A molecular dynamics study of interfaces: from pure liquids to biological membranes
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Summary

The aim of this work is to study, by computer simulations, various interfaces and their properties. We have used different interface models: a simple two phases system (liquid-vapour alkane, an oil-like molecule), a hydrophobic-hydrophilic interface (liquid-liquid water-hexane, an alkane), a similar interface containing a surfactant lipopeptide (surfactin), and a biological membrane made of spanning lipids from archaeabacteria. This work has been done using the molecular dynamics technique (MD), and almost all the models have been described at an atomic scale, providing a realistic representation of the modelled materials.

First, we introduce in chapter 1 the terms used in this work, define the scope of the thesis, and give a very brief description of the molecular dynamics (MD) technique.

The first part (A) of the manuscript reports both the study of a liquid-vapour alkane model (chapter 2) and the study of a hexane-water liquid-liquid interface (chapter 3). We present in the former chapter a method of interfacial tension calculation, and probe it for a range of linear alkane lengths, two ranges of temperature, and two sets of force field parameters (set of parameters which give a representation of the molecular properties and dynamics). The implementation of the method used gives interfacial tension predictions in nice agreement with experiments. In the latter chapter, we study the topology and properties of the interface. The interfacial broadening from capillary waves (small waves occurring at the interface and responsible for an 'interfacial width') is, for the first time, investigated both qualitatively and quantitatively, for a non-ideal liquid-liquid system. We found that the interfacial widths calculated from computer simulations are much smaller than the widths predicted from the capillary waves theory. We suggest that the apparent disagreement comes from the correlation length parameter (defined as the minimum length between two particles with uncorrelated motions) often taken as a molecular length or diameter in the literature.
The second part (B, chapter 4) of the manuscript concerns the study of a bio-surfactant (surfactin, a lipopeptide composed of seven amino-acid residues and a long aliphatic chain, which is oil-like) at the water-hexane interface. This molecule is an efficient surfactant, decreasing the water surface tension by a factor 2 at low concentration. Moreover, experimental results suggest that this molecule exhibits various interesting biological properties. This is the first extensive and realistic MD simulation of surfactin done at a hydrophobic-hydrophilic interface. We have investigated the molecular motions, the peptide folding, the intra- and inter-molecular hydrogen bonds, and the dynamics of the surfactin. This surfactant exhibits a 'chimeric' geometry depending on the interfacial concentration of surfactants. The molecule has a stable structure and is tensioactive at a sufficient interfacial concentration. Below this limit, the molecule is in a 'horse-saddle' shape, but none of the hydrogen bonds is conserved, and the dihedral angles characteristic for the amino-acid residues (Ramachandran angles) fluctuate a lot.

The last part (C, chapter 5) presents the first long MD study of five tetraether lipid membrane models. The models differ with respect to the number of cyclopentane rings per lipid molecule, and their positions. Cyclopentane rings are supposed to maintain the low permeability of the membrane at high temperatures. We have investigated their effects on the membrane properties by the study of the five different models. Furthermore, the absolute configuration of the the carbons linking the rings to the rest of the chain differs from one side of the chain to the other one (which means they are chiral, thus, as two hands, cannot be superimosed). We investigate the membrane physical properties and the membrane organization. We report the dependence of the lipid membrane topology on the lipid structure, and more specifically the presence of rings on the aliphatic chains. Moreover, we correlate the pressure profile to the absolute configuration of the aliphatic carbons, by the comparison between the pressure profiles of each hydrophobic side of the membrane.