

Water/Oil Interfacial Tension Reduction - An Interfacial Entropy Driven Process

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Supporting Information

In addition to the details provided in the main text

- Table S1 shows the comparison of IFT calculated using the NP_nAT and NVT ensembles at 2.1×10^{-6} mol/m² of SDS surface density at different temperatures. The results indicate that both ensembles give similar results, suggesting that the algorithm used to calculate the IFT in our study is appropriate.
- Table S2 displays information about the SDS surface excess concentration calculated from various experimental studies in literature. The data indicate that the surface densities of SDS used in our simulations are within the range of the experimental values.
- Figure S1 presents the results of simulated water/*n*-dodecane IFT as a function of temperature and compared to the experimental data from Zeppieri et al.¹ The results show that MD simulations capture correctly the trend of temperature dependence of water/*n*-dodecane IFTs. It is worth noting that the calculated water/dodecane IFTs are within 10% of the experimental data, therefore justifying our choice of force fields for water and *n*-dodecane to predict oil/water interfacial tension.
- Figure S2 shows the evolution of the water/dodecane interfacial tension and the potential energy of the simulated systems as a function of simulation time, indicating that the simulations presented here are conducted for sufficiently long times.
- Figure S3 depicts the distribution of interfacial water molecules (identified by the ITIM algorithm) along the *Z* direction of the simulation box. The distribution was then fitted to a Gaussian distribution to calculate the full width at half maximum, which is referred as the interfacial width and interfacial roughness.
- Figure S4 shows distribution of interfacial dodecane, water, and SDS molecules along the *Z* direction of the simulation box. The interfacial molecules are identified using the ITIM algorithm with a probe sphere radius of 1.5 Å.
- Figure S5 displays simulation snapshots showing the co-existence of SDS and dodecane molecules at the interface from low to high SDS surface densities. At low SDS surface densities, oil molecules align parallel to the water surface. Whereas at intermediate and high SDS surface densities, interfacial oil molecules tend to be more isotropically oriented.
- Figure S6 shows the probability distribution of the angle formed between the dipole moment vector of interfacial water molecules and the interfacial normal vector at various SDS surface densities.
- Figure S7 shows a comparison between the IFT values calculated for water/air and water/dodecane as a function of SDS surface density calculated at 293.15 K and 1 bar. The results indicate that when oil is present, the IFT reduction is greater than that of the water/air system. This information further signifies the contribution of the (interfacial) oil molecules in the IFT reduction.
- Figure S8 displays representative principal motions for the saturated SDS molecules (top), and the *cis* unsaturated ones (bottom). These motions were reconstructed by performing a principal component analysis (PCA) on the

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MD trajectories of the simulated systems. The PCA analysis was conducted using *gmx covar* and *gmx ana eig* tools implemented in the GROMACS simulation package² to create a covariance matrix from coordinates of all atoms of the surfactant of interest. The principal motions are represented by eigenvectors (orthogonal collective modes) and eigenvalues (variances) of the covariance matrix. The eigenvectors reveal the overall direction of motion of the atoms whereas the eigenvalues indicate the spatial scale of the motions. The motion projected on eigenvector 1 resembles a folding process, whereas the motion projected on eigenvector 2 represents either a folding or a twisting process. The information of the the radius of gyration, $R_{gyration}$, and the end-to-end tail length, d_{tail} , for SDS surfactants is also displayed in this Figure. This information supports our conclusions regarding the effect of surfactants in modulating the interfacial entropy.

- Figure S9 displays the torsional angle potentials of the original and the modified TraPPE/UA force fields. We also show in this figure the order parameters obtained for the alkyl tails of SDS surfactants using the two torsional potentials. This information is used to modify the force fields used to simulate SDS, and to further quantify the entropy of the surfactant molecules at the interface.

Table S1 IFT of *n*-dodecane/water systems with a surface density of 2.1×10^{-6} mol/m² of SDS at three different temperatures using two distinct ensembles NVT and NP_{*n*}AT.

	NP _{<i>n</i>} AT	NVT
293.15K	46.2 ± 0.9	45.8 ± 1.5
313.15K	43.8 ± 0.8	43.1 ± 0.2
333.15K	41.0 ± 0.5	42.4 ± 0.8

Table S2 Maximum surface excess concentration of SDS from different studies in literature.

