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# Computersimulation of Free Liquid Surfaces

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Structure and dynamics on the microscopic level are important for the understanding of reactions taking place in liquid surfaces and liquid / liquid interfaces. We use different experimental techniques which are briefly described: besides conventional methods for studying macroscopic properties like surface tension we use a spectroscopic approach to gain information on a molecular level.

After outlining this spectroscopic technique experimental results are introduced. They have motivated to the computer simulation studies described afterwards.

In the present article we focus on binary liquid mixtures, one of them being miscible (formamide and benzyl alcohol) the other one exhibiting a miscibility gap (formamide and hexane).

In both cases we examine whether experimental results can be supplemented by the simulation. A special interest deals with the question how much orientational and dynamical properties of one liquid are affected by the presence of a second species.

While many computer simulations examine bulk properties we present a special strategy to create a liquid lamella with two interfaces liquid / vacuum. This gives the opportunity to study molecular properties for different surroundings, namely the liquid bulk and the surface exposed to vacuum.

## 1 Introduction

A large part of research done in our group focusses on the characterization of liquid surfaces based on experimental techniques. The composition of the surface region, molecular orientation and the kinetics of adsorption processes are of interest.

Different experimental techniques are used to monitor these properties: a macroscopic method to study changes in the liquid surface due to surfactants is the static or dynamic surface tension (tensiometry). Using concepts developed in thermodynamics like the Gibbs adsorption equation such measurements lead to properties like the surface excess of the different components in a mixture.

Since these experiments do not trace features on a molecular scale a special interest in our group is the application of spectroscopic methods to elucidate system parameters on a molecular level.

One technique being an established tool to characterize solid surfaces due to its high surface sensitivity is electron spectroscopy: illumination of the sample leads to electron emission, which originate from a layer being only several Å up to a few nm thick. Analysis of the energy and angular distribution of these photoelectrons gives a handle on target composition, binding properties and structural information. Variation of photon energy and

electron emission angle allows recording of concentration depth profiles. In the early 70th electron spectroscopy was used for studying liquid surfaces for the first time<sup>1</sup> (X-ray Photoelectron Spectroscopy XPS, ESCA). In 1986 MIES (Metastable Induced Electron Spectroscopy) was introduced as perfect surface sensitive type of electron spectroscopy<sup>2</sup>: the projectile beam consists of excited helium atoms having an electronic energy of  $\sim 20eV$ . The thermal kinetic energy of  $\sim 50mV$  prevents the helium atoms from penetrating into the target material. MIES is chemically sensitive, traces molecular orientation in the outermost surface layer and allows quantitative analysis of particle ratios.

Electron spectroscopy averages over a certain time and sample volume. With our equipment adsorption processes as function of the age of the liquid surface can be studied. The regime accessible goes from  $\sim 2 - 25ms$  or from a few hundred  $ms$  up to a few  $s$ , depending on the type of target arrangement chosen. This allows to monitor diffusion processes perpendicular to the liquid surface. A lateral movement is not traced by the experiment but can be evaluated from computer simulation. In case of an inner surface for polar / unpolar systems with miscibility gap the high surface sensitivity of electron spectroscopy prevents a study due to the limited mean free path of  $e^-$ . In this case MD simulation is an ideal tool to gain details of inner surfaces.

In the following section we first describe experimental studies that gave rise to our simulations. Afterwards results of the computer simulations are outlined.

## 2 Motivation for the Simulation Due to Experimental Results

### 2.1 The Binary Liquid System Formamide / Benzyl Alcohol

The system formamide (FA) and benzyl alcohol (BA), which is miscible for molar fractions ranging from 0 to 1, was investigated both with electron spectroscopy and with tensiometry. Both methods reveal BA to be the surface active component, its surface tension being  $39 \frac{mN}{m}$  compared to  $52 \frac{mN}{m}$  in case of FA.

With MIES which is sensitive for the molecular orientation it could be seen that both species show preferential orientation in the liquid surface: The FA lies more or less flat in the time average whereas BA tends to expose the benzene ring to vacuum. The surface active BA starts to form a layer on top of the formamide when its concentration is increased. It is assumed that this layer shows holes for a certain ratio BA/FA in which FA is embedded with an orientation determined by the dipole moment of the benzyl alcohol.

The aim of our simulation study is to elucidate this ordering process at the interface liquid / vacuum and trace differences between bulk and surface properties.

### 2.2 The Binary Liquid System Formamide / Hexane

The general interest in 2-phase-systems polar / unpolar with a miscibility gap with regard to industrial application is expressed in many studies with water as polar component and a second unpolar liquid .

