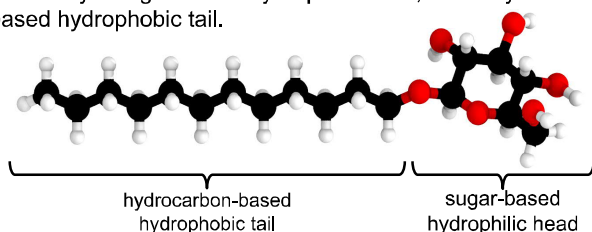


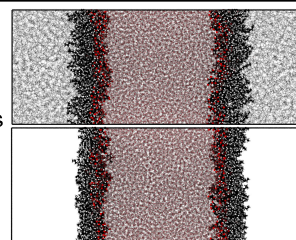
## INTRODUCTION

- Using atomistic molecular dynamics simulations, it is now possible to model systems that closely resemble those studied in the laboratory.
- The impressive visual graphics and the detailed molecular insight obtained from the calculations distract from the fact that these representations and their quantitative predictions are only as good as the quality of the underlying force fields which are used to describe the intermolecular interactions.
- The main issue is finding the right intermolecular potential with the appropriate balance of accuracy, transferability and representability.
- The systems under study herein include alkyl polyglucosides (APG) molecules; biocompatible and degradable surfactants formed by a sugar-based hydrophilic head, and a hydrocarbon-based hydrophobic tail.



## METHODOLOGY

- Two different interfacial environments are considered: water/air interface and water/oil interface (where the oil phase is represented by *n*-decane molecules). Each system has two layers of surfactant molecules.
- In terms of molecular description, the new generation of the polymer compatible force field (*pcff+*) is used in this work. The *pcff+* force field traces its origin to the family of the COMPASS force field, which has been optimized to model polymers containing organic compounds.



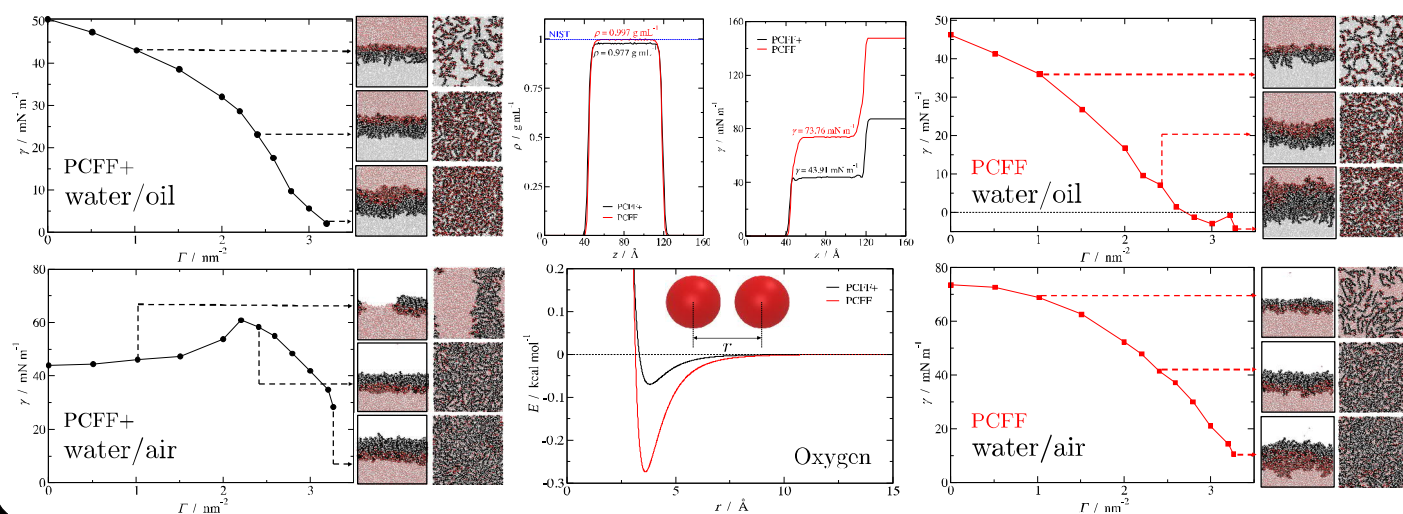
$$E_{vdW} = \varepsilon \left[ 2 \left( \frac{\sigma}{r} \right)^9 - 3 \left( \frac{\sigma}{r} \right)^6 \right]$$

- The interfacial tension is measured through the Irving-Kirkwood (IK) method, which integrates the difference between the normal and the tangential pressure through the coordinate perpendicular to the interface (*z*):

$$\gamma = \int_{-\infty}^{+\infty} \left[ \langle P_{zz}(z) \rangle - \frac{\langle P_{xx}(z) \rangle + \langle P_{yy}(z) \rangle}{2} \right] dz$$

## RESULTS

- The plots from the left-hand side display the interfacial tension,  $\gamma$ , as a function of the number of surfactants per interfacial area,  $\Gamma$ , at 298.15 K. The use of the *pcff+* water model leads to an unexpected behaviour, showing a maximum in the tension curve for the water-air interface.
- From the simulation snapshots, it is possible to observe that before that point, the surfactants are clustering on the surface, which is also unexpected in this context.
- Employing a compatible water model with a different parametrization (actually an older model, labelled here as *pcff*) the issue resolves itself. The *n*-decane and the APG molecules were kept with the *pcff+* parameters.
- The *pcff* water model provides a more accurate value for the interfacial tension. This corrects the trend of the interfacial tension of the APG at the water-air interface (right-hand side plots).



## CONCLUSIONS

- The accurate description of the interfacial tension of *n*-dodecyl- $\beta$ -glucoside (APG12) at both water/oil and water/air interfaces is crucially dependent on the properties of the water force field employed. Even though the *pcff+* model has been optimized to fit the bulk water properties, it falls at reproducing the correct physics at the interface.
- The example raises the general question of how much faith we can/should have on the predictions of molecular dynamics simulations and the importance of testing the validity of the potentials against experimental results.