References	System	SDS surface excess concentration
Langmuir 2018, 34, 21, 5978–5989	Water/ <i>n</i> -dodecane/SDS	5.2×10^{-6} mol/m ²
J. Phys. Chem. B 2016, 120, 29, 7265–7274	Water/ <i>n</i> -hexane/SDS	$\sim 8.0 \times 10^{-6}$ mol/m ²
J. Am. Chem. Soc. 2010, 132, 7, 2122–2123 Colloids and Surfaces A: Physicochem.	Water/ <i>n</i> -hexadecane/SDS	3.3×10^{-6} mol/m ²
Eng. Aspects 2002, 196, 19–24	Water/air/SDS	$>4 \times 10^{-6}$ mol/m ²
J. Phys. Chem. 1967, 71, 3, 738–745	Water/ <i>n</i> -dodecane/SDS	3.39×10^{-6} mol/m ²

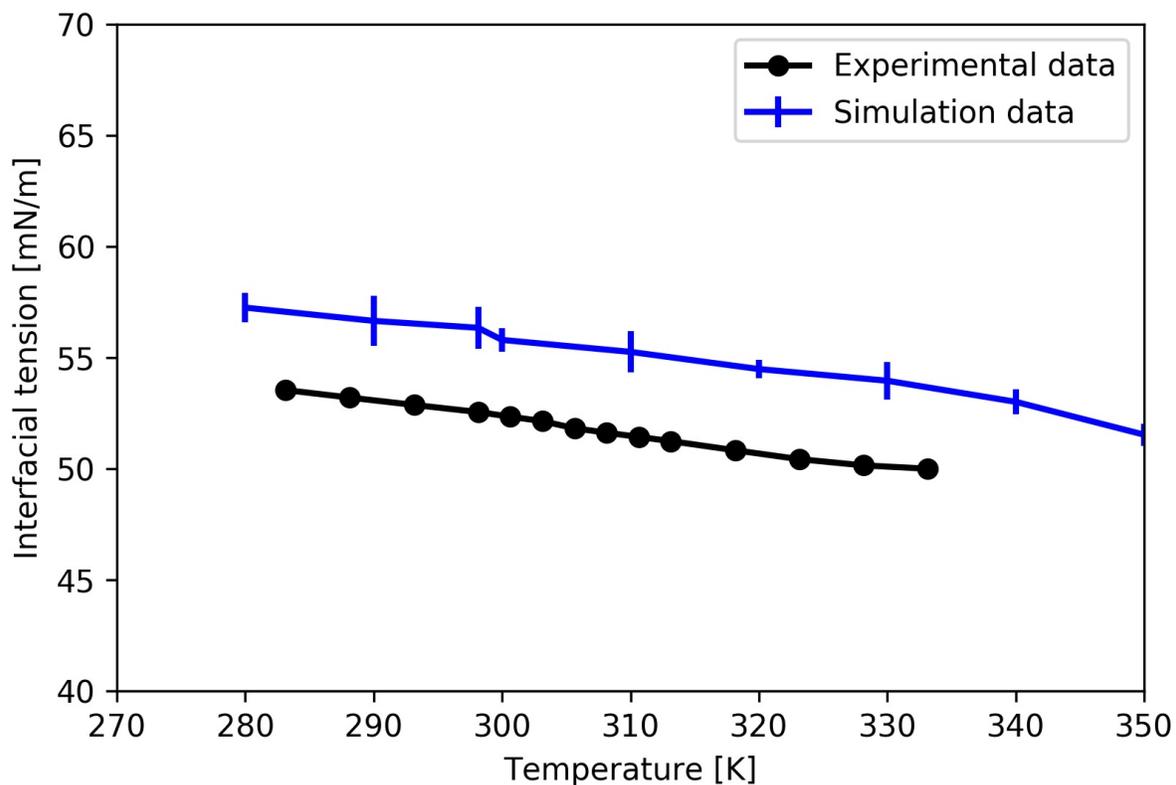


Fig. S1 Water/dodecane interfacial tensions as a function of temperature. Simulation results and experimental data are presented as blue and black lines, respectively.

