Lateral Equations of State of Surfactants at Interfaces: A Multiscale Perspective

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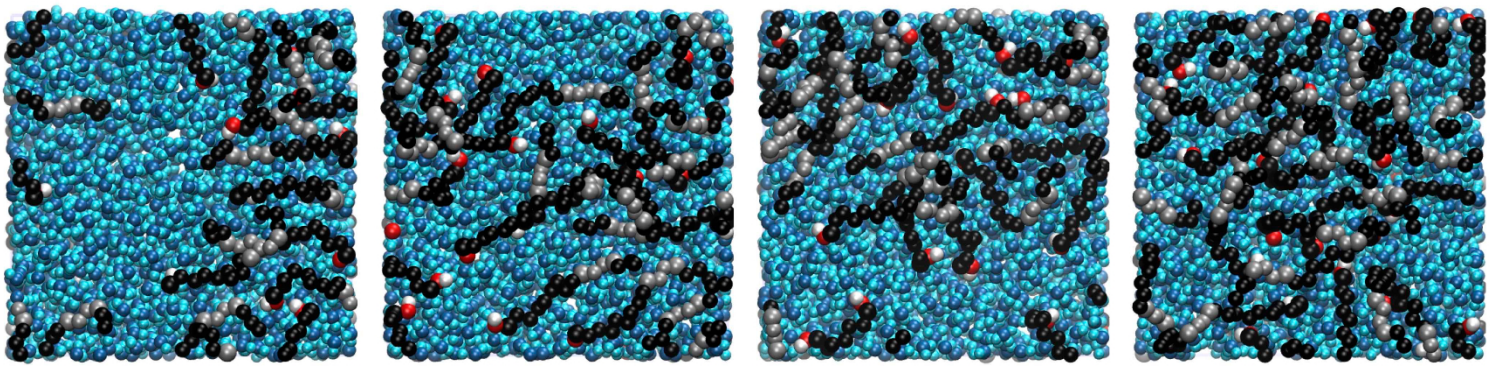
Surfactant molecules are commonly characterized by their lateral equation of state, which encodes the thermodynamic properties of the interface onto which they adsorb. This concept underpins a wide range of applications. For instance, the critical micelle concentration (CMC) of amphiphilic molecules in solution can be inferred from surface tension measurements. However, the underlying physics is intrinsically complex, as it involves the interplay between two coupled equations of state: one in the bulk phase, governing intermolecular interactions, and another at the interface, where competing attractive and repulsive surface interactions may arise. As a result, extracting unambiguous macroscopic properties from experimental observables remains challenging. For example, a plateau in surface tension may reflect either micelle formation in the bulk or saturation of the interface.

To address these issues, we perform classical molecular dynamics simulations within a multiscale framework to determine lateral equations of state as accurately as possible in representative systems. In the context of solvent [1] extraction, the adsorption of a diamide extractant at the liquid–liquid interface is characterized in detail, revealing its coupling to aggregation processes in the organic phase. We also investigate bombykol, an amphiphilic pheromone [2] potentially present at aerosol surfaces, to elucidate how interfacial behavior may influence long-range insect communication. Additional applications related to flottation [3] processes are currently under investigation.

Our results highlight that, whenever interfacial concentrations cannot be directly measured, the apparent lateral equation of state reflects a subtle balance between bulk and interfacial equilibria. This coupling complicates the interpretation of surface tension data alone, as distinct physical mechanisms—including interfacial phase transitions—may produce similar signatures.

More broadly, this multiscale approach, combining colloid and interface theory with molecular simulation, provides a unified framework in which seemingly puzzling phenomena emerge as natural consequences of underlying thermodynamic constraints. For example, the frequently observed synergy in extractant mixtures can be rationalized by an increase in configurational entropy, while abrupt changes in surface tension may be interpreted as signatures of frustration effects within interfacial assemblies.

Keywords:
Surfactant, equation of state, surface tension, aggregation, saturation, molecular dynamics, pheromones, solvent extraction



Molecular Dynamics Simulations of Bombykol at the Air–Water Interface

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