# LANGMUIR



pubs.acs.org/Langmui

# Surfactant Assemblies on Selected Nanostructured Surfaces: Evidence, Driving Forces, and Applications

# Alberto Striolo\*

Department of Chemical Engineering University College London, London, WC1E 7JE United Kingdom

# Brian Patrick Grady

School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, Oklahoma 73019, United States

ABSTRACT: Surfactant adsorption at solid-liquid interfaces is critical for a number of applications of vast industrial interest and can also be used to seed surface-modification processes. Many of the surfaces of interest are nanostructured, as they might present surface roughness at the molecular scale, chemical heterogeneity, as well as a combination of both



surface roughness and chemical heterogeneity. These effects provide lateral confinement on the surfactant aggregates. It is of interest to quantify how much surfactant adsorbs on such nanostructured surfaces and how the surfactant aggregates vary as the degree of lateral confinement changes. This review focuses on experimental evidence on selected substrates, including gold- and carbon-based substrates, suggesting that lateral confinement can have pronounced effects both on the amount adsorbed and on the morphology of the aggregates as well as on a systematic study, via diverse simulation approaches, on the effect of lateral confinement on the structure of the surfactant aggregates. Atomistic and coarse-grained simulations conducted for surfactants on graphene sheets and carbon nanotubes are reviewed, as well as coarse-grained simulations for surfactant adsorption on nanostructured surfaces. Finally, we suggest a few possible extensions of these studies that could positively impact a few practical applications. In particular, the simultaneous effect of lateral confinement and of the coadsorption of molecular compounds within the surface aggregates is expected to yield interesting fundamental results with long-lasting consequences in applications ranging from drug delivery to the design of advanced materials.

# ■ INTRODUCTION

The use of surfactants is widespread in modern technology, and the literature reflects the corresponding wide interest from both fundamental and applied perspectives. The fundamentals of surfactant and colloidal sciences have been summarized clearly and concisely in several monographs,<sup>1-3</sup> which became the cornerstones of educational programs. Current research focuses on diverse aspects of surfactant science, from the synthesis of bespoke surfactants with tailored properties (e.g., gemini, polymerizable, and biodegradable surfactants) to their use as platforms to manufacture advanced materials (e.g., coatings and porous and nanostructured materials) and from toxicological studies and the production of biosurfactants<sup>4,5</sup> to pioneering their use in applications such as environmental remediation and drug delivery. A few reviews on these various research fields relevant to the subject of this article are briefly summarized below.

Surfactants adsorb at a wide variety of interfaces: solidliquid, liquid-liquid, and liquid-gas. The ability of surfactants to yield a compact dense layer at the air-water or liquid-liquid interface is responsible for lowering the interfacial tension. Czajka et al.6 reviewed the performance of three classes of surfactants (those based on hydrocarbons, fluorocarbons, and silicones). This review yields structure-function relationships that could be extremely valuable for the design of novel

surfactants effective at reducing interfacial tension. In addition, the review discusses what makes a surfactant environmentally friendly, which is generally described as a surfactant that degrades quickly after use. The present article is concerned with the solid-liquid interface, where surfactants adsorb and change the surface energy of the solid.

Surfactants are used to stabilize emulsions, sometimes in the presence of particles. Maestro et al.' reviewed particles at interfaces and how surfactants could affect the properties of such interfaces. The discussion included a number of observations, ranging from the ability of particle-surfactant systems to reduce the interfacial tension to phenomena responsible for packing at an interface. The effect of both particles and surfactants on the rheological properties of interfaces and on the ability of such systems to stabilize emulsions was discussed. In complex systems such as emulsions containing particles, surfactants could adsorb at liquid-liquid as well as at solid-liquid interfaces that are not homogeneously flat.

The largest current application for surfactants is in cleaning products, which in turn can be divided into many categories



Received: March 6, 2017 **Revised:** May 1, 2017 Published: May 18, 2017



Figure 1. Schematic of typical aggregates formed on solid surfaces exposed to aqueous surfactant systems. In the left panel are the structures observed on a hydrophilic surface (from top to bottom cylinders, spheres, and bilayers). In the right panel, the corresponding structures observed on a hydrophobic surface are shown (from top to bottom hemicylinders, hemispheres, and monolayers). The hydrophilic surfactant headgroups are shown as blue spheres in this schematic, and the hydrophobic tailgroups are shown as black lines.

including laundry detergents, hard-surface cleaners, dishwashing (both hand and automatic), and personal care (shampoos, hand soaps, etc.). An application that is growing substantially is the use of surfactants in subsurface operations. Camarillo et al.<sup>8</sup> reviewed the available information for chemicals used in hydraulic fracturing operations in California and discussed possible technologies and processes for managing the environmental impact of such operations. It has recently been reported that the use of surfactants in hydraulic fracturing fluids can enhance shale gas production.<sup>9</sup> Mao et al.<sup>10</sup> reviewed the possible use of surfactants in the remediation of contaminated soils, in which case important factors include the critical micelle concentration (CMC) of the surfactants, their adsorption on the soils, their toxicity and biocompatibility, and their ability to displace and remove heavy metals and other contaminants from the soil. Trellu et al.<sup>11</sup> expanded on these observations and also considered the technologies that can be implemented to treat the surfactant-containing fluids used to decontaminate the soils. Indeed, surfactants are more and more useful for tertiary oil recovery (i.e., enhanced oil recovery, EOR). In EOR, surfactants are used predominantly to achieve three goals: increase the capillary number, decrease the interfacial tension, and alter the wettability of various systems. Kamal<sup>12</sup> reviewed surfactants used for EOR, paying particular attention to gemini surfactants, which offer some advantages compared to traditional surfactants, because they offer low CMCs, good water solubility, and unusual micellar structure and aggregate behavior. The primary limitation of the use of surfactants in subsurface operations is the tendency of surfactants to adsorb on a rock surface, which could prevent the products from reaching the interface where the surfactant is intended to operate. Therefore, it is important to understand how surfactants adsorb on rock surfaces, which can be heterogeneous and certainly differ from atomically smooth homogeneous surfaces such as those on which many controlled academic experiments tend to be conducted.

Understanding adsorption on irregular surfaces is also important for the aforementioned laundry detergent applications, where particle removal is a critical function for a surfactant. Furthermore, surfactants are often used, in the form of corrosion inhibitors, to prevent, limit, and delay metal corrosion. Indeed, Malik et al.<sup>13</sup> discussed the effect of parameters such as temperature, surfactant concentration, and mode of adsorption on the ability of surfactants to inhibit metal corrosion.

Surfactants can also be used in biological applications. For example, they can be used to prevent protein adsorption on surfaces as well as to modulate protein-protein interactions, but their efficacy depends on the mode of action and on their molecular features. Lee et al.<sup>14</sup> reviewed the role of surfactants in the prevention of the loss of activity of protein-based pharmaceuticals. Surfactants can also be used to immobilize enzymes on solid substrates and/or to disperse such enzymes in organic solvents. Adlercreutz reviewed several techniques that could be used to immobilize lipases in organic media, sometimes even enhancing their biological activity.<sup>15</sup> The resultant complexes show different properties depending on the surfactants used and on the procedures followed to prepare them. To put these applications in the context of the present article, it is useful to point out that the enzyme surface is not uniform, from either a chemical or morphological point of view. Thus, it is expected that the morphology of the adsorbed surfactant aggregates will depend on the features of the complex enzyme surface, on the presence of solvents, cosolvents, and/or other surfactants, and on the amount of surfactant adsorbed. These are the general aspects explored by this focused review. Surfactants can also be used to decorate nanoparticles, in which case surface-active agents are used to impart specific functions to the nanostructures, thus facilitating their use as biomarkers, catalysts, and therapeutics. Heinz et al.<sup>16</sup> recently reviewed such applications, with emphasis on the design principles for surfactants to optimize their performance.

A surfactant dissolved in water adsorbs to a molecularly smooth solid surface in one of six general morphologies as determined via atomic force microscopy (AFM). On a hydrophilic surface, spheres, cylinders, and flat bilayers have been imaged, whereas on a hydrophobic surface, hemispheres, hemicylinders, and flat monolayers have been found. A schematic for these morphologies is provided in Figure 1. Zhang and Somasundaran reviewed techniques used to study the adsorption on a solid surface of pure and mixed surfactant systems, including anionic–cationic, anionic–nonionic, nonionic–nonionic, and nonionic–cationic.<sup>17</sup> Direct AFM imaging at surfactant concentrations above half the CMC suggests that adsorbed aggregates can undergo transitions from sphere to cylinders to flat bilayers, especially with added salt.<sup>18–20</sup> Some data from techniques including neutron scattering, neutron

reflectivity, and ellipsometry suggest that the same surfactants yield patchy or fully covered bilayers,<sup>21-24</sup> although Zhang and Somasundaran discuss a few exceptions to these observations. Schonhoff reviewed a number of NMR-based approaches able to probe adsorbed surfactant aggregates.<sup>25</sup> Although the initial studies were focused on flat solid surfaces, more recent studies focus on surfactant adsorption on colloidal surfaces. Although the colloidal surfaces are curved, on the length scale of an individual surfactant molecule such surfaces appear flat for the most part. Such colloidal systems include hollow colloids and surfactant structures within which smaller compounds (e.g., molecular drugs) adsorb. NMR requires systems with large interfaces to enhance the signal-to-noise ratio. Another powerful technique is the combination of neutron reflectivity and of small-angle neutron scattering. Penfold et al.<sup>26</sup> recently reviewed how these techniques, sometimes combined with dynamic light scattering and microscopy, have been used to study surfactant adsorption and aggregate structure. These authors considered biosurfactants such as rhamnolipids and sophorolipids as well as some surfactants obtained from surfactin. Neutron reflectivity can probe the surfactant adsorbed amounts on an interface and quantify the distribution of surfactant fragments (e.g., head vs tail groups) in the direction perpendicular to the interface as well as the composition of the adsorbed films as a function of the bulk solution composition. Insights from such studies allow us to understand how to better tune the formulation of a surfactant system to control the properties of the adsorbed film. Small-angle neutron scattering and light scattering can probe the structure of surfactant aggregates, including micelles and vesicles. On the basis of results from such techniques, Penfold et al.<sup>26</sup> suggest that nature has fine-tuned the composition of surfactant systems to optimize different biological applications. Perhaps lessons can be learned from these observations to enhance applications.