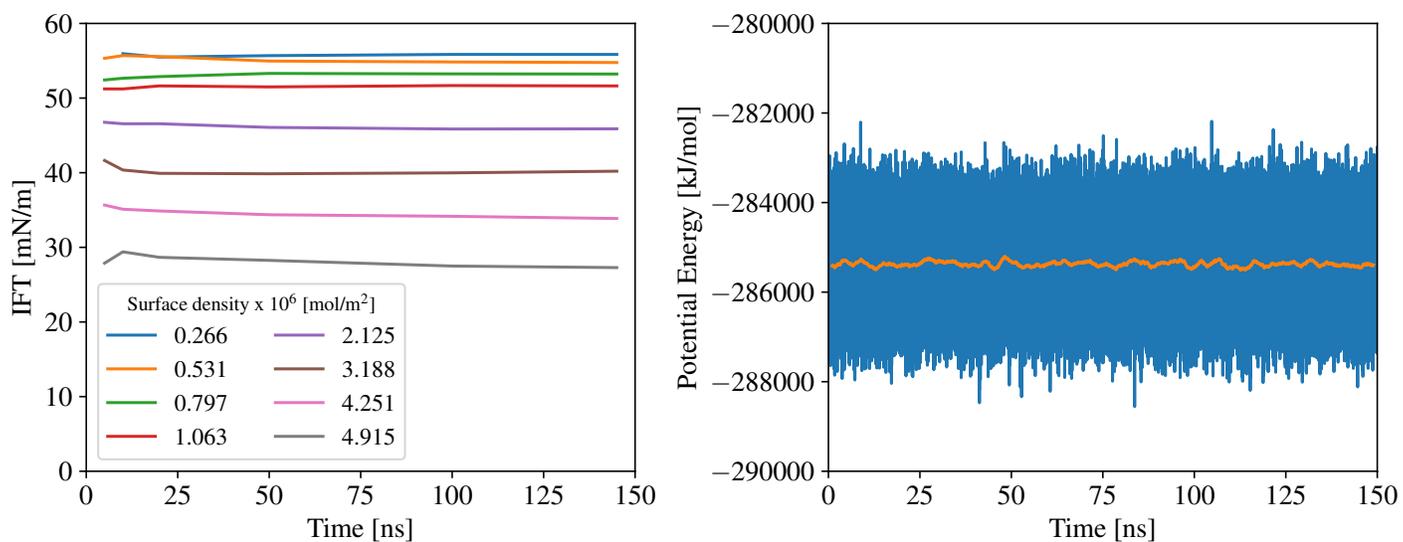


Fig. S2 Left: Interfacial tension as a function of simulation time at different SDS surface densities. For all simulations, the IFT values are stable after 100 ns. Right: Evolution of potential energy of the simulated system with 4.915 mol/m² of SDS. The orange curve represents the moving average values of the blue curve.

