

COARSE-GRAINED SIMULATIONS OF OIL-WATER-SURFACTANT MIXTURES

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EXTENDED ABSTRACT

Mixtures of oil and water are naturally unstable but they can be stabilized by addition of surfactant molecules to form microemulsions. Microemulsions are macroscopically homogeneous mixtures but present, at the microscopic scale, large heterogeneities with water-rich and oil-rich domains separated by a surfactant film. The properties of this film are essential for microemulsions as a whole; amongst them, interfacial tension plays a crucial role as it is strongly related with the microemulsion structure [1].

Intensive research in this area have shown that interfacial tension at the oil-water interface can be modified by several factors including the chemistry of the surfactant hydrophilic part (ionic or non-ionic), the number and length of the hydrophobic parts, surfactant concentration, addition of a co-surfactant, addition of salts [2,3,4]. . . In order to understand the interplay between the different species in presence and eventually to tailor new surfactants or even surfactant mixtures, several attempts have been made to compute interfacial tension from molecular dynamics, Monte Carlo or coarse-grained simulation tools. As usual, the prediction of thermodynamical properties using approaches based on statistical mechanics, requires both an efficient tool to sample the phase space of the system and an empirical forcefield that describes intermolecular interactions as accurately as possible.

Monte Carlo and Molecular Dynamics simulations make an intensive use of empirical forcefields that can accurately predict surface tension in simple liquids or liquid mixtures. By using a system description at the atomistic level, a good understanding of processes can be gained. However, the time and length scales involved in the simulation of oil-water-surfactant usually go beyond what is commonly attainable today with these tools. Therefore, coarse-grained simulations, where particles represent several molecules, or groups of atoms inside a given molecule, are nowadays used as an alternative tool to study such complex systems. One of the most commonly used tool is dissipative particle dynamics proposed by Hoogerbrugge and Koelman [5].

In this paper, we will try to review the difficulties that arise from studying such systems using coarse-grained models [6], in particular when direct comparison with experimental data is wished (see Fig. 1 and Fig. 2).

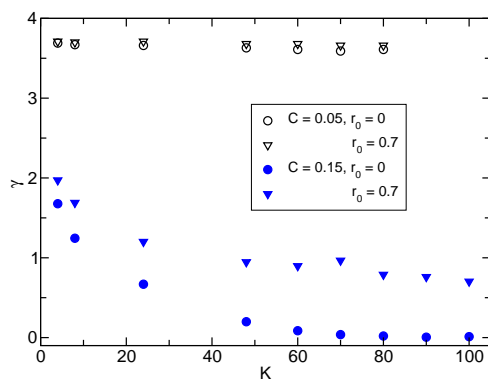


Figure 1. Interfacial tension γ in a model oil-water-surfactant mixture, versus the intramolecular bonding force constant K for different equilibrium bond lengths r_0 and different surfactant concentrations. At large surfactant concentration, surface tension strongly depends on surfactant intramolecular parameters.

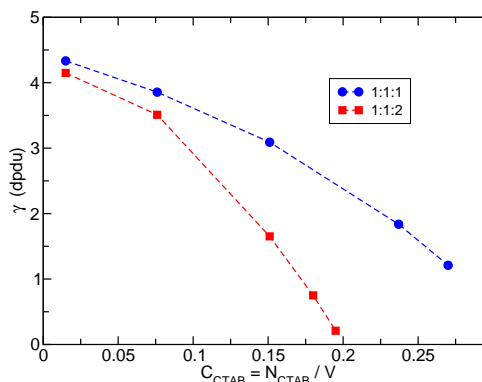


Figure 2. Interfacial tension γ in a model oil-water-surfactant mixture, versus total surfactant concentration in boxes with different shapes (cubic and parallelepipedic). It is shown that interfacial tension depends on box shape if plotted versus total surfactant concentration. Rather, "bulk concentration" or "interfacial concentration" must be used in order to get meaningful results.

We will present the conditions under which chemical (and thermodynamical...) equilibrium is reached and show that spurious effects can arise such as *box shape* effects. We will discuss the possible solutions that have been proposed to handle electrostatic interactions in coarse-grained models, and how consistent forcefield can be derived to describe accurately such systems. Last but not least, we will wonder how dynamical informations can be obtained from dissipative particle dynamics simulations.

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