Molecular simulations have also been used to investigate the properties of surfactant assemblies at various solid–liquid interfaces.<sup>27–30</sup> For example, Tummala et al.<sup>31</sup> simulated sodium dodecyl sulfate (SDS) and hexaethylene glycol monododecyl ether (C12E6) separately at the silica-water interface. The results revealed the importance of the distribution of charged groups on the solid surface, which can determine the features of the adsorbed surfactant aggregates. Shi et al.<sup>32</sup> simulated the same two surfactants at the watervacuum interface, changing the surfactant density. The results were analyzed in terms of the orientation of the surfactant tails with respect to the interface, morphology of the aggregates, and surfactant mobility. The role of the headgroups was clearly highlighted. The results from these simulations are in general agreement with experimental observations. However, the time and length scales accessible using modern all-atom molecular simulations are at most on the order of hundreds of nanoseconds, whereas in some cases hours or even longer times are required to reach proper equilibration in experimental studies. Furthermore, the reliability of simulation studies depends on the availability of accurate force fields and on the implementation of appropriate algorithms. Much emphasis is currently on developing adequate approaches to interrogating systems of technological importance using coarse-grained and multiscale approaches as well as in developing adequate force fields. Although the promising outcomes of some recent efforts are discussed herein, much needs to be done to achieve a synergistic use of computational studies within the important field of surfactant self-assembly. Heinz and Ramezani-Dakhel

recently provided a comprehensive overview of the state of the art in simulations as applied to investigate interfacial systems.<sup>33</sup>

## EXPERIMENTAL EVIDENCE OF THE EFFECTS OF LATERAL CONFINEMENT

This focused review considers surfactant adsorption on nanostructured surfaces. Nanostructured surfaces can refer to morphological variations, surface chemical variations, or both types of variations simultaneously occurring. This review is concerned with variations in the lateral direction, but we should briefly describe work that has been done with nanostructure in the direction perpendicular to the surface (i.e., frontal).

Both theoretical and experimental results have been reported on the effect of frontal confinement for surfactant systems. Experiments are typically carried out using the surface force apparatus, where the force is measured precisely as a function of the distance between two approaching (or receding) molecularly smooth surfaces, usually mica.<sup>34–39</sup> Self-consistent-field theoretical calculations have been reported for nonionic surfactants under frontal confinement.<sup>40</sup> The results showed that, at close enough separation distances (i.e., the removal point), one of the two adsorbed layers desorbs. At distances slightly larger than the removal point, the amount of surfactant adsorbed on one surface is larger and that adsorbed on the other smaller than that observed on freestanding surfaces. Thus, frontal confinement affects surfactant adsorption but only at wall–wall separations comparable to the surfactant length.

The fundamental question addressed by the studies reviewed here is the following: do the aggregates shown in Figure 1 on a flat homogeneous surface change, and if so how in the presence of lateral confinement? A few experimental observations strongly suggest that when surfaces are not uniform, perhaps because of geometric features comparable in size to several surfactant molecules, the adsorbed self-assembled surfactant aggregates differ compared to those reported (e.g., via AFM measurements) on homogeneous, atomically flat surfaces. An indirect observation of this phenomenon was provided by Marquez et al.,<sup>41</sup> who adsorbed surfactants on a surface to seed the so-called "template assisted admicellar polymerization".<sup>42</sup> Admicellar polymerization refers to a process by which monomers segregate within surfactant self-assembled aggregates. The monomers are then polymerized to obtain the final permanent polymeric structures. Harwell, O'Rear, and coworkers introduced the process<sup>43</sup> that is now being applied, for example, to change the wettability of textiles<sup>44</sup> and for the synthesis of nanostructures.<sup>45</sup> Marquez et al.<sup>41,42</sup> used latex spherical particles to template a solid substrate (e.g., graphite) and then applied admicellar polymerization. The final polymeric structures reported were described as "nanopillars, nanorings, honeycombs and honeytubes" based on atomic force microscopy (AFM) observations. Parameters of importance for determining the final structures included the surfactant chain length, the surfactant concentration, the monomer concentration, the polymerization time, the temperature, and the size of the latex particles. In general, the morphology of the resultant polymeric structures suggests that polymerization took place only far from the latex spheres, suggesting that the presence of the latex spheres affects the morphology of the surfactant self-assembled aggregates at distances much larger than the length of a surfactant molecule; similar work with adsorbed polymers indicates that the latex spheres do not inhibit adsorption far from the spheres.<sup>46</sup> Unfortunately, direct

#### Langmuir

characterization of the surfactant aggregates could not be attempted. To better understand the molecular mechanisms responsible for the experimental observations such as those reported by Marquez et al., one would require a quantification of the surfactant aggregates formed at solid—liquid interfaces

form of confinement for the surfactant aggregates. Irregular lateral confinement (e.g., surface roughness) has been shown to affect surfactant adsorption in a number of studies. Direct evidence of the effect of lateral confinement on the morphology of surfactant self-assembled aggregates was reported by Schniepp et al.<sup>47,48</sup> These authors improved the resolution of the AFM so that they could directly image the structure of surfactant self-assemblies on rough gold substrates. They demonstrated that the structures are quite different compared to those observed on flat substrates and that whereas on perfectly smooth solid crystals the orientational order of the adsorbed surfactant aggregates is influenced by the crystal symmetry, on rough surface features. Some of these results are reproduced in Figure 2.

when the solid substrate is not flat but instead provides some



**Figure 2.** Experimental AFM data for gold surfaces in contact with SDS solutions at 10 mM concentration. (a) SDS yields hemicylinders oriented parallel to one of the three symmetric directions (shown by the yellow arrows) when large flat areas are available; the orientation changes at the topographic steps surrounding these areas, as highlighted by the blue arrows and ellipsoids. (c) Enlargement of the image in panel b. (b and c) When the surfaces are rougher, orientational order for the assembled aggregates is possible only on flat areas, and disordered structures are also observed (blue circles in panel c). (d) When the surfaces have a smaller grain size, the adsorbed micelles do not show preferred orientations. Reprinted with permission from ref 47. Copyright (2008) American Chemical Society.

The procedure of Marquez et al.<sup>41,42</sup> necessarily includes components other than the surfactants. In particular, monomers need to be present to promote the polymerization reaction. It is therefore possible that the structure of the selfassembled aggregates is affected not only by confinement effects but also by the adsorption of the monomers within the surfactant aggregates. It is possible that the two effects, one due to lateral confinement and the other due to coadsorbents, are synergistic. To probe, indirectly, the effect of monomers on the structure of the surface aggregates, one could use the quartz crystal microbalance, especially when the instrument is equipped with the ability to monitor the dissipation of the interfacial film (QCM-D).

Grady, Striolo, and their co-workers used the QCM-D to address two issues: (a) the possible coadsorption of various molecular compounds within the self-assembled aggregates on a surface<sup>49</sup> and (b) the effect of surface roughness on the measured adsorption.<sup>50,51</sup> Shi et al.<sup>49</sup> measured the adsorption of C12E6 and CTAB from aqueous solutions containing controlled amounts of toluene, phenol, and 1-hexanol. The data are interpreted by assuming that CTAB yields a patchy cylindrical structure whereas C12E6 yields a monolayer on the support considered. The coadsorbents have the effect of almost doubling the amount adsorbed in the case of CTAB, in which case the aggregates become more rigid in the presence of the coadsorbent. These data were interpreted with the possible morphological change from cylindrical to flat monolayer. In the case of C12E6, small changes were observed both in the amount adsorbed and in the rigidity of the adsorbed aggregates, suggesting that the flat adsorbed films did not change their morphology in the presence of the coadsorbents. Regrettably, the QCM-D data cannot provide information regarding the composition of the adsorbed aggregates nor direct evidence of their morphology.

Regarding the effect of surface roughness on the adsorbed amount, Wu et al.51 used the QCM-D to measure CTAB adsorption on surfaces with root-mean-square roughnesses of 2.3, 3.1, and 5.8 nm as measured by AFM. The data collected at 25 °C showed that, for bulk concentrations below 0.8 times the CMC or above 1.2 times the CMC, the adsorbed amount normalized by the estimated actual surface area (which increases as the roughness increases) decreases as the surface roughness increases. These data suggest that the surface roughness prevents the formation of a completely homogeneous surfactant film, suggesting that surfactant coverage is patchy when the surface roughness is significant. On the contrary, when the bulk CTAB concentration is around the CMC, the amount adsorbed increases with the surface roughness. The increased surfactant adsorption around the CMC is often related to the presence of impurities in the system.<sup>52</sup> The results also showed that the dissipation increased with surface roughness in this region, suggesting the possibility that flexible, possibly metastable surfactant aggregates were promoted by significant surface roughness. Hsieh et al.5 reported additional evidence of the effect of surface heterogeneity on adsorption. This group used conductometric titration to measure aqueous SDS adsorption on functionalized graphene sheets. The results suggest "the presence of regions on functionalized graphene sheets on which SDS adsorption does not occur". This appears to be an effect of lateral confinement, provided by the limited size of the graphene sheets, by the functional groups present on the graphene surface, by undulations of the graphene surface, or by a combination of these factors. To relate these fundamental observations to applications, Hsieh et al.<sup>54</sup> reported that the stability of aqueous dispersions of functionalized graphene sheets strongly depends on the concentration of SDS, with stable dispersions obtained when the SDS is able to form a



Figure 3. (Top) Atomistic simulation snapshots for aqueous SDS surfactants on graphene sheets and graphene nanoribbons of various sizes. The green spheres represent either  $CH_2$  or  $CH_3$  groups in the surfactant tails, the red spheres represent oxygen atoms, and the yellow spheres represent sulfur. Water molecules are not shown for clarity. Adapted with permission from ref 55. Copyright (2010) Royal Society of Chemistry. (Bottom) Time evolution of a dissipative particle dynamics simulation for a system containing coarse-grained surfactants and one graphene sheet. The red spheres represent the surfactant headgroups, and the blue spheres represent the tailgroups. (a) Initial configuration in which the surfactants are randomly dispersed throughout the box. Some micelles start forming at 0.4 ns (b) and grow, whereas adsorption starts (c). As adsorption proceeds, the amount of surfactants available in solution decreases. After 70.5 ns (f), all surfactants are adsorbed and yield an aggregate whose morphology is reminiscent of that obtained from atomistic simulations.<sup>55</sup> Adapted with permission from ref 72. Copyright (2012) Royal Society of Chemistry.

monolayer on the functionalized graphene sheet but is not large enough to form adsorbed micelles.