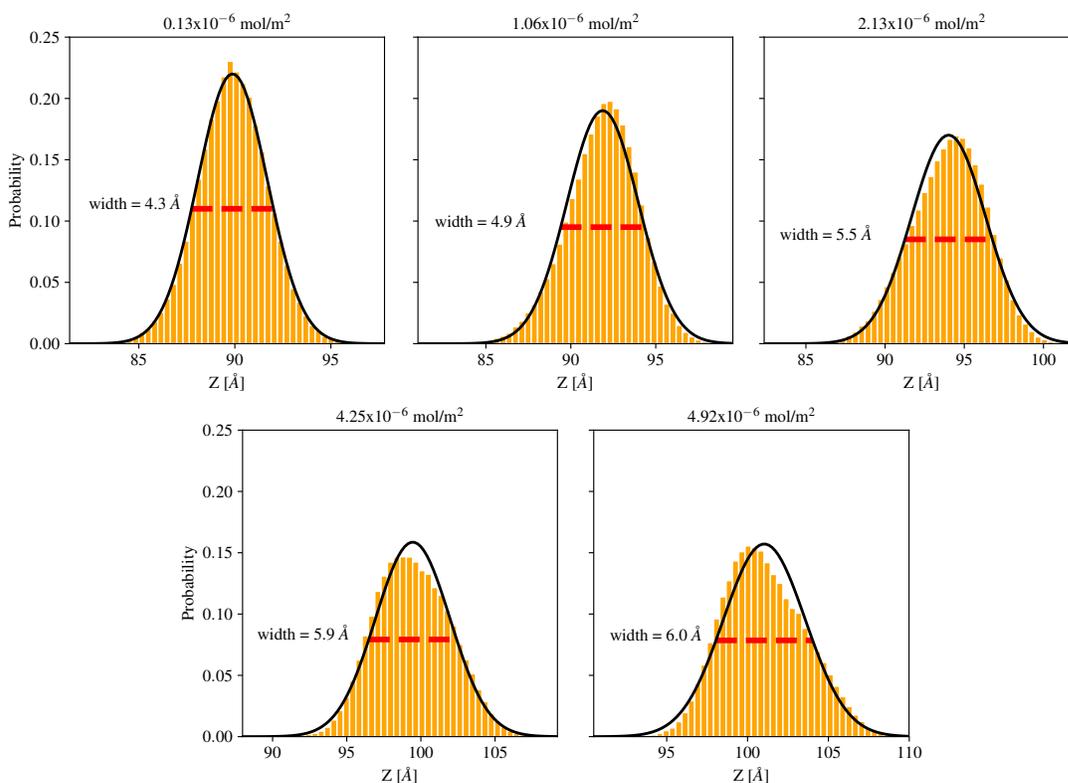


Fig. S3 Distributions of interfacial water molecules (identified using the ITIM algorithm) along the Z direction of the simulation box calculated at various SDS surface densities. The distribution was then fitted to a Gaussian distribution to calculate the full width at half maximum, which is referred as the interfacial width or interfacial roughness.

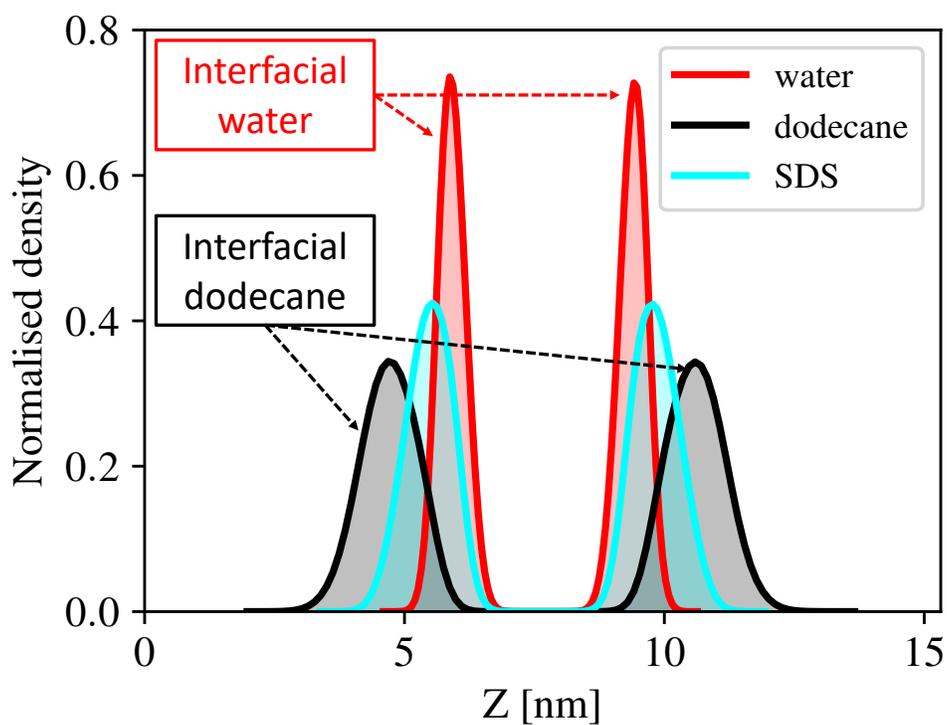


Fig. S4 Probability distribution of the interfacial water, dodecane, and SDS molecules along the Z direction of the simulation box identified by the ITIM algorithm using a probe sphere with a radius of 1.5 \AA .

