated water for a long time, no single atomistic model captures all its properties (phase transitions, structure, transport).<sup>26</sup> To study surfactants, it is important that the models reproduce interfacial tension, and capture salt-specific effects, because salts affect density, surface tension, solubility, diffusion, adsorption, etc.

Unfortunately, the water model of choice is not easily identifiable. For example, Pethes simulated density, dielectric constant and self-diffusion for aqueous LiCl using three popular models for water: the single point charge extended (SPC/E), the transferable intermolecular potential 4 points (TIP4P), and the TIP4P specifically derived for Ewald summations (TIP4P-Ew).<sup>27</sup> None of the tested models satisfactorily predicted all quantities. However, because the TIP4P-Ew water model replicates water's dielectric constant,<sup>28</sup> and parameters for Na and Cl ions are available,<sup>29</sup> perhaps, it could simulate aqueous surfactants, provided it is able to accurately simulate brines.

Coarse-grained (CG) simulations can access larger system sizes and longer simulation times, at the expense of atomistic details and sometimes yielding artificial dynamics. For a review on CG models of water, we refer to Hadley and McCabe.<sup>30</sup> Douglas and co-workers recently developed a minimal CG explicit model in which water-ion dispersion interactions are tuned to reproduce the ion solvation energy.<sup>31</sup> The model semi-quantitatively reproduces ion-specific properties, including density, viscosity, compressibility, diffusion and surface tension, yielding results consistent with experiments. Perhaps this model could become useful in describing aqueous surfactants, once the needed parameters (e.g., those between surfactants and water) are derived.

Once the water model is chosen, one has to derive the models for surfactants, surfaces, and chemical additives. Generic CG force fields have been implemented to describe, e.g., self-assembly.<sup>32</sup> These approaches are helpful in discovering primary driving forces. Several approaches attempt to maintain consistency between CG simulations and either experimental data or atomistic models. In thermodynamics-based approaches, CG parameters are obtained from reference data, e.g., surface tension and partition coefficients.<sup>33</sup> Khedr and Striolo recently demonstrated a systematic approach to derive CG parameters for oil-water systems containing surfactants. Starting from experimental Flory-Huggins data, they obtained parameters that yield realistic values for the water-benzene interfacial tension as well as CMC, size and shape of C<sub>12</sub>E<sub>6</sub> surfactants micelles.<sup>34</sup> In structure-based approaches, the CG parameters are adjusted until selected structural properties are reproduced, e.g., structure function,<sup>35</sup> mean forces,<sup>36</sup> or relative entropy.<sup>37</sup> The CG parameters could be adjusted iteratively, in an approach known as Iterative Boltzmann Inversion.<sup>38</sup>

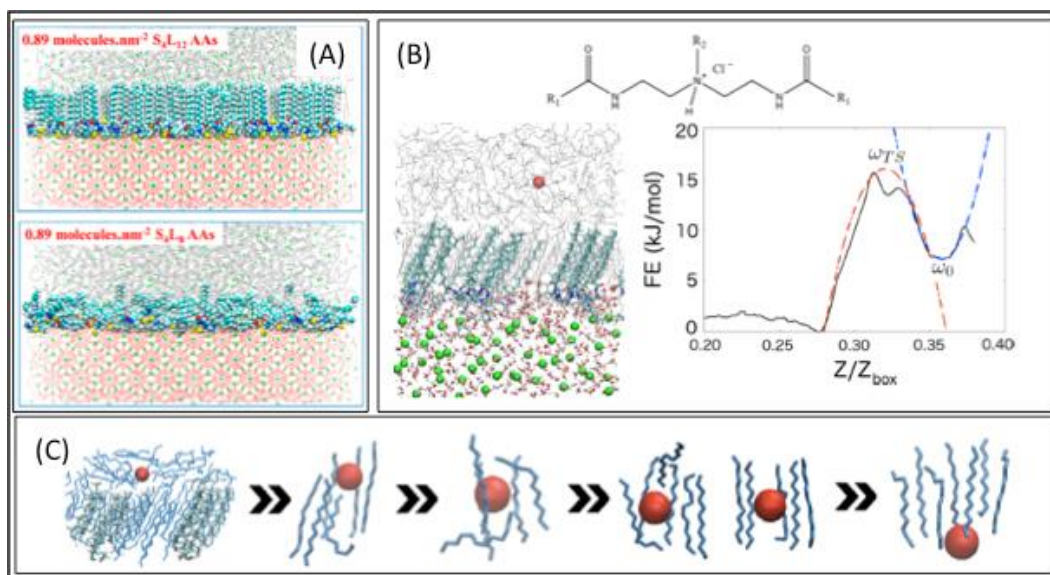
**Time Scales.** The time scale accessible to simulations strongly depends on the choice of resolution. For example, atomistic simulations can sample surfactant systems for a few hundreds of nanoseconds within state-of-the-art supercomputing systems. To access the time scales typical of surfactants exchange between different micelles (i.e., microseconds), one requires CG approaches. Algorithms have been proposed to switch between different levels of resolution within a single simulation. One such approach is the Adaptive Resolution Scheme (AdResS), which implements a force-interpolation scheme across an interfacial region between atomistic and CG areas.<sup>39</sup> AdResS has been shown to satisfactorily reproduce atomistic structural and dynamical properties for several systems, including oligonucleotides.<sup>40</sup> By implementing AdResS, it might be possible to describe surfactant aggregates at atomistic resolution, while supernatant and other compounds could be described at CG resolution.