The remainder of this article considers a systematic investigation regarding how lateral confinement affects the properties of adsorbed surfactant aggregates. Building on the experimental observations from Aksay and co-workers, 47,48,53,54 the discussion starts from simulations of the adsorption of surfactants on graphene sheets. These simulations are typically conducted at atomistic resolution. For completeness, we briefly discuss the limitations of atomistic models and a few current strategies to generate mesoscopic approaches suitable for studying surfactant systems. We then discuss surfactant adsorption on carbon nanotubes, for which the circumference of the nanotubes, which can be changed systematically, provides lateral confinement. Finally, the discussion focuses on an attempt to systematically investigate surfactant adsorption on structured surfaces, on which lateral confinement is provided by trenches, edges, and chemical heterogeneity. These systems are not yet comparable to those considered by Marquez et al.,<sup>41,42</sup> but extensions of these initial studies could provide the needed link. These extensions are discussed in the form of possible future directions, where some potential applications of these fundamental studies are also proposed.

### SIMULATION EVIDENCE OF THE EFFECTS OF LATERAL CONFINEMENT

Surfactant Adsorption on Graphene Nanosheets. To study the features of surfactant aggregates on graphene sheets, one could employ molecular simulations because they allow us to quantify, sometimes at the atomistic level, the properties of the systems under investigation. Within the scope of this focused review, the goal of such investigations is to quantify how the aggregates change compared to those obtained on flat, homogeneous substrates. Along these lines, Tummala et al.55 simulated SDS on graphene nanosheets and nanoribbons. The results were compared to those available for the same surfactant on a graphite substrate under similar conditions (temperature, pressure, salt concentration, and surfactant surface density). Circular graphene nanosheets of size 2, 5, and 10 nm were considered, as were graphene nanoribbons infinite in one direction, and with a width of 2 or 5 nm along the other direction. The substrates were maintained rigid. The simulations on a homogeneous graphitic substrate, 56,57 on which no lateral confinement is present, show that SDS yields hemicylindrical micelles, with morphology in quantitative agreement with AFM experiments.<sup>58</sup> By comparison, the results obtained on graphene nanosheets showed that the edge of the graphene sheets effectively acts as a confining agent (Figure 3). As a consequence, SDS can yield multiple adsorbed layers, hemispheres, and hemicylinders depending on the size and shape of the graphene support. Many others have studied the properties of surfactant aggregates adsorbed on graphene sheets. Yang et al.<sup>59</sup> recently reviewed a number of such simulation studies as well as calculations conducted to quantify the effect of such surfactants on the stabilization of dispersions containing graphene sheets. As discussed by Yang et al., simulations have so far considered relatively simple systems containing, for example, SDS, sodium dodecyl benzenesulfonate (SDBS), and sodium cholate (SC). The results show in general that the structure of the surfactant aggregates depends on the size of the graphene sheet.

Molecular simulations conducted at atomistic resolution are currently limited by the availability of adequate computing resources. Note, for example, that Tummala et al.55 were limited to consider graphene supports of size 10 nm at most, which is much smaller than the size of graphene sheets used in most experimental applications.<sup>53,54</sup> In addition to the size of the systems that can be simulated, atomistic simulations can probe the systems of interest only for relatively short times, in general not exceeding a few hundred nanoseconds using the most advanced computational resources. (Many simulations in the literature do not reach 100 ns.) These simulation times are much shorter than the typical times required for surfactants to exchange between surface and bulk aggregates, which are on the order of microseconds. As such, one cannot determine the amount of surfactant adsorbed in equilibrium with a bulk system using atomistic simulations. Instead, it is customary to impose a surface density as an initial condition and use the simulation to interrogate the aggregate structure expected at such coverage. Hence, some of the structures predicted by simulations may be metastable, especially if the surfactants are not able to desorb.

Alternative approaches exist, and they include Monte Carlo and coarse-grained simulations. In Monte Carlo simulations, two consecutive configurations representative of a system are not connected by equations of motion but instead require only that the configurations belong to the same ensemble. This allows the exploration of the properties of the equilibrated system, provided truly new configurations can be accepted at a reasonable rate during the study. Coarse-grained simulations allow savings in computational time by reducing the number of details that are explicitly considered. For example, one coarsegrained bead can be representative of several water molecules, whereas in atomistic simulations every atom of each water molecule is explicitly described. Details of either Monte Carlo or coarse-grained simulations are provided elsewhere.<sup>60,61</sup>

To provide a few examples, we refer to Panagiotopoulos and co-workers, who implemented a number of Monte Carlo techniques to determine the CMC of models meant to represent ionic and nonionic surfactants.<sup>62–64</sup> The results show that atomistic models tend to underpredict the CMC of the surfactants they mean to describe. The same group investigated the CMC for coarse-grained models,<sup>65</sup> showing that the corresponding models underpredicted the CMC for zwitterionic surfactants, whereas there is reasonable agreement with experiments for ionic surfactants. Although the models were found to yield a good representation of the size of the micelles, the coarse-grained models in general are not able to describe the temperature dependence of the CMC because they do not describe the solvent structure appropriately.

Limitations of coarse-grained models include the fact that, depending on the parametrization, they might lose a direct atomistic representation of the chosen surfactant system. However, they offer the possibility of simulating reasonably large systems for times exceeding those required for the exchange of surfactants between different aggregates. As such, these models could be considered to be adequate when one is interested in extracting general guidelines and guiding principles regarding the physical behavior of self-associating systems at the expense of atomic-level accuracy.

It is not always clear how to connect atomistic to mesoscale simulations, which indeed is a current challenge within the simulation community. Various approaches have been attempted, each with its own merits. For systems similar to those considered here, Noro et al.<sup>66</sup> proposed procedures for linking atomistic and mesoscale simulations based on thermodynamics arguments. Fan and Striolo<sup>67,68</sup> ensured that observables such as contact angles would be faithfully replicated between atomistic and mesoscale simulations of similar systems. Lane et al.<sup>69</sup> demonstrated that atomistic models can be used to directly calculate forces between silica nanoparticles of size 5 nm in solution, even when the nanoparticles are grafted with poly(ethylene oxide) oligomers; then these massive atomistic simulation results (the authors report that 1 ns of simulation requires 140 h on 1024 Intel Xeon processors) can serve as the basis to derive coarse-grained models to study, for example, the dynamic deformation of ultrasoft colloids exposed to drag.<sup>70</sup> As an example demonstration of the effectiveness of coarse-grained approaches, we refer to Anderson et al.,<sup>71</sup> who simulated triblock copolymers, which have a structure similar to a particular class of surfactants sold under the trade name Pluronic, and showed that under appropriate conditions these models yield micellar structures. These authors report that in their simulations it was possible to observe frequent exchanges of polymer chains between different micelles in the micellar crystal, demonstrating that long time scales can be probed by coarse-grained approaches.

In Figure 3, we provide a comparison between insights that can be achieved using atomistic vs coarse-grained simulations. From the atomistic point of view, we select simulation snapshots from Tummala et al.,55 obtained for SDS on graphene sheets of size 2, 5, and 10 nm and on graphene nanoribbons of size 2 and 5 nm. The surface available for each SDS surfactant was ~0.45–0.48 nm<sup>2</sup>. From the coarse-grained point of view, we refer to Min et al.,<sup>72</sup> who employed dissipative particle dynamics to investigate the adsorption and selfassembly of surfactants, meant to replicate SDS, on graphene sheets. Note the time evolution of the system, which starts from a disordered nonadsorbed state and yields surfactant aggregates on the flexible graphene sheet. The coarse-grained simulations were in agreement with some of the insights provided by atomistic models and in addition allowed Min et al.<sup>72</sup> to sample systems with varying surfactant concentrations.

**Surfactant Adsorption on Carbon Nanotubes.** One application in which both atomistic and coarse-grained models have been implemented relates to the stabilization of carbon nanotubes, CNTs, in aqueous dispersions. Practically, several techniques have been attempted to stabilize these dispersions, including the chemical functionalization of the CNT walls,<sup>73</sup> the design of appropriate solvents,<sup>74</sup> and the use of surface-active agents, including polymers,<sup>75</sup> DNA,<sup>76</sup> and surfactants.<sup>77</sup> Using DNA, it has been possible to differentiate left- and right-handed CNTs.<sup>78</sup> Using surface-active agents has the advantage that the CNTs remain pristine and adsorption is usually easily reversed via dilution; therefore, the intrinsic properties of

#### Langmuir

nanotubes are not compromised by the stabilization step. Within the scope of the present article, we point out that when surfactants adsorb on the external surface of a CNT they are effectively confined laterally because the circumference of the CNT is limited, and the support, which is an atomically smooth rolled over graphene sheet, provides a curved surface on which adsorption occurs. In this case, though, the curvature, in particular for single-walled carbon nanotubes, is comparable to the length of an individual surfactant molecule. The curvature of the support and hence the degree of lateral confinement can be easily changed systematically with the CNT diameter.

Experimental evidence suggests that some surfactants are not effective at stabilizing aqueous CNTs dispersions. Others are effective but not specific, and a few surfactants are found to be effective specifically for stabilizing dispersions containing CNTs of a given diameter.<sup>79–83</sup> This wealth of experimental data is extremely beneficial for allowing us to interrogate and possibly identify the molecular phenomena responsible for the macroscopic differences just summarized. To identify differences between the surfactants, one needs to implement atomistic models, despite their limitations in predicting CMC and in probing system sizes and simulation times that have experimental relevance. As a consequence, a careful choice of system conditions and a systematic investigation of the effect of surfactant surface density are necessary.

Within this philosophical approach, Tummala and Striolo<sup>84</sup> simulated aqueous surfactant SDS on CNTs. The simulations were conducted within the equilibrium molecular dynamics formalism under ambient conditions. SDS is known to be weakly effective at stabilizing aqueous dispersions of CNTs, irrespective of the CNT diameter. To gather insights on the molecular reasons for these observations, the simulations were conducted on (6, 6), (12, 12), and (20, 20) single-walled CNTs at increasing surface density. In all cases, the simulations showed that the SDS yield disordered aggregates, with the exception that at low surfactant concentrations the SDS tailgroups align parallel to the CNT axis to reduce effects due to the curvature of the support. The results contributed to settling a discussion regarding the possible organization of surfactants on CNTs, with some groups expecting the surfactants to yield cylindrical micelles with the surfactants oriented radially from the CNT axis. The simulation results agree with the interpretation of experimental neutron scattering data proposed by Yurekli et al.,85 supportive of disordered aggregates formed on the CNTs. Although the simulation results of Tummala et al.<sup>84</sup> showed that the curvature of the support and the lateral confinement strongly affect the morphology of the self-assembled SDS aggregates (the former especially at low surfactant loadings), it was not yet clear how the structure of the aggregates could be related to the ability of the surfactants to stabilize aqueous CNT dispersions.