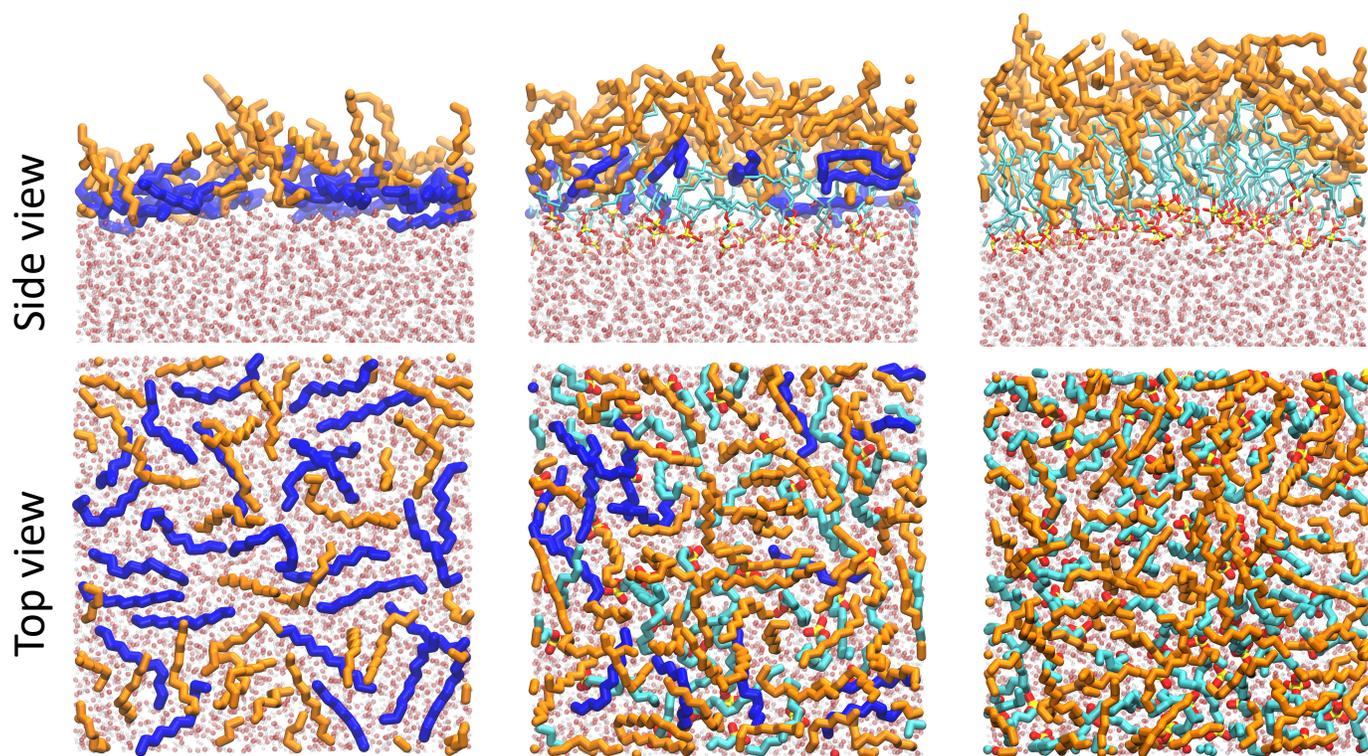


Fig. S5 From left to right: simulation snapshots showing the co-existence of SDS and dodecane molecules at the interface from low to high SDS surface densities. Oxygen atoms (present in water and SDS headgroups) are highlighted in red, hydrogen atom in white, SDS alkyl tails in cyan, whereas interfacial dodecane molecules identified using the ITIM algorithm are in orange and blue. The blue dodecane molecules are those that are found close and aligned parallel to the water surface.