When one is interested in sampling the equilibrium states of a complex system without observing the natural progression from one equilibrated state to the next, enhanced-sampling algorithms might be attractive. One such algorithm widely used is umbrella sampling.<sup>41</sup> This approach is useful when the free energy depends on one collective variable (e.g., the distance between the center of mass of two surfactant micelles). An alternative enhanced sampling approach is metadynamics.<sup>42</sup> In this approach, the free energy landscape is represented as a sum of Gaussians, generated as the simulation progresses. Recent developments allow one to extract dynamical properties from metadynamics results.<sup>43</sup> When multi-dimensional collective variables are needed to properly explore the free energy landscape, such as is expected for surfactants adsorption on heterogeneous surfaces, metadynamics could become inefficient. Several alternatives have been proposed. Gil-Ley and Bussi,<sup>44</sup> for example, proposed concurrent metadynamics simulations integrated in replica-exchange approaches, while Tribello et al.<sup>45</sup> proposed to reduce the problem dimensionality using 'sketch-maps'. To speed up the exploration of complex free-energy landscapes, Roux and co-workers recently proposed a hybrid propagator algorithm that sequentially considers:<sup>46</sup> (i) a system simulated via standard MD; (ii) a 'boosting' phase described by a time-dependent Hamiltonian; (iii) a Monte Carlo Metropolis criterion to accept or reject the configuration resulting from step (ii). This algorithm might be suitable for investigating surfactants adsorption on heterogeneous substrates, as in stage (ii) of the approach one could implement ad hoc biased Hamiltonians that allow the systems investigated to escape from metastable states. Several approaches are certainly feasible, and one will have to identify the most promising one for the specific system of interest.

**Validation.** Once the simulations are conducted, it is essential to validate the results. At present, indirect validation approaches are prevalent, because of the difficulty in observing surfactant aggregates on structured surfaces. As experimental methods improve, direct validation will become possible. When this will be the case, one will have to select the surfactants. Some surfactants and the structures of their self-assembled films are discussed in connection with **Figure 3**. Once the surfactants are chosen, one will have to systematically study adsorbed aggregates on heterogeneous substrates. Structured surfaces whose features changed systematically from ~10 nm to ~0.1 $\mu$ m are required. Such materials can be prepared using nanoimprint lithography, following Hamon et al.,<sup>14</sup> as well as block copolymer templating, an approach that allows to generate structures with 5-100 nm features.<sup>47</sup> In the latter approach, co-assembly using surfactants as 'structure-directing agents' can yield porous materials with pores of size 1-5 nm. Larger pores (5-30 nm and larger) can be obtained using block copolymers. These materials could be used as a QCM-D or ellipsometer sensors to measure quantitatively the amount of surfactant adsorption on heterogeneous substrates.

**Performance prediction.** Once the structure of the interfacial surfactants' films formed has been predicted, and possibly confirmed on various substrates, one could be interested in correlating it with the surfactant performance in specific applications. While in some applications surfactants change the substrate wettability, in others they modulate the effective interaction between surfaces,<sup>2</sup> the molecular traffic at the interface, etc. Sicard et al.<sup>24</sup> recently quantified molecular traffic at interfaces using simulations. The application of interest was the prevention of hydrate formation in

oil and gas pipelines. Specifically, the industry has used surfactants, known as anti-agglomerants, to permit the formation of small hydrate particles, but to prevent their agglomeration. The surfactants are expected to reduce the attraction between different hydrate particles. Bui et al.<sup>48,49</sup> recently suggested that these surfactants could also delay the diffusion of methane to the aqueous phase within which hydrate particles grow. Sicard et al.<sup>24</sup> first implemented metadynamics to identify possible transport pathways for methane across the interfacial film, and then umbrella sampling to extract free energy profiles along such pathways. The transition state theory was then invoked to extract time constants representative of methane diffusion. A pictorial summary of the approach is provided in **Figure 4**. It is also possible to directly extract these time constants by implementing methadynamics.<sup>43</sup> Sicard et al.<sup>24</sup> showed that the two approaches yield similar results. The simulation protocol just summarized allows one to understand the molecular mechanisms responsible for molecular traffic, with the promise that innovative surfactants or additives could perhaps be designed to enhance performance.



**Figure 4.** Atomistic simulations for surfactants used to manage gas hydrates in pipelines.<sup>48</sup> Panel (A) compares two surfactant films at hydrate-hydrocarbon interfaces: the ordered film (top) yields good performance, as opposed to the disordered one (bottom). Panel (B) shows the chemical structure of the surfactants (top), a simulation set-up (left), and a typical free energy profile experienced by one methane molecule diffusing across the interfacial film (right).<sup>24</sup> Panel (C) highlights how hydrocarbon molecules act as gate-keepers to control methane diffusion across the interfacial film; understanding this mechanism could lead to new surfactants and formulations for advanced applications. Figure reproduced from Refs. [24,48].

## Conclusions

Surfactants adsorption at interfaces is widely used in modern advanced applications. However, our ability to predict the structure of adsorbed surfactant films is based on studies performed for model systems on well characterised,



often homogeneous surfaces. A few cases in which experiments and simulations have identified differences in surfactants behaviour due to surface heterogeneity have been summarised here. Because it is widely known that surface heterogeneities strongly affect the performance of surfactant formulations, it is argued that the community should carefully characterize the adsorption of surfactants, and that of their formulations on structured substrates. A few possible methods have been overviewed, with the possibility of employing computational approaches to design formulations that overcome current technological barriers. It is recommended to use molecular simulations, at various length scales, in conjunction with experiments. However, it is our opinion that computational modelling and simulations are mature enough to begin proposing guidelines for improving the performance of surfactant formulations.

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**Conflicts of interests.** The Author declares no conflicts of interests.

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