One possible way forward was to calculate potential of mean force (PMF) profiles between two CNTs, maintained parallel to each other,<sup>86,87</sup> with the underlying principle being that when the PMF shows a large maximum at intermediate separations, a strong kinetic barrier delays CNT agglomeration. Tummala et al.<sup>88</sup> conducted such calculations for CNTs covered by SDS and FMN. By comparing the features of the PMF profiles, a few guidelines were proposed to stabilize aqueous CNT dispersions: (a) the surfactants should provide long-range repulsions to reduce the likelihood of agglomeration and (b) the surfactants should not be easily removed when two CNTs approach each other. Several molecular dynamics simulations suggest that because of both lateral confinement and curvature, selected surfactants can provide the aforementioned properties specifically for a CNT with a given diameter. For example, Suttipong et al.<sup>89</sup> simulated SDBS on (6, 6), (12, 12), and (20, 20) single-wall CNTs. SDBS is effective at stabilizing aqueous CNT dispersions irrespective of their diameter or chirality. Because commercial SDBS samples typically contain isomeric mixtures, Suttipong et al.<sup>89</sup> considered two SDBS isomers: one only had one linear tailgroup, but the other, referred to as "branched" in the paper, had two short tailgroups. The simulation results suggested that whereas the linear SDBS behaves very similarly to SDS, the branched one shows self-assembled aggregates with features that are strongly dependent on the CNT diameter. Thus, the branched SDBS could be used to selectively isolate narrow CNTs. Unfortunately, this is not observed experimentally. To reconcile the simulations with experimental evidence, mixtures containing both SDBS isomers were simulated.<sup>90</sup> The resultant aggregates show disordered features on all CNTs considered, possibly explaining why these surfactants are equally effective at stabilizing aqueous dispersions of CNTs with diverse diameters.

Additional simulation results also suggest that it is possible to change the properties of the self-assembled SDS aggregates by changing the salts in the dispersion, with a strong dependence on the CNT diameter. These results were in quantitative agreement with experimental observations collected using UV–vis–NIR absorbance spectra.<sup>91</sup> Allen et al.<sup>92</sup> recently reported salt-specific effects for monolayers formed by SDS surfactants. These simulations show that although the arrangement of SDS molecules did not change depending on the counterion, some of the ions lost their hydration structures. Comparing the data obtained on CNTs vs those observed on flat interfaces suggests that the curvature of the support can strongly influence the response of surfactants to counterions, which could be useful to develop advanced sensors.

A number of simulation studies are now available for surfactants on CNTs of different diameters.<sup>93–97</sup> For the scope of the present article, these reports are useful because they clearly show how lateral confinement and the curvature of the support modulate the structure of the self-assembled surfactant aggregates. Direct experimental validation of the simulations is difficult because it requires the ability to differentiate surfactants within the adsorbed aggregates. Shastry et al.98 employed twodimensional diffusion-ordered NMR to assess the adsorption of mixtures containing SDS and SC surfactants on CNTs as well as perturbations in the micellar structures. These experiments were conducted on samples containing single-walled CNTs of similar diameter (~1.3 to 1.4 nm) but different chirality and electronic type (metallic vs semiconductive). The results suggested that when the bulk surfactant composition was 3:2 w/w SDS/SC, the metallic CNTs are essentially covered only by SC, whereas the mixture of the two surfactants covers the semiconducting CNTs. On the contrary, molecular dynamics simulations for SC and SDS surfactant aggregates on CNTs yield similar structures.<sup>84,86,99</sup> Because density-gradient separations such as ultracentrifugation, using different surfactant systems, can sort single-walled CNTs by electronic type,<sup>100</sup> chirality,<sup>101</sup> and diameter,<sup>102</sup> it appears that the force fields need to be improved toward accounting for electronic differences among the CNTs. One possible way forward is the inclusion in the force fields of an explicit description of  $\pi$ interactions and effective polarization effects.<sup>103-107</sup>



**Figure 4.** (Top) Radial density distributions of tailgroups (left), headgroups (middle), and counterions (right) for SDS adsorbed on (6, 6) CNTs. These atomistic simulation results are shown at three surfactants densities on the CNTs in the presence of either Na<sup>+</sup> or Cs<sup>+</sup>. Adapted with permission from ref 91. Copyright (2013) Royal Society of Chemistry. (Middle) Equilibrium coarse-grained simulation structures for surfactant adsorbed on CNTs (the surfactant concentration decreases from left to right); different surfactant molecular structures are considered (e.g., 11T indicates surfactants with 11 beads in their tailgroups). Blue represents tailgroups, and red represents headgroups. Adapted from ref 110. Copyright (2009) John Wiley and Sons. (Bottom) Adsorption isotherms from coarse-grained simulations of SC on (6, 6), (12, 12), and (20, 20) CNTs (left) and the calculated surface electrical potential as a function of surfactant concentration (right). The vertical dashed black lines identify three CNTs, the dashed horizontal white line identifies the SC bulk CMC, and the bold continuous white line identifies the conditions under which the electrical potential is maximized. Adapted with permission from ref 108. Copyright (2015) American Chemical Society.

To make an indirect connection with experiments, one could consider the agglomeration of CNTs in aqueous dispersions, but atomistic molecular dynamics simulations are no longer adequate. Blankschtein and co-workers demonstrated how it is



**Figure 5.** Representative simulation snapshots for coarse-grained simulations conducted for surfactant adsorbed on hydrophobic surface stripes surrounded by surfactant-repellent surfaces. In panal a, from top to bottom, the results are shown as the width of the hydrophobic stripe increases.  $L_s$  is the length of one surfactant molecule. Although on homogeneous, hydrophobic flat surfaces the surfactant yields a flat monolayer, the simulations show that a hemisphere forms on the narrower hydrophobic stripe and a hemicylinder forms on the hydrophobic stripe with a width of at least 0.61 times the length of the surfactant. In panel b, we show simulation snapshots obtained when two parallel hydrophobic stripes with a width that is 0.46 times the length of one surfactant are close to each other. Hemicylinders can form when the distance is small, and metastable structures are observed at intermediate separations. Adapted with permission from ref 114. Copyright (2014) Royal Society of Chemistry.

possible to use a coarse-grained simulation approach to bridge between molecular insights and experiments. Specifically, Shih et al.<sup>108</sup> carried out large-scale simulations at the coarse-grained level, quantified the surface coverage of SC on CNTs as a function of bulk concentration, and extracted the surface electrical potential. This information was then used to inform models derived from the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory to study the CNT stability. These very important results (summarized in Figure 4) showed that optimal surfactant concentrations exist for each carbon nanostructure (graphene sheets were also considered). Note that the optimal concentration is different depending on the CNT diameter. In another contribution, Lin et al.<sup>109</sup> showed that kinetic models of colloidal aggregation, informed using simulations-derived parameters, can reproduce experimental data for the stability of graphene dispersions.

Various coarse-grained simulations have been conducted for surfactants adsorbing on CNTs.<sup>110–112</sup> It is worth repeating that coarse-grained simulations are in general not able to capture the details of the molecular behavior but allow researchers to describe the formation of micelles of various shapes and sizes in equilibrium with the surfactant adsorbed on the CNTs. The simulations confirm that the aggregates selfassembled on the CNTs have different morphologies than those expected on flat homogeneous substrates. Angelikopoulos and Bock<sup>111</sup> compared the adsorption of coarse-grained surfactants on individual CNTs and on their bundles. Adsorption was driven by aggregation on the individual CNTs, but it follows Langmuir isotherms on bundles, where the regions between two neighboring CNTs provided nucleation sites for adsorption. The high-energy adsorption sites, formed at the intersection between neighboring CNTs in the bundle, are effectively due to the nonflat topography of the support, which yields both lateral confinement and a heterogeneous energy landscape.

In Figure 4, we pictorially summarize some of the results that have been reported for surfactant adsorbed on CNTs. At the atomistic level, we refer to the simulation results reported by Suttipong et al.<sup>91</sup> In these simulations, dodecyl sulfate surfactants were simulated on (6, 6), (12, 12), and (20, 20) CNTs at various concentrations. The surfactants were in the presence of either Na<sup>+</sup> or Cs<sup>+</sup> counterions. The atomistic simulations provide detailed information such as the radial distribution of the headgroups, that of the counterions, that of water, and so forth from the surface of the CNTs, allowing for a quantitative comparison to experimental spectroscopic data. At the coarse-grained level, we refer to the dissipative particle dynamics simulations reported by Calvaresi et al.<sup>110</sup> These authors considered surfactants with one bead representing the headgroup. They then considered tailgroups composed of various numbers of beads, from 3 to 11. The coarse-grained simulations allowed them to determine the structure of the surfactant aggregates that form on the CNTs when the surfactant type and the surfactant concentration change. It is notable that some of the micellar aggregates reported do not form when the CNTs are not present nor when adsorption occurs on a flat homogeneous surface. In the bottom portion of Figure 3, we refer to Shih et al.,<sup>108</sup> who used coarse-grained simulations to quantify the adsorption isotherms for SC on CNTs of different diameters and then used the results to calculate the surface electrical potential and therefore the stability of the aqueous dispersions containing either CNTs or graphene sheets, depending on the bulk surfactant concentration.

Surfactant Adsorption on Structured Surfaces. Although the CNT external surface is a prototype of lateral confinement, in many practical applications surfactants adsorb on flat surfaces, on which lateral confinement can be provided by either molecular-scale roughness (e.g., asperities, trenches, and step edges) or chemical heterogeneity. It is also possible that these two forms of lateral confinement occur simultaneously. At the atomistic level, Sammalkorpi et al.<sup>113</sup> simulated SDS on graphitic substrates on which line defects (i.e., surface steps) were present: the steps were found to localize the formation of surfactant aggregates and to induce a specific orientation. The authors suggested that "extended defects could be employed to localize and orient surfactant aggregates". As discussed above, atomistic models cannot allow one to study large aggregates and the exchange of surfactants, whereas coarse-grained approaches allow us to interrogate such phenomena.

Suttipong et al.<sup>114–116</sup> employed the dissipative particle dynamics<sup>117</sup> coarse-grained approach to study surfactant adsorption on a variety of patterned surfaces. The surfactant model was parametrized to yield a flat monolayer on a homogeneous hydrophobic flat surface exposed to an aqueous solution containing the surfactant at a concentration well above the CMC. A second model surface was constructed on which no surfactant could adsorb (i.e., a surfactant-repellent surface). It was then possible to prepare patterned surfaces on which, for example, stripes of hydrophobic surface were surrounded by surfactant-repellent surfaces. The width of the hydrophobic stripes can then be used as a measure of lateral confinement: the narrower the stripe, the more extensive the lateral confinement. By conducting simulations in which the width of the hydrophobic stripe was varied systematically, it was possible to quantify the degree of lateral confinement at which the flat surfactant monolayer transitions to a hemicylinder, to a very mobile and unstable hemisphere, and to the absence of adsorption.<sup>114</sup> Some of the results are summarized in Figure 5.