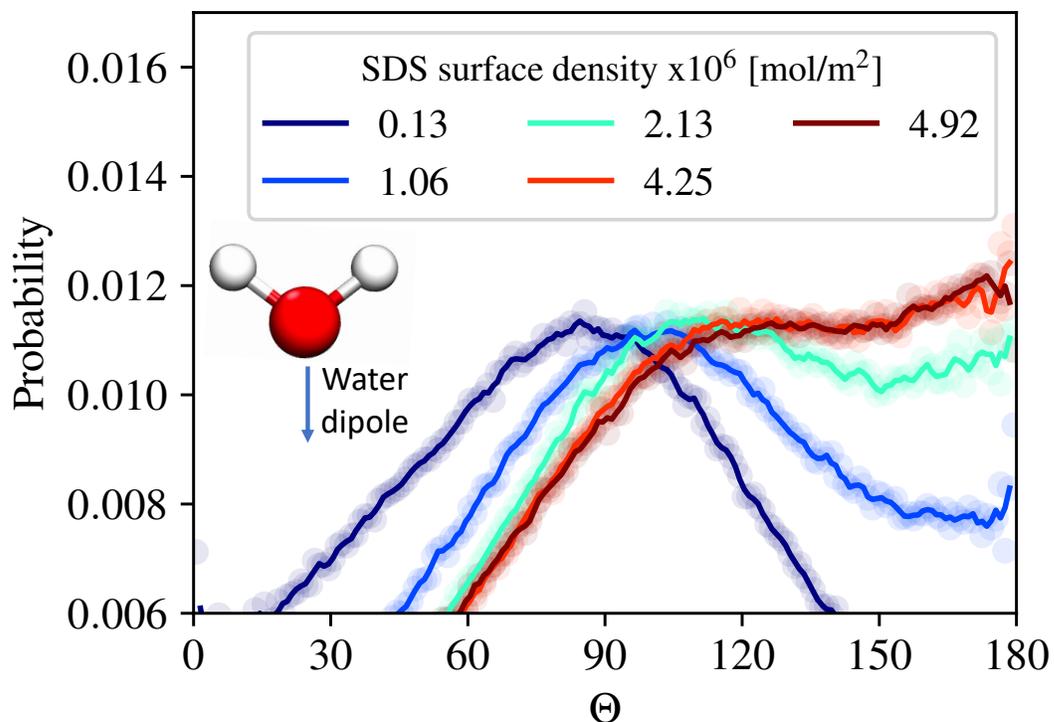


Fig. S6 Probability distribution of the angle formed between the water dipole moment vector and the interfacial normal vector (the Z direction) at different surface densities of SDS. A 90-degree angle indicates that the dipole moment vector of water is parallel to the interface's plane, whereas a 180-degree angle indicates that the dipole moment vector of water points away from the interface toward the bulk water phase.

