



Reprint of “Role of the fluidity of a liquid phase in determining the surface properties of the opposite phase”[☆]

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ABSTRACT

Molecular dynamics simulations of the water–CCl₄ interface have been done in two different ways. In the first simulation the CCl₄ phase has been frozen in an equilibrium configuration, and only the water molecules have been allowed to move, whilst in the other one no such artificial freezing has been done. This way the effect of the fluid-like structure and fluid-like dynamics of the CCl₄ phase on the surface properties of the aqueous phase could be investigated separately. Due to the separate thermostating of the two types of molecules in the simulations all the differences seen between the interfacial properties of water in the two systems can indeed be attributed to the rigid vs. fluid nature of the organic phase, and not to the thermal contact with a phase of zero temperature. The obtained results reveal that the rigidity of the opposite phase introduces an ordering both in the layering structure and orientation of the surface water molecules. The enhanced orientational ordering leads to a stronger lateral hydrogen bonding structure of the molecules within the subsequent molecular layers beneath the surface, and hence also to a slower exchange of the water molecules between the surface and the bulk aqueous phase.

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1. Introduction

Investigation of the molecular level properties of various fluid (i.e., liquid–vapour and liquid–liquid) interfaces became the focus of intensive scientific research in the past fifteen years. Although fluid interfaces play a key role in a number of processes of fundamental scientific interest, in living systems, and in numerous industrial applications, such investigations were previously largely prevented by the lack of suitable experimental methods that can selectively probe interfacial molecules. The recent development and spread of this kind of methods, such as nonlinear (e.g., sum frequency generation or second harmonic generation) spectroscopies [1,2] or x-ray and

neutron reflectivity measurements [3] enabled scientists to meaningfully address such problems, and thus resulted in a rapidly growing number of such studies [4–24].

Experimental investigations can be well complemented by computer simulation studies, since simulation methods can provide us with a three dimensional model of atomistic resolution of the system of interest. Thus simulations can offer deeper insight into the appropriately chosen model of the system than conventional experiments are likely to reach [25]. The rapid development of the routinely available computing power has led to a significant increase in the number and quality of simulation studies of fluid interfaces [26–55], which has paralleled the similar development in the experimental fields in the past two decades.

However, when simulating fluid interfaces at atomistic resolution one has to face the problem that finding the exact location of the interface in such systems is not a trivial task at all. The problem originates from the fact that fluid interfaces are corrugated by capillary waves due to the thermal motion of the molecules. The task of finding the real, capillary wave-corrugated intrinsic interface is analogous with that of finding the full list of molecules that are located right at the surface of their phase (i.e., in contact with the opposite phase) at every instant along the simulated trajectory. Until recently, the majority of the interfacial simulation studies simply neglected this problem,

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and used the (ideally planar) Gibbs dividing surface instead of the real, capillary wave-corrugated intrinsic interface. However, it is now clear that this neglect leads to systematic error in the calculated structural properties [47,56] and composition [44,45,50] of the interface, and even in the thermodynamic properties of the system studied [51]. Thus, for instance, the critical mixing line of the water–benzene system was found to appear at 100–200 K lower temperature than its real location when the interface between the two phases is treated in a non-intrinsic way. [51]. Further, when comparing simulation results with experimental data it is essential to calculate the quantities of interest exactly on the same set of molecules that are probed in the experiment, i.e., the molecules that are located at the real, intrinsic surface of their phase.

The first method designed to determine the intrinsic surface of a fluid phase, proposed by Chacón and Tarazona [57] was followed in the past decade by several alternative approaches, [40,41,56,58–60] some of which do not even require the interface to be macroscopically planar [58,60]. Amongst these methods the Identification of the Truly Interfacial Molecules (ITIM) [56] has turned out to be an excellent compromise between computational cost and accuracy [59]. In an ITIM analysis the molecules located at the boundary of their phase are detected by moving a probe sphere of a given radius along a large set of test lines from the bulk opposite phase; and the molecules of the phase of interest that are first touched by the probe sphere along any of the test lines are marked as being interfacial [56]. The ITIM method has successfully been applied recently to a set of liquid–liquid [43,46,47,51] and liquid–vapour [44,45,48–50,52–55] interfacial systems. The use of an intrinsic surface analysis method, such as ITIM has the additional advantage that various surface properties, such as intrinsic density [41,42,57,60,61] or free energy profiles [62,63], roughness of the intrinsic surface [49,53,56] and its relation with the surface tension [64], lateral percolation of the surface molecules [51,55,56], dynamics of exchange of the molecules between the surface layer and the bulk phase [43–50,53,65], adsorption of molecules at the surface and its extent in terms of molecular layers [44,45,50], or immersion of large surface molecules (e.g., surfactants) into the bulk phase [65–67] can be meaningfully addressed this way.