It was also possible to quantify synergistic effects, which are observed when two stripes with a width of less than the length of one surfactant molecule are parallel yet very close to each other. Some of these results are also summarized in Figure 5. Under the conditions just listed, the surfactant aggregates adsorb on both stripes, taking advantage of surfactant surfactant and surfactant—surface synergistic interactions. When the same stripes are slightly further from each other, metastable aggregates were observed, which could be the signature of the pronounced QCM-D dispersion data obtained experimentally for surfactant adsorption on rough surfaces.<sup>51</sup> On the contrary, when the stripes are wide enough that surfactants yield stable hemicylinders, or flat monolayers, on each stripe, no synergistic effects were observed, independently of how close the parallel stripes are placed to each other.

Other patterned surfaces considered included those obtained when two hydrophobic stripes intersect each other perpendicularly.<sup>116</sup> In this case, the region where the two stripes intersect can behave either as a preferential adsorption site or as a defect, depending on the stripe width. When the stripes are narrow, the surfactants yield a stable, long-lived hemisphere at the stripes' intersection even though they would not adsorb on either one of the individual stripes. When the stripes are wide enough that the surfactants yield a hemicylinder on an individual stripe, their intersection forces the hemicylinders to intersect, which seems to prevent complete coverage of the hydrophobic portions of the surfaces. This observation was explained by the possibility that the intersection of the two hemicylinders induces energetically unfavorable strains on the surfactant aggregates.

When surfactant adsorption occurs within trenches<sup>115</sup> and hence lateral confinement is due both to the chemical features of the surface and to its geometrical details, the surfactant aggregates can become significantly different compared to those expected on a flat, homogeneous hydrophobic substrate (i.e., a flat monolayer). In particular, on hydrophobic trenches of moderate width, the surfactant aggregates become monolayers, trilayers, and multilayers as the trench depth increases. For completeness, we point out that in these model systems the walls of the trenches were considered to be hydrophobic. Whereas experimental techniques such as AFM would not be able to distinguish between these aggregates because it probes only the top of the surfactant aggregate exposed to the aqueous system, the QCM-D could be able to detect differences in the amount of surfactant adsorbed on surfaces of varying roughness.<sup>51</sup>

Suttipong et al.<sup>116</sup> also showed that the adsorption of surfactants on hydrophobic edges depends strongly on the pitch angle, suggesting that the surfactant aggregates experience an energetic penalty when they are stretched; the energy penalty is similar to an elastic contribution to the free energy of the system.

Others reported that the behavior of surface-active compounds strongly depends on the presence of surface patterns and lateral confinement effects. For example, Das et al.<sup>118</sup> considered skin lipids. They conducted atomistic simulations to show that the equilibrium phase for these compounds is inverse micellar, and then they showed, using a variety of techniques including coarse-grained simulations, how a patterned surface promotes the formation of lamellar layering. Although the experiments of Marquez et al.<sup>41</sup> contained both surfactants and monomers, the simulations discussed so far considered pure surfactants. As suggested by QCM-D experiments,<sup>49</sup> the coadsorption of smaller compounds could change the morphology of self-assembled surfactant aggregates, which could compound the effect of lateral confinement on the surfactant aggregates. Among investigations on the coadsorption of different compounds within self-assembled aggregates, Akinshina et al.<sup>119</sup> considered the partitioning of compounds such as monoglycerides and fatty acids within self-assembled bilayers, showing that the mechanical properties of the bilayers are strongly affected by the molecular guests. Similar studies could be conducted for molecular guests coadsorbed within self-assembled surfactant aggregates on different surfaces, even in the presence of lateral confinement, not only to connect mesoscale simulations such as those reported by Suttipong et al.<sup>116</sup> to experimental investigations such as those of Shi et al.<sup>4</sup> but also to enable the incorporation of molecular-level insights, such as those discussed here, into the enhancement of practical applications such as controlled drug delivery and new material synthesis.

#### SUMMARY AND POSSIBLE FUTURE DIRECTIONS

In this focused review, selected examples were chosen to provide experimental evidence according to which lateral confinement has strong effects on the structure of selfassembled surfactant aggregates. These observations stimulated a number of simulation studies that focused on surfactant adsorption on graphene sheets, carbon nanotubes, and structured surfaces. In general, the simulation results corroborate semiquantitatively some macroscopic experimental observations. In some cases, as for example in the explanation of the stability of dispersions,<sup>109</sup> the simulations provide parameters for theoretical calculations that are in good quantitative agreement with experiments for the stability of aqueous dispersions of graphene sheets and of carbon nanotubes. In other circumstances, as for example in the case of surfactant adsorption on metallic vs semiconductive carbon nanotubes,<sup>98</sup> evidence suggests that the atomistic force fields are not yet able to predict the preferential adsorption of different surfactants on carbon nanotubes. Certainly, developing adequate force fields could be important to furthering our ability to sort carbon nanotubes and also other carbon-based nanostructures depending on their intrinsic properties. Understanding and manipulating self-assembly will allow us to control the structure and properties of interfacial structures, which is of extreme importance for synthesizing multifunctional structures and devices. El Garah et al.<sup>120</sup> recently showed an example in which exquisite control of a molecular-level structure could be achieved at the graphite-liquid interface by manipulating the interactions between molecules via appropriate design and careful synthesis.

The coadsorption of different compounds in surfactant aggregates can affect the morphology of the surface aggregates<sup>49</sup> as well as their mechanical properties.<sup>119</sup> A systematic investigation of the combined effect of the presence of coadsorbents and of lateral confinement on the features of surfactant self-assembled aggregates would be very intriguing, and the results could have direct application in the fields of controlled drug delivery and advanced cosmetics, in which case a coadsorbent could be used to trigger a change in the conformation of the surfactant assemblies. Pioneering studies have initiated this line of research. For example, Lin et al.<sup>121</sup> combined coarse-grained molecular dynamics simulations and photoluminescence experiments to identify the physical phenomena responsible for the potential use of carbon nanotube-polymer complexes as sensors for the detection of various analytes, including sugars and amino acids. As a second example, Lin et al.<sup>122</sup> investigated the adsorption of diazonium salts on carbon nanotubes covered with different surfactants (SC, SDS, and CTAB) as a starting point for controlling the functionalization of the nanotubes.

Understanding the changes in surfactant self-assembled aggregates as a function of lateral confinement has important consequences not only in the field of nanotechnology but also in several other applications with significant industrial interest. For example, in flow assurance applications, in which sometimes surfactants are used to prevent the formation of large hydrate plugs within pipelines, quantifying how the surfactant features change depending on the size of the water droplets and/or of the hydrate particles could be useful for quantifying how the surfactants can be used to prevent the agglomeration of such entities within the hydrocarbons. Simulations suggest that surfactant films adsorbed on small spherical water droplets or on a small spherical hydrate particle differ substantially from the surfactant films expected on a flat interface.<sup>123</sup> These and other studies<sup>124</sup> suggest that the integrity of the surfactant film affects its ability to prevent the transport of, for example, methane or water across the interface. Bui et al.<sup>124</sup> suggest that these phenomena could relate to the surfactant performance as antiagglomerants. The initial observations should be extended to include lateral confinement effects due to surface defects on the hydrate particles.

Other applications that are likely to depend on lateral confinement effects are corrosion inhibition,<sup>13</sup> enhanced oil recovery,<sup>12</sup> environmental remediation,<sup>10,11</sup> and hydraulic fracturing<sup>8</sup> because the substrates on which surfactants adsorb during these operations are not atomically flat and chemically homogeneous but instead show significant heterogeneity. Another large-scale application that could benefit from the quantitative understating of the effect of lateral confinement on the properties of surfactant self-assembled aggregates is mineral flotation, in which case rocks are crushed until a sufficient amount of the desired mineral (e.g., copper) is exposed. Although the simulations reported by Suttipong et al.<sup>114-116</sup> considered surfactant adsorption on a hydrophobic surface of limited lateral extension, to be relevant to mineral flotation, studies should be conducted for the inverse problem in which surfactant adsorption occurs on a hydrophilic surface (the mineral of interest) surrounded by gangue, which provides lateral confinement.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: a.striolo@ucl.ac.uk.

#### ORCID 0

Alberto Striolo: 0000-0001-6542-8065

#### Notes

The authors declare no competing financial interest. **Biographies** 



Alberto Striolo received his Ph.D. in chemical engineering from the University of Padova, Italy, in 2002. After a postdoctoral research experience, in 2005 he joined the University of Oklahoma as a faculty member in the School of Chemical, Biological and Materials Engineering. He spent a sabbatical leave at Princeton University and at the Lawrence Berkeley National Laboratory, Berkeley, California. In 2013, he joined University College London, in the U.K., where he is Professor of Molecular Thermodynamics. He currently holds the position of Deputy Head of Department (Enterprise), he directs the MSc program Global Management of Natural Resources, and he coordinates two consortia (ShaleXenvironmenT and Science4CleanEnergy) supported by the European Commission within the auspices of the Horizon 2020 research portfolio. His research interests focus on solid—fluid interfaces of technological importance.



Brian Grady received a B.S. from the University of Illinois in 1987 and a Ph.D. from the University of Wisconsin in 1994, both in chemical engineering. Since 1994, he has been employed by the University of Oklahoma as a faculty member in the School of Chemical, Biological and Materials Engineering, with a 1-year sabbatical in 2000–2001 at the Max Planck Institute of Colloids and Interfaces in Potsdam, Germany. He is currently the David and Hilda Bourne Chair of Chemical Engineering at the University of Oklahoma. He is also the Director of the Institute for Applied Surfactant Research at the University at Oklahoma as well as the current Chair of the Surfactants and Detergent Division of the American Oil Chemists Society. He is also the organizer of the 2018 Surfactants in Solution Meeting.

#### ACKNOWLEDGMENTS

This overview stems from a body of work that was initiated several years ago in collaboration with Prof. Daniel Resasco at the University of Oklahoma. A.S. is profoundly indebted to all of the members of his research group, past and present, for their efforts, enthusiasm, and dynamism. Much of the work presented here was produced by a number of very talented students. Dr. Naga Rajesh Tummala was responsible for planting the seeds of fruitful simulation studies that were then carried out for a number of systems by Dr. Manaswee Suttipong. Dr. Liu Shi was responsible for conducting a number of experiments with the QCM-D that were instrumental in supporting our computational studies. Financial support was provided by the National Science Foundation, the Oklahoma Center for the Advancement of Science and Technology, the U.S. Department of Energy, the U.K. Engineering and Physical Sciences Research Council under grant number EP/N007123/1, and the industrial sponsors of the Institute for Applied Surfactant Research (IASR) at the University of Oklahoma. A.S. is grateful to several institutions for granting his group access to supercomputing facilities, in particular, NERSC, OSCER, UCL, and ARCHER.