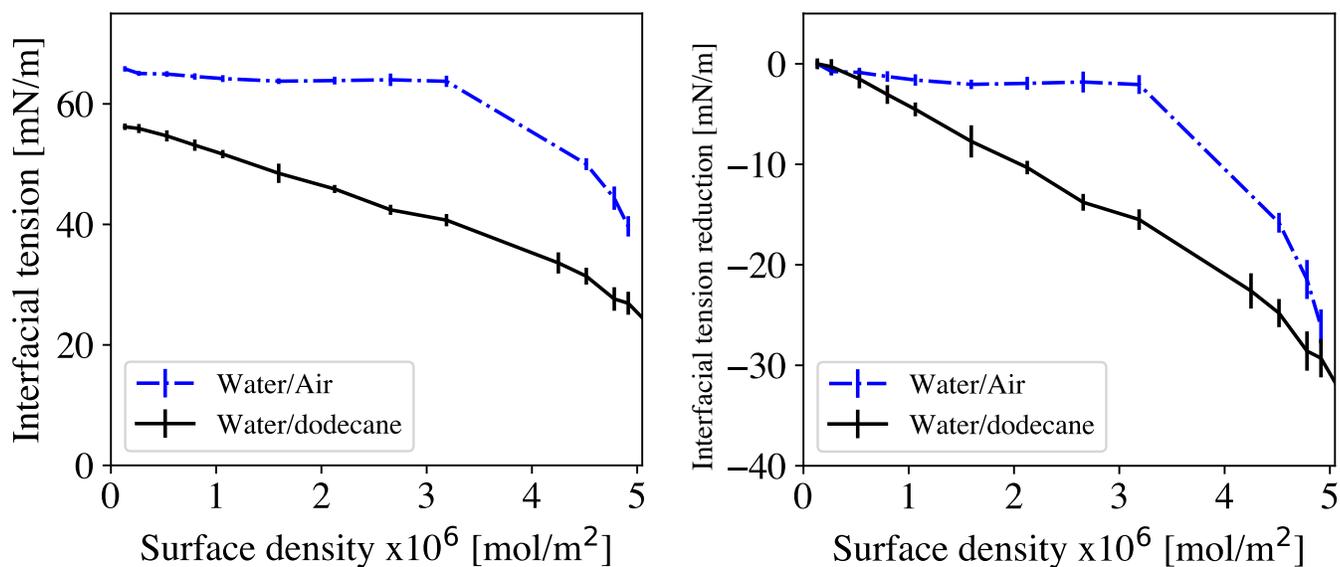


Fig. S7 Left: IFT values obtained for water/air and water/dodecane as a function of SDS surface density calculated at 293.15 K and 1 bar. Right: IFT reduction (as compared to the system without SDS) as a function of SDS surface density calculated for water/air and water/dodecane systems

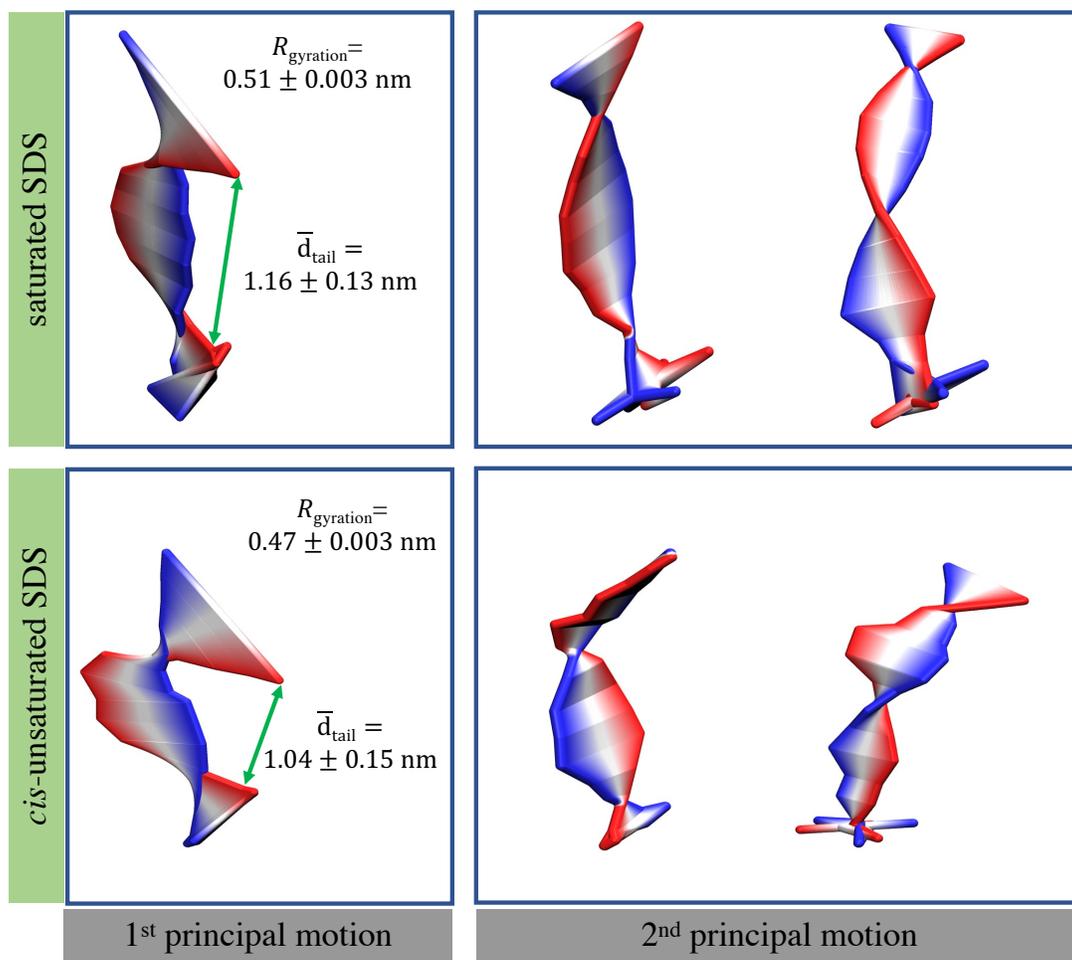


Fig. S8 From left to right: concerted motion projected on *eigenvector* 1 (the first principal motion) and *eigenvector* 2 (the second principal motion) of saturated (top) and unsaturated in *cis* conformation (bottom) SDS surfactants. The radius of gyration, $R_{gyration}$, and the end-to-end tail length, d_{tail} , are also displayed for the saturated and *cis*-unsaturated SDS. Color scale ranging from red to blue represents the amplitude of the two extreme projections along a trajectory on the average structure and 200 interpolated frames.