In our experimental studies we have replaced water by formamide in order to benefit from its lower vapor pressure. In two types of experiments we have investigated the influence of a phase transfer catalyst (tetrabutylammoniumiodide = TBAI) onto the interface formamide / alkanes. In both studies we find that the alkanes can form a closed thin

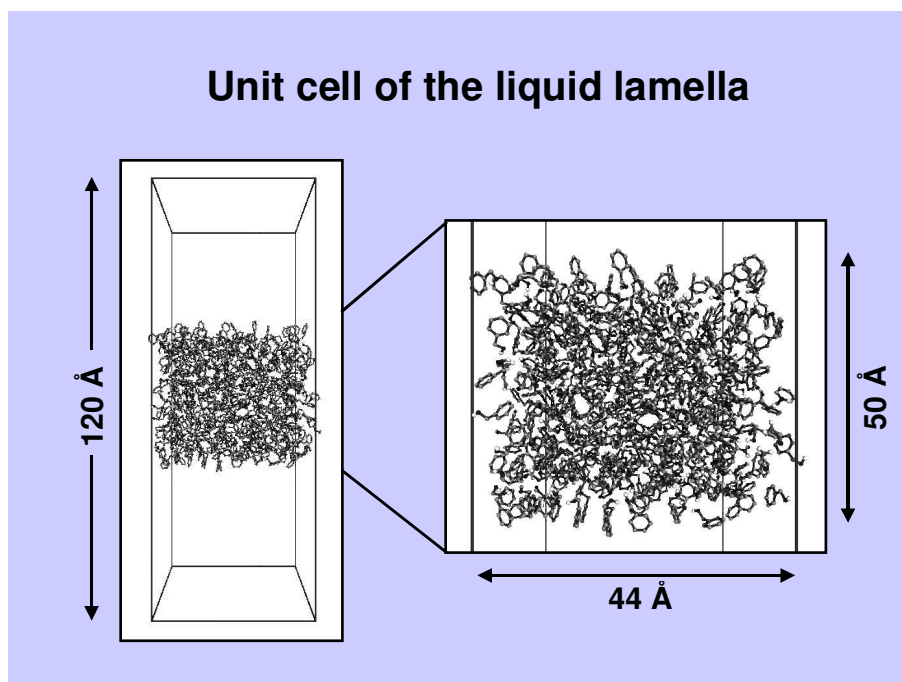


Figure 1. Schematic picture of the boundary conditions used: The simulation box is elongated in Z-direction in order to create 2 surfaces liquid / vacuum.

(mono)layer on the liquid formamide. Addition of TBAI destroys the closed alkane layer and leads to accumulation of both, TBAI and alkane, below the surface.

In addition to the limitation due to its time averaging the high surface sensitivity of electron spectroscopy prevents us from studying the interface polar / unpolar in usual 2-phase-systems which are macroscopically large. The only experimental approach using electron spectroscopy uses a very thin layer of alkane with a thickness not higher than the mean free path of the electrons which amounts to a few nm. Here MD-simulation is an appropriate method to overcome these experimental obstacle in order to model 2-phase-systems in general.

### 3 Special Features for Simulating Liquid Surfaces

A high percentage of computer simulation carried out deals with bulk properties. The use of three dimensional boundary conditions allows to study in principle macroscopically extended systems by looking at a simulation box of typically a few 100Å edge size.

In case of our simulation of liquid surfaces we follow a different strategy (fig. 1): we use a simulation box which has no cubic shape but is elongated in Z-direction (the later surface normal). A liquid slab is then centered in Z and periodically continued in X- and Y-direction. The Z-size is large enough to avoid interaction between the actual simulation box and its copy below and above.

The slab geometry has the advantage that two interfaces liquid / vacuum are created. This can either be used to improve statistics or one can imbed some surfactant in one surface in order to compare the *pure* surface with the enriched one. This gives the possibility of studying molecular properties in three different surroundings: the bulk liquid and two different interfaces liquid / vacuum.

On the other hand the extend in Z must not be too high in order to keep the number of vectors calculated in the Ewald summation as small as possible.

## 4 Simulation Results

### 4.1 Introduction

This section deals with results from our MD simulation. Parameters of the different systems are listed in tables 1, 2.

### 4.2 Binary System Formamide and Benzyl Alcohol

molecular parameters				
	name	formular	sites	number
species 1	benzyl alcohol	$C_6H_5CH_2OH$	9	420
species 2	formamide	$HCONH_2$	5	80
simulation parameters				
program	computer	knots	Box X,Y,Z [Å]	timestep [fs]
DL-POLY	CRAY T3E Jülich	32	44, 44, 120	2
	local workstation	1		
run parameters				
simulated time [ps]		temperature [K]		
1385		300		

Table 1. MD-simulation benzyl alcohol + formamide, parameters.