# **REFERENCES**

(1) Rosen, M. J. Surfactants and Interfacial Phenomena, 2nd ed.; Wiley: New York, 1989.

(2) Kissa, E. Fluorinated Surfactants: Synthesis, Properties, Applications; Marcel Dekker: New York, 1994.

(3) Zana, R.; Xia, J. Gemini Surfactants: Synthesis, Interfacial and Solution-Phase Behavior, and Applications; CRC Press, 2003.

(4) Ron, E. Z.; Rosenberg, E. Natural roles of biosurfactants. *Environ. Microbiol.* **2001**, 3 (4), 229–236.

(5) Desai, J. D.; Banat, I. M. Microbial production of surfactants and their commercial potential. *Microbiol. Mol. Biol. Rev.* **1997**, *61* (1), 47–64.

(6) Czajka, A.; Hazell, G.; Eastoe, J. Surfactants at the Design Limit. *Langmuir* **2015**, *31* (30), 8205–8217.

(7) Maestro, A.; Santini, E.; Zabiegaj, D.; Llamas, S.; Ravera, F.; Liggieri, L.; Ortega, F.; Rubio, R.; Guzman, E. Particle and Particle-Surfactant Mixtures at Fluid Interfaces: Assembly, Morphology, and Rheological Description. *Adv. Condens. Matter Phys.* **2015**, 2015, 917516.

(8) Camarillo, M. K.; Domen, J. K.; Stringfellow, W. T. Physicalchemical evaluation of hydraulic fracturing chemicals in the context of produced water treatment. *J. Environ. Manage.* **2016**, *183*, 164–174.

(9) He, K.; Xu, L.; Gao, Y. F.; Yin, X. L.; Neeves, K. B. Evaluation of surfactant performance in fracturing fluids for enhanced well productivity in unconventional reservoirs using Rock-on-a-Chip approach. *J. Pet. Sci. Eng.* **2015**, *135*, 531–541.

(10) Mao, X. H.; Jiang, R.; Xiao, W.; Yu, J. G. Use of surfactants for the remediation of contaminated soils: A review. *J. Hazard. Mater.* **2015**, 285, 419–435.

(11) Trellu, C.; Mousset, E.; Pechaud, Y.; Huguenot, D.; van Hullebusch, E. D.; Esposito, G.; Oturan, M. A. Removal of hydrophobic organic pollutants from soil washing/flushing solutions: A critical review. *J. Hazard. Mater.* **2016**, *306*, 149–174.

(12) Kamal, M. S. A Review of Gemini Surfactants: Potential Application in Enhanced Oil Recovery. J. Surfactants Deterg. 2016, 19 (2), 223–236.

(13) Malik, M. A.; Hashim, M. A.; Nabi, F.; AL-Thabaiti, S. A.; Khan, Z. Anti-corrosion Ability of Surfactants: A Review. *Int. J. Electrochem. Sci.* **2011**, *6*, 1927–1948.

(14) Lee, H. J.; McAuley, A.; Schilke, K. F.; McGuire, J. Molecular origins of surfactant-mediated stabilization of protein drugs. *Adv. Drug Delivery Rev.* **2011**, *63* (13), 1160–1171.

(15) Adlercreutz, P. Immobilisation and application of lipases in organic media. *Chem. Soc. Rev.* 2013, 42 (15), 6406–6436.

(16) Heinz, H.; Pramanik, C.; Heinz, O.; Ding, Y. F.; Mishra, R. K.; Marchon, D.; Flatt, R. J.; Estrela-Lopis, I.; Llop, J.; Moya, S.; Ziolo, R. F. Nanoparticle decoration with surfactants: Molecular interactions, assembly, and applications. *Surf. Sci. Rep.* **2017**, *72* (1), 1–58.

(17) Zhang, R.; Somasundaran, P. Advances in adsorption of surfactants and their mixtures at solid/solution interfaces. *Adv. Colloid Interface Sci.* **2006**, 123-126, 213-229.

(18) Grant, L. M.; Tiberg, F.; Ducker, W. A. Nanometer-scale organization of ethylene oxide surfactants on graphite, hydrophilic silica, and hydrophobic silica. *J. Phys. Chem. B* **1998**, *102* (22), 4288–4294.

(19) Manne, S.; Gaub, H. E. Molecular-Organization of Surfactants at Solid-Liquid Interfaces. *Science* **1995**, *270* (5241), 1480–1482.

(20) Warr, G. G. Surfactant adsorbed layer structure at solid/solution interfaces: impact and implications of AFM imaging studies. *Curr. Opin. Colloid Interface Sci.* **2000**, 5 (1–2), 88–94.

(21) Tiberg, F.; Jonsson, B.; Tang, J.; Lindman, B. Ellipsometry Studies of the Self-Assembly of Nonionic Surfactants at the Silica Water Interface - Equilibrium Aspects. *Langmuir* **1994**, *10* (7), 2294– 2300.

(22) Thirtle, P. N.; Li, Z. X.; Thomas, R. K.; Rennie, A. R.; Satija, S. K.; Sung, L. P. Structure of nonionic surfactant layers adsorbed at the solid/liquid interface on self-assembled monolayers with different surface functionality: A neutron reflection study. *Langmuir* **1997**, *13* (20), 5451–5458.

(23) Cummins, P. G.; Penfold, J.; Staples, E. Nature of the Adsorption of the Nonionic Surfactant Pentaethylene Glycol Monododecyl Ether on a Ludox Silica Sol. *J. Phys. Chem.* **1992**, *96* (20), 8092–8094.

(24) Kline, S. R.; Kaler, E. W. Aggregation of colloidal silica by n-alkyl sulfates. *Langmuir* **1996**, *12* (10), 2402–2407.

(25) Schonhoff, M. NMR studies of sorption and adsorption phenomena in colloidal systems. *Curr. Opin. Colloid Interface Sci.* 2013, 18 (3), 201–213.

(26) Penfold, J.; Thomas, R. K.; Shen, H. H. Adsorption and selfassembly of biosurfactants studied by neutron reflectivity and small angle neutron scattering: glycolipids, lipopeptides and proteins. *Soft Matter* **2012**, *8* (3), 578–591.

(27) Liu, Z.; Yu, J. G.; O'Rear, E. A.; Striolo, A. Aqueous Dual-Tailed Surfactants Simulated on the Alumina Surface. *J. Phys. Chem. B* 2014, *118* (32), 9695–9707.

(28) Santos-Carballal, D.; Du, Z. M.; King, H. E.; de Leeuw, N. H. A computational study of the interaction of organic surfactants with goethite alpha-FeO(OH) surfaces. *RSC Adv.* **2016**, *6* (94), 91893–91903.

(29) Yuan, F.; Wang, S. H.; Larson, R. G. Potentials of Mean Force and Escape Times of Surfactants from Micelles and Hydrophobic Surfaces Using Molecular Dynamics Simulations. *Langmuir* **2015**, *31* (4), 1336–1343.

(30) Darkins, R.; Sushko, M. L.; Liu, J.; Duffy, D. M. Adhesion of Sodium Dodecyl Sulfate Surfactant Mono layers with TiO2 (Rutile and Anatase) Surfaces. *Langmuir* **2013**, *29* (37), 11609–11614.

(31) Tummala, N. R.; Shi, L.; Striolo, A. Molecular dynamics simulations of surfactants at the silica-water interface: Anionic vs nonionic headgroups. *J. Colloid Interface Sci.* **2011**, *362* (1), 135–143.

(32) Shi, L.; Tummala, N. R.; Striolo, A. C12E6 and SDS Surfactants Simulated at the Vacuum-Water Interface. *Langmuir* **2010**, *26* (8), 5462–5474.

(33) Heinz, H.; Ramezani-Dakhel, H. Simulations of inorganicbioorganic interfaces to discover new materials: insights, comparisons to experiment, challenges, and opportunities. *Chem. Soc. Rev.* **2016**, 45 (2), 412–448.

(34) Fielden, M. L.; Claesson, P. M.; Verrall, R. E. Investigating the adsorption of the gemini surfactant "12–2-12" onto mica using atomic force microscopy and surface force apparatus measurements. *Langmuir* **1999**, *15* (11), 3924–3934.

(35) Claesson, P.; Horn, R. G.; Pashley, R. M. Measurement of Surface Forces between Mica Sheets Immersed in Aqueous Quaternary Ammonium Ion Solutions. *J. Colloid Interface Sci.* 1984, 100 (1), 250–263.

(36) Kekicheff, P.; Christenson, H. K.; Ninham, B. W. Adsorption of Cetyltrimethylammonium Bromide to Mica Surfaces Below the Critical Micellar Concentration. *Colloids Surf.* **1989**, 40 (1–2), 31–41.

(37) Claesson, P. M.; Eriksson, J. C.; Herder, C.; Bergenstahl, B. A.; Pezron, E.; Pezron, I.; Stenius, P. Forces between Nonionic Surfactant Layers. *Faraday Discuss. Chem. Soc.* **1990**, *90*, 129–142.

(38) Waltermo, A.; Sjoberg, M.; Anhede, B.; Claesson, P. M. Adsorption of an Ethoxylated Amine Surfactant on Mica and Its Effect on the Surface Forces. *J. Colloid Interface Sci.* **1993**, *156* (2), 365–376.

(39) Rutland, M.; Waltermo, A.; Claesson, P. pH-Dependent Interactions of Mica Surfaces in Aqueous Dodecylammonium Dodecylamine Solutions. *Langmuir* **1992**, 8 (1), 176–183.

(40) Leermakers, F. A. M.; Koopal, L. K.; Lokar, W. J.; Ducker, W. A. Modeling of confinement-induced phase transitions for surfactant layers on amphiphilic surfaces. *Langmuir* **2005**, *21* (24), 11534–11545.

(41) Marquez, M.; Kim, S.; Jung, J.; Truong, N.; Teeters, D.; Grady, B. P. Factors affecting the synthesis of polymeric nanostructures from template assisted admicellar polymerization. *Langmuir* **2007**, *23* (20), 10008–10019.

(42) Marquez, M.; Patel, K.; Carswell, A. D. W.; Schmidtke, D. W.; Grady, B. P. Synthesis of nanometer-scale polymeric structures on surfaces from template assisted admicellar polymerization: A comparative study with protein adsorption. *Langmuir* **2006**, *22* (19), 8010–8016.

(43) Wu, J. Y.; Harwell, J. H.; Orear, E. A. Two-Dimensional Reaction Solvents - Surfactant Bilayers in the Formation of Ultrathin Films. *Langmuir* **1987**, *3* (4), 531–537.