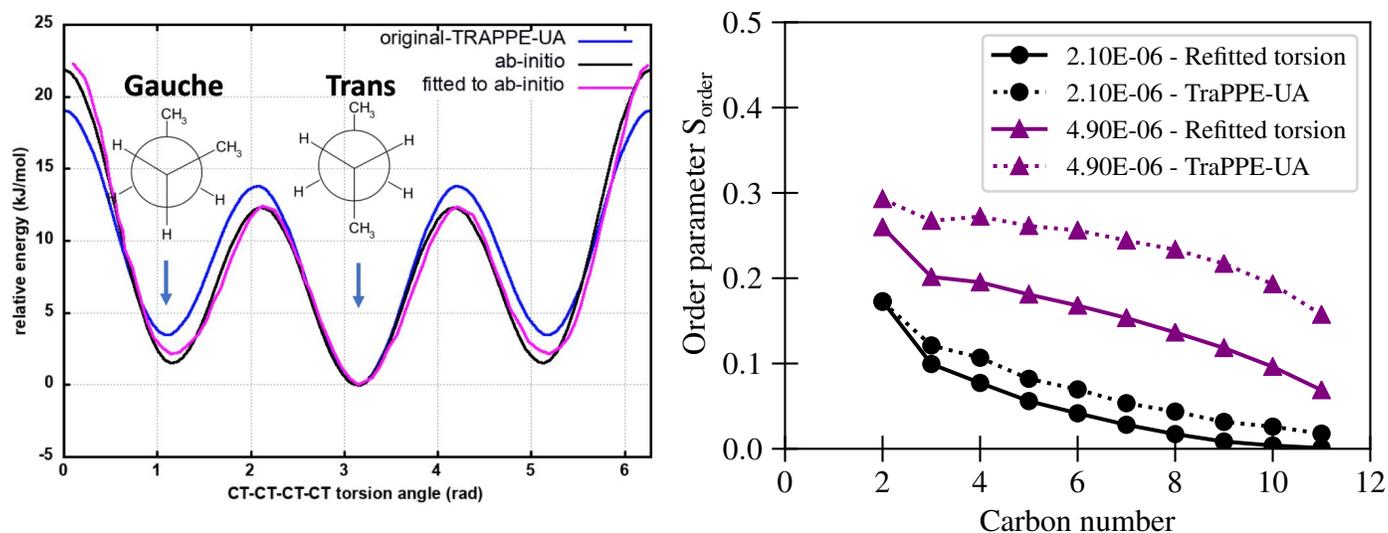


Fig. S9 Left panel: Torsional angle potentials calculated for C-C-C-C in alkyl chain. Different curves represent the torsional angle potentials for the original TraPPE-UA force field (blue), *ab-initio* data (black),³ and fitted to the *ab-initio* data (purple). The energy well in the middle represents the torsional angle potential of the trans conformation, while the other ones are the potentials of the gauche conformation. Right panel: order parameters obtained for the alkyl tail of the SDS surfactant when implementing a modification of the original TraPPE-UA force field in which the torsional angle potential was fit to reproduce *ab-initio* data (bold lines) and the original TraPPE-UA (dotted lines). Different colours represent the results obtained at different surface densities of SDS surfactants.

Notes and references

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- 2 M. J. Abraham, T. Murtola, R. Schulz, S. Páll, J. C. Smith, B. Hess and E. Lindah, *SoftwareX*, 2015, **1-2**, 19–25.
- 3 S. W. Siu, K. Pluhackova and R. A. Böckmann, *J. Chem. Theory Comput.*, 2012, **8**, 1459–1470.