In this paper we address another fundamental question, namely the role of the fluidity of one phase in determining the surface properties of the other one at the liquid–liquid interface. At a liquid–liquid interface two dynamically fluctuating fluid phases meet. It is reasonable to assume that some coupling exists between these fluctuations of the phases. It is natural to ask then how would one of the two liquid phases behave if the fluctuations of the other one were stopped. To address this question we performed molecular dynamics simulations of the water–CCl₄ system in two ways. In the first simulation the molecules of the organic phase were frozen in an equilibrium configuration of the liquid–liquid system, and only the water molecules were allowed to move. This way, the CCl₄ phase was turned into a glass-like phase, and hence it could not adapt to the fluctuations occurring at the surface of the aqueous phase, neither could the capillary waves of CCl₄ exhibit any interference with those of the aqueous surface. In the other simulation, used here for reference, no such artificial freezing has been done, and hence the real water–CCl₄ interface has been simulated. It should be emphasized that the first simulation is not intended to, and does not correspond to any physically relevant system. Computer simulation provides a unique opportunity to formally decouple several factors that cannot be done in real systems, making it possible to analyze their role separately from each other. Our approach takes advantage of this opportunity, by decoupling the fluid-like structure and dynamics of the organic phase in order to analyze their separate roles in determining the properties of the surface of the aqueous phase. The properties of the water surface obtained in the two ways are then compared in terms of density profiles of the subsequent subsurface layers, surface roughness, dynamics of exchange of the bulk phase and surface

molecules, as well as orientation and percolation of the surface molecules.

The paper is organized as follows. In Section 2 details of the simulations performed are given. The obtained results are discussed in detail in Section 3. Finally, in Section 4 the main conclusions of this study are summarized.

2. Computational details

Molecular dynamics simulations of the water–CCl₄ liquid–liquid interface have been performed on the isothermal–isobaric (N,p,T) ensemble at 298 K and 1 bar. The rectangular basic simulation box consisted of 4000 water and 2000 CCl₄ molecules. The Y and Z edges of the basic box, being parallel with the macroscopic interface have been set to be 50 Å long, whilst the X axis has been left to fluctuate according to the semi-isotropic pressure coupling applied.

Water and CCl₄ molecules have been described by the rigid TIP4P [68] and OPLS [69] potential models, respectively. According to these models, the total potential energy of the system has been calculated as the sum of the pair interaction energy terms, the latter being equal to the sum of the Lennard–Jones and Coulomb contributions of all the pairs of the interaction sites of the two molecules. The geometry of the water and CCl₄ molecules have been kept unchanged by means of the SETTLE [70] and LINCS [71] algorithms, respectively. All interactions have been truncated to zero beyond the cut-off distance of the molecule centres of 12.5 Å; the long range part of the electrostatic interaction has been taken into account using the Ewald summation method in its smooth particle mesh (PME) implementation [72].

Simulations have been performed using the GROMACS simulation package [73]. The temperature and pressure of the system have been controlled by the Nosé–Hoover [74,75] and Parinello–Rahman [76] algorithms, respectively. The equations of motion have been solved in time steps of 2 fs. Initial configurations have been taken from an earlier simulation of us, thus, even the starting configurations supposed to be in equilibrium [43]. Nevertheless, we further equilibrated the system for 5 ns, during which energetic and structural properties did not change tendentially. After this equilibration, two simulations have been performed. In the first of these simulations, referred to here as I or the “frozen” simulation, the CCl₄ molecules have been fixed at their initial positions, and only the water molecules have been moved. Technically this has been done by setting the temperature of the CCl₄ phase to zero. However, since the water and CCl₄ molecules have been thermostatted separately, this treatment has not led to a cooling down of the aqueous phase (i.e., slowing down of the water molecules) at all. In other words, the separate thermostating has introduced a perfect virtual non-interacting thermal insulator between the two phases. In the other run, called as II or the “reference” simulation CCl₄ molecules have also been moved in the regular manner, according to the forces acting on them. In both cases a 5 ns long trajectory has been simulated, along which 2500 sample configurations per system, separated by 2 ps long trajectories each, have been saved for further evaluation. The calculated interfacial properties have been averaged for the 2500 sample configurations, including both liquid–liquid interfaces present in the basic simulation box.

The intrinsic surface of the aqueous phase has been identified by means of the ITIM method [56]. In the ITIM analyses a probe sphere of the radius of 1.25 Å has been used, according to the suggestion of Jorge et al. [59]. The test lines along which the probe was moved have been arranged in a 100 × 100 grid across the interfacial plane YZ . This resolution corresponds to a distance of 0.5 Å of two neighbouring grid lines, which is sufficient to get an accurate mapping of the water surface [59]. The ITIM procedure has been repeated three times by disregarding the set of molecules identified in the previous steps. This way, the first three molecular layers beneath the surface of the aqueous phase have been identified separately [56]. An

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