(44) Kothary, P.; Yanumet, N.; O'Rear, E. A. Surfactant effects on application of a hydrophobic, fluoropolymer coating to cotton by admicellar polymerization. *Fibers Polym.* **2013**, *14* (5), 710–717.

(45) Carswell, A. D. W.; O'Rear, E. A.; Grady, B. P. Adsorbed surfactants as templates for the synthesis of morphologically controlled polyaniline and polypyrrole nanostructures on flat surfaces: From

spheres to wires to flat films. J. Am. Chem. Soc. 2003, 125 (48), 14793-14800.

(46) Taylor, Z. R.; Patel, K.; Spain, T. G.; Keay, J. C.; Jernigen, J. D.; Sanchez, E. S.; Grady, B. P.; Johnson, M. B.; Schmidtke, D. W. Fabrication of Protein Dot Arrays via Particle Lithography. *Langmuir* **2009**, 25 (18), 10932–10938.

(47) Schniepp, H. C.; Shum, H. C.; Saville, D. A.; Aksay, I. A. Orientational order of molecular assemblies on rough surfaces. *J. Phys. Chem. C* 2008, *112* (38), 14902–14906.

(48) Schniepp, H. C.; Shum, H. C.; Saville, D. A.; Aksay, I. A. Surfactant aggregates at rough solid-liquid interfaces. *J. Phys. Chem. B* **2007**, *111* (30), 8708–8712.

(49) Shi, L.; Ghezzi, M.; Caminati, G.; Lo Nostro, P.; Grady, B. P.; Striolo, A. Adsorption Isotherms of Aqueous C12E6 and Cetyltrimethylammonium Bromide Surfactants on Solid Surfaces in the Presence of Low Molecular Weight Coadsorbents. *Langmuir* 2009, 25 (10), 5536–5544.

(50) Gutig, C.; Grady, B. P.; Striolo, A. Experimental studies on the adsorption of two surfactants on solid-aqueous interfaces: Adsorption isotherms and kinetics. *Langmuir* **2008**, *24* (9), 4806–4816.

(51) Wu, S. Q.; Shi, L.; Garfield, L. B.; Tabor, R. F.; Striolo, A.; Grady, B. P. Influence of Surface Roughness on Cetyltrimethylammonium Bromide Adsorption from Aqueous Solution. *Langmuir* **2011**, 27 (10), 6091–6098.

(52) Pagac, E. S.; Prieve, D. C.; Tilton, R. D. Kinetics and mechanism of cationic surfactant adsorption and coadsorption with cationic polyelectrolytes at the silica-water interface. *Langmuir* **1998**, *14* (9), 2333–2342.

(53) Hsieh, A. G.; Punckt, C.; Korkut, S.; Aksay, I. A. Adsorption of Sodium Dodecyl Sulfate on Functionalized Graphene Measured by Conductometric Titration. *J. Phys. Chem. B* **2013**, *117* (26), 7950–7958.

(54) Hsieh, A. G.; Korkut, S.; Punckt, C.; Aksay, I. A. Dispersion Stability of Functionalized Graphene in Aqueous Sodium Dodecyl Sulfate Solutions. *Langmuir* **2013**, *29* (48), 14831–14838.

(55) Tummala, N. R.; Grady, B. P.; Striolo, A. Lateral confinement effects on the structural properties of surfactant aggregates: SDS on graphene. *Phys. Chem. Chem. Phys.* **2010**, *12* (40), 13137–13143.

(56) Tummala, N. R.; Striolo, A. Role of counterion condensation in the self-assembly of SDS surfactants at the water-graphite interface. *J. Phys. Chem. B* **2008**, *112* (7), 1987–2000.

(57) Dominguez, H. Self-aggregation of the SDS surfactant at a solid-liquid interface. J. Phys. Chem. B 2007, 111 (16), 4054–4059.

(58) Manne, S.; Cleveland, J. P.; Gaub, H. E.; Stucky, G. D.; Hansma, P. K. Direct Visualization of Surfactant Hemimicelles by Force Microscopy of the Electrical Double-Layer. *Langmuir* **1994**, *10* (12), 4409–4413.

(59) Yang, J.; Yang, X. N.; Li, Y. P. Molecular simulation perspective of liquid-phase exfoliation, dispersion, and stabilization for graphene. *Curr. Opin. Colloid Interface Sci.* **2015**, 20 (5–6), 339–345.

(60) Frenkel, D.; Smit, B. Understanding Molecular Simulation: From Algorithms to Applications, 2nd ed.; Academic Press: San Diego, CA, 2002.

(61) Allen, M. P.; Tildesley, D. J. Computer Simulation of Liquids; Oxford University Press: New York, 1987.

(62) Santos, A. P.; Panagiotopoulos, A. Z. Determination of the critical micelle concentration in simulations of surfactant systems. *J. Chem. Phys.* **2016**, *144* (4), 044709.

(63) Jusufi, A.; Panagiotopoulos, A. Z. Explicit- and Implicit-Solvent Simulations of Micellization in Surfactant Solutions. *Langmuir* **2015**, *31* (11), 3283–3292.

(64) Sanders, S. A.; Sammalkorpi, M.; Panagiotopoulos, A. Z. Atomistic Simulations of Micellization of Sodium Hexyl, Heptyl, Octyl, and Nonyl Sulfates. *J. Phys. Chem. B* **2012**, *116* (8), 2430–2437. (65) Sanders, S. A.; Panagiotopoulos, A. Z. Micellization behavior of coarse grained surfactant models. *J. Chem. Phys.* **2010**, *132* (11), 114902.

(66) Noro, M. G.; Paul, P. K. C.; Warren, P. B. Linking atomistic and mesoscale simulations of water-soluble polymers. *J. Am. Chem. Soc.* **2003**, *125* (24), 7190–7191.

(67) Fan, H.; Striolo, A. Mechanistic study of droplets coalescence in Pickering emulsions. *Soft Matter* **2012**, *8* (37), 9533–9538.

(68) Fan, H.; Striolo, A. Nanoparticle effects on the water-oil interfacial tension. *Phys. Rev. E* 2012, *86* (5), 051610.

(69) Lane, J. M. D.; Ismail, A. E.; Chandross, M.; Lorenz, C. D.; Grest, G. S. Forces between functionalized silica nanoparticles in solution. *Phys. Rev. E* **2009**, *79* (5), 050501.

(70) Singh, S. P.; Winkler, R. G.; Gompper, G. Nonequilibrium Forces between Dragged Ultrasoft Colloids. *Phys. Rev. Lett.* **2011**, *107* (15), 158301.

(71) Anderson, J. A.; Lorenz, C. D.; Travesset, A. Micellar crystals in solution from molecular dynamics simulations. *J. Chem. Phys.* 2008, 128 (18), 184906.

(72) Min, S. H.; Lee, C.; Jang, J. Dissipative particle dynamics modeling of a graphene nanosheet and its self-assembly with surfactant molecules. *Soft Matter* **2012**, *8* (33), 8735–8742.

(73) Ramanathan, T.; Fisher, F. T.; Ruoff, R. S.; Brinson, L. C. Amino-functionalized carbon nanotubes for binding to polymers and biological systems. *Chem. Mater.* **2005**, *17* (6), 1290–1295.

(74) Davis, V. A.; Parra-Vasquez, A. N. G.; Green, M. J.; Rai, P. K.; Behabtu, N.; Prieto, V.; Booker, R. D.; Schmidt, J.; Kesselman, E.; Zhou, W.; Fan, H.; Adams, W. W.; Hauge, R. H.; Fischer, J. E.; Cohen, Y.; Talmon, Y.; Smalley, R. E.; Pasquali, M. True solutions of singlewalled carbon nanotubes for assembly into macroscopic materials. *Nat. Nanotechnol.* **2009**, *4* (12), 830–834.

(75) Bhattacharya, S.; Samanta, S. K. Soft-Nanocomposites of Nanoparticles and Nanocarbons with Supramolecular and Polymer Gels and Their Applications. *Chem. Rev.* **2016**, *116* (19), 11967–12028.

(76) Johnson, R. R.; Johnson, A. T. C.; Klein, M. L. Probing the structure of DNA-carbon nanotube hybrids with molecular dynamics. *Nano Lett.* **2008**, *8* (1), 69–75.

(77) Wang, H. Dispersing carbon nanotubes using surfactants. *Curr. Opin. Colloid Interface Sci.* **2009**, 14 (5), 364–371.

(78) Ao, G. Y.; Streit, J. K.; Fagan, J. A.; Zheng, M. Differentiating Left- and Right-Handed Carbon Nanotubes by DNA. J. Am. Chem. Soc. **2016**, 138 (51), 16677–16685.

(79) Fagan, J. A.; Haroz, E. H.; Ihly, R.; Gui, H.; Blackburn, J. L.; Simpson, J. R.; Lam, S.; Walker, A. R. H.; Doorn, S. K.; Zheng, M. Isolation of > 1 nm Diameter Single-Wall Carbon Nanotube Species Using Aqueous Two-Phase Extraction. *ACS Nano* **2015**, *9* (5), 5377– 5390.

(80) Fagan, J. A.; Zheng, M.; Rastogi, V.; Simpson, J. R.; Khripin, C. Y.; Batista, C. A. S.; Walker, A. R. H. Analyzing Surfactant Structures on Length and Chirality Resolved (6,5) Single-Wall Carbon Nanotubes by Analytical Ultracentrifugation. *ACS Nano* **2013**, *7* (4), 3373–3387.

(81) McDonald, T. J.; Engtrakul, C.; Jones, M.; Rumbles, G.; Heben, M. J. Kinetics of PL quenching during single-walled carbon nanotube rebundling and diameter-dependent surfactant interactions. *J. Phys. Chem. B* **2006**, *110* (50), 25339–25346.

(82) Matarredona, O.; Rhoads, H.; Li, Z. R.; Harwell, J. H.; Balzano, L.; Resasco, D. E. Dispersion of single-walled carbon nanotubes in aqueous solutions of the anionic surfactant NaDDBS. *J. Phys. Chem. B* **2003**, *107* (48), 13357–13367.

(83) Green, A. A.; Hersam, M. C. Nearly Single-Chirality Single-Walled Carbon Nanotubes Produced via Orthogonal Iterative Density Gradient Ultracentrifugation. *Adv. Mater.* **2011**, *23* (19), 2185.

(84) Tummala, N. R.; Striolo, A. SDS Surfactants on Carbon Nanotubes: Aggregate Morphology. *ACS Nano* **2009**, *3* (3), 595–602.

(85) Yurekli, K.; Mitchell, C. A.; Krishnamoorti, R. Small-angle neutron scattering from surfactant-assisted aqueous dispersions of carbon nanotubes. *J. Am. Chem. Soc.* **2004**, *126* (32), 9902–9903.

(86) Lin, S. C.; Blankschtein, D. Role of the Bile Salt Surfactant Sodium Cholate in Enhancing the Aqueous Dispersion Stability of Single-Walled Carbon Nanotubes: A Molecular Dynamics Simulation Study. J. Phys. Chem. B 2010, 114 (47), 15616–15625.

(87) Xu, Z. J.; Yang, X. N.; Yang, Z. A Molecular Simulation Probing of Structure and Interaction for Supramolecular Sodium Dodecyl Sulfate/Single-Wall Carbon Nanotube Assemblies. *Nano Lett.* **2010**, *10* (3), 985–991.

(88) Tummala, N. R.; Morrow, B. H.; Resasco, D. E.; Striolo, A. Stabilization of Aqueous Carbon Nanotube Dispersions Using Surfactants: Insights from Molecular Dynamics Simulations. *ACS Nano* **2010**, *4* (12), 7193–7204.

(89) Suttipong, M.; Tummala, N. R.; Kitiyanan, B.; Striolo, A. Role of Surfactant Molecular Structure on Self-Assembly: Aqueous SDBS on Carbon Nanotubes. J. Phys. Chem. C 2011, 115 (35), 17286–17296.

(90) Suttipong, M.; Striolo, A. Equimolar mixtures of aqueous linear and branched SDBS surfactant simulated on single walled carbon nanotubes. *RSC Adv.* **2015**, *5* (109), 90049–90060.

(91) Suttipong, M.; Tummala, N. R.; Striolo, A.; Batista, C. S.; Fagan, J. Salt-specific effects in aqueous dispersions of carbon nanotubes. *Soft Matter* **2013**, *9* (14), 3712–3719.

(92) Allen, D. T.; Saaka, Y.; Pardo, L. C.; Lawrence, M. J.; Lorenz, C. D. Specific effects of monovalent counterions on the structural and interfacial properties of dodecyl sulfate monolayers. *Phys. Chem. Chem. Phys.* **2016**, *18* (44), 30394–30406.

(93) Poorgholami-Bejarpasi, N.; Sohrabi, B. Role of surfactant structure in aqueous dispersions of carbon nanotubes. *Fluid Phase Equilib.* **2015**, *394*, 19–28.

(94) Samarajeewa, D. R.; Dieckmann, G. R.; Nielsen, S. O.; Musselman, I. H. Modifying the electronic properties of single-walled carbon nanotubes using designed surfactant peptides. *Nanoscale* **2012**, *4* (15), 4544–4554.

(95) Samarajeewa, D. R.; Dieckmann, G. R.; Nielsen, S. O.; Musselman, I. H. Doping single-walled carbon nanotubes with surfactant peptides containing electron-donor substituents and nitrogen heterocycles. *Carbon* **2013**, *57*, 88–98.

(96) De Leo, F.; Sgrignani, J.; Bonifazi, D.; Magistrato, A. Structural and Dynamic Properties of Monoclonal Antibodies Immobilized on CNTs: A Computational Study. *Chem. - Eur. J.* **2013**, *19* (37), 12281–12293.

(97) Carvalho, E. J. F.; dos Santos, M. C. Surfactant-nanotube interactions in water and nanotube separation by diameter: atomistic simulations. *Eur. Phys. J. B* **2010**, *75* (2), 147–150.

(98) Shastry, T. A.; Morris-Cohen, A. J.; Weiss, E. A.; Hersam, M. C. Probing Carbon Nanotube-Surfactant Interactions with Two-Dimensional DOSY NMR. *J. Am. Chem. Soc.* **2013**, *135* (18), 6750–6753.

(99) Carvalho, E. J. F.; dos Santos, M. C. Role of Surfactants in Carbon Nanotubes Density Gradient Separation. *ACS Nano* **2010**, *4* (2), 765–770.

(100) Hersam, M. C. Progress towards monodisperse single-walled carbon nanotubes. *Nat. Nanotechnol.* **2008**, 3 (7), 387–394.

(101) Ghosh, S.; Bachilo, S. M.; Weisman, R. B. Advanced sorting of single-walled carbon nanotubes by nonlinear density-gradient ultracentrifugation. *Nat. Nanotechnol.* **2010**, *5* (6), 443–450.

(102) Green, A. A.; Hersam, M. C. Colored semitransparent conductive coatings consisting of monodisperse metallic single-walled carbon nanotubes. *Nano Lett.* **2008**, *8* (5), 1417–1422.

(103) Williams, C. D.; Dix, J.; Troisi, A.; Carbone, P. Effective Polarization in Pairwise Potentials at the Graphene-Electrolyte Interface. *J. Phys. Chem. Lett.* **2017**, *8* (3), 703–708.

(104) Wang, C. H.; Yang, G. W.; Jiang, Y. Structure and property of multiple amino acids assembled on the surface of a CNT. *Phys. E* 2017, 85, 7-12.

(105) Welch, C. M.; Camden, A. N.; Barr, S. A.; Leuty, G. M.; Kedziora, G. S.; Berry, R. J. Computation of the binding free energy of peptides to graphene in explicit water. *J. Chem. Phys.* **2015**, *143* (4), 045104.

(106) Kim, S. N.; Kuang, Z. F.; Slocik, J. M.; Jones, S. E.; Cui, Y.; Farmer, B. L.; McAlpine, M. C.; Naik, R. R. Preferential Binding of Peptides to Graphene Edges and Planes. *J. Am. Chem. Soc.* **2011**, *133* (37), 14480–14483. (107) Zhou, X. Y.; Wang, B.; Lan, T.; Chen, H. Q.; Wang, H. L.; Tao, Y.; Li, Z. H.; Ibrahim, K.; Wang, D. Q.; Feng, W. Y. Chirality of Graphene Oxide-Humic Acid Sandwich Complex Induced by a Twisted, Long-Range-Ordered Nanostructure. *J. Phys. Chem.* C 2016, 120 (45), 25789–25795.

(108) Shih, C. J.; Lin, S. C.; Strano, M. S.; Blankschtein, D. Understanding the Stabilization of Single-Walled Carbon Nanotubes and Graphene in Ionic Surfactant Aqueous Solutions: Large-Scale Coarse-Grained Molecular Dynamics Simulation-Assisted DLVO Theory. J. Phys. Chem. C 2015, 119 (2), 1047–1060.

(109) Lin, S. C.; Shih, C. J.; Strano, M. S.; Blankschtein, D. Molecular Insights into the Surface Morphology, Layering Structure, and Aggregation Kinetics of Surfactant-Stabilized Graphene Dispersions. J. Am. Chem. Soc. 2011, 133 (32), 12810–12823.

(110) Calvaresi, M.; Dallavalle, M.; Zerbetto, F. Wrapping Nanotubes with Micelles, Hemimicelles, and Cylindrical Micelles. *Small* **2009**, *5* (19), 2191–2198.

(111) Angelikopoulos, P.; Bock, H. The Differences in Surfactant Adsorption on Carbon Nanotubes and Their Bundles. *Langmuir* 2010, 26 (2), 899–907.

(112) Angelikopoulos, P.; Bock, H. The science of dispersing carbon nanotubes with surfactants. *Phys. Chem. Chem. Phys.* **2012**, *14* (27), 9546–9557.

(113) Sammalkorpi, M.; Panagiotopoulos, A. Z.; Haataja, M. Surfactant and Hydrocarbon Aggregates on Defective Graphite Surface: Structure and Dynamics. *J. Phys. Chem. B* **2008**, *112* (41), 12954–12961.

(114) Suttipong, M.; Grady, B. P.; Striolo, A. Self-assembled surfactants on patterned surfaces: confinement and cooperative effects on aggregate morphology. *Phys. Chem. Chem. Phys.* **2014**, *16* (31), 16388–16398.

(115) Suttipong, M.; Grady, B. P.; Striolo, A. Surfactant Aggregates Templated by Lateral Confinement. J. Phys. Chem. B 2015, 119 (17), 5467-5474.

(116) Suttipong, M.; Grady, B. P.; Striolo, A. Surfactants adsorption on crossing stripes and steps. *Soft Matter* **2017**, *13* (4), 862–874.

(117) Groot, R. D.; Warren, P. B. Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation. *J. Chem. Phys.* **1997**, *107* (11), 4423–4435.

(118) Das, C.; Noro, M. G.; Olmsted, P. D. Lamellar and Inverse Micellar Structures of Skin Lipids: Effect of Templating. *Phys. Rev. Lett.* **2013**, *111* (14), 148101.

(119) Akinshina, A.; Das, C.; Noro, M. G. Effect of monoglycerides and fatty acids on a ceramide bilayer. *Phys. Chem. Chem. Phys.* **2016**, *18* (26), 17446–17460.

(120) El Garah, M.; Bonilla, A. S.; Ciesielski, A.; Gualandi, A.; Mengozzi, L.; Fiorani, A.; Iurlo, M.; Marcaccio, M.; Gutierrez, R.; Rapino, S.; Calvaresi, M.; Zerbetto, F.; Cuniberti, G.; Cozzi, P. G.; Paolucci, F.; Samori, P. Molecular design driving tetraporphyrin selfassembly on graphite: a joint STM, electrochemical and computational study. *Nanoscale* **2016**, *8* (28), 13678–13686.

(121) Lin, S. C.; Zhang, J. Q.; Strano, M. S.; Blankschtein, D. Understanding selective molecular recognition in integrated carbon nanotube-polymer sensors by simulating physical analyte binding on carbon nanotube-polymer scaffolds. *Soft Matter* **2014**, *10* (32), 5991–6004.

(122) Lin, S. C.; Hilmer, A. J.; Mendenhall, J. D.; Strano, M. S.; Blankschtein, D. Molecular Perspective on Diazonium Adsorption for Controllable Functionalization of Single-Walled Carbon Nanotubes in Aqueous Surfactant Solutions. *J. Am. Chem. Soc.* **2012**, *134* (19), 8194–8204.

(123) Phan, A.; Bui, T.; Acosta, E.; Krishnamurthy, P.; Striolo, A. Molecular mechanisms responsible for hydrate anti-agglomerant performance. *Phys. Chem. Chem. Phys.* **2016**, *18* (36), 24859–24871.

(124) Bui, T.; Phan, A.; Monteiro, D.; Lan, Q.; Ceglio, M.; Acosta, E.; Krishnamurthy, P.; Striolo, A. Evidence of Structure-Performance Relation for Surfactants Used as Anti-agglomerants for Hydrate Management. *Langmuir* **2017**, 33 (9), 2263–2274.