We carried out simulations for both liquids and for the mixture<sup>4,5,8</sup>. This offers the opportunity to explore how much molecular features are influenced by the second component.

The experimental studies of BA reveal a strong preferential ordering of the benzyl alcohol in the surface region as well as an exceptionally large surface potential of several hundred  $mV$ . According to experimental studies the surface molecules in the liquid BA orient in such a way that the benzene rings point towards the vacuum and the polar group is directed towards the bulk of the liquid.

The simulation confirms the experimental results concerning the orientation of surface molecules. The surface potential resulting from the simulation is  $350mV$ . Thus sign and magnitude are in accordance with the experimental work.

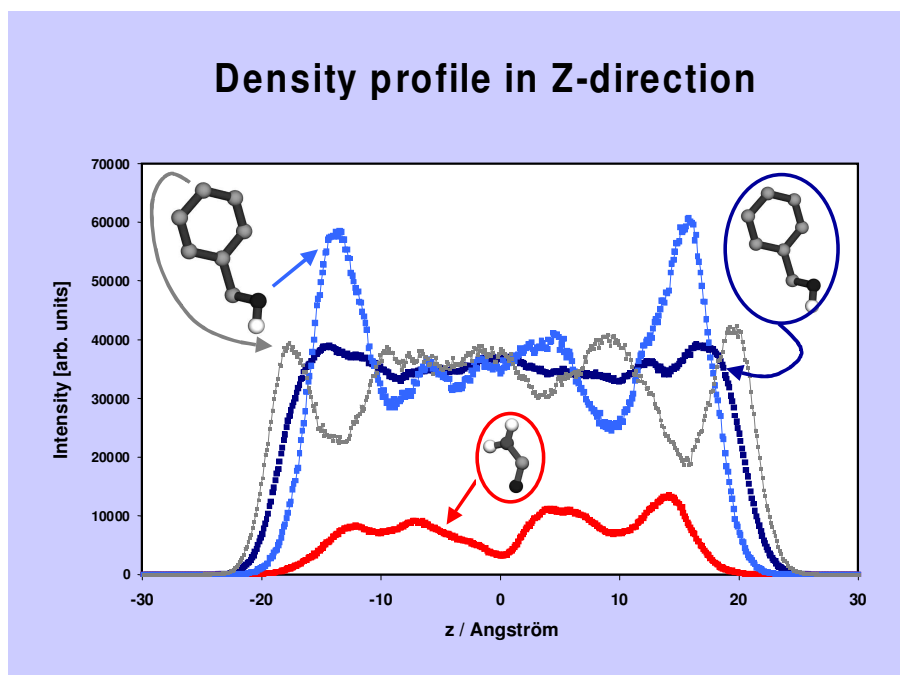


Figure 2. Density profile for the binary system formamide / benzyl alcohol. The preferential orientation of the benzyl alcohol can be seen: the benzene ring is exposed to vacuum while the O-H-group points towards the bulk of the liquid.

An examination of the structure of hydrogen bonds by means of bond angle distribution and bond state distribution reveals that the hydrogen bond is nearly unchanged when switching from bulk to surface.

The orientation of surface molecules causes a specific dynamic behaviour of individual components of the molecule. We find a speed up of the reorientation of certain axes when going from bulk to surface which depends on the separation of these axes from the polar group. This originates from the fact that benzene ring of surface molecules experiences a less dense region than axes near the polar group or the polar group itself.

In addition the average local environment of a polar group for surface molecules is very similar to that of bulk molecules.

The simulation of a NVE-ensemble of pure formamide shows that on the average the molecular plane is oriented perpendicular to the liquid surface with N and O pointing towards the liquid bulk and the CH-group exposed to vacuum. At first glance this seems to be a contradiction to the experimental finding where the plane is mainly parallel to the surface (see sec. 2.1). This puzzle can be solved by keeping in mind that MD averages the molecular orientation over a broad distribution. In the experiment it is taken into account how long the molecules remain in a certain orientation. Since there is a higher probability to trace the molecule in the turning points of a rotation the orientation parallel is overemphasized in the spectroscopic data.

Furthermore it could be seen that the liquid structure is dominated by a H-bonded network reaching from bulk into the surface region. Close to the surface smaller parts of H-bonded molecules separate from the main cluster. Studying dynamic properties shows that movement around certain axes of formamide is slower in the surface region originating from the preferential orientation of the molecules.

The binary system consisting of 420 BA and 80 FA molecules shows that features of the pure component are not much influenced by the second species: The liquid surface consists preferentially of BA, benzene rings are exposed to vacuum, the hydroxy group points into the bulk. It is no rigid arrangement and the ordering does not continue into the bulk. FA molecules are found mainly in the neighbourhood of hydroxy groups below the first molecular layer. The close distance ordering results from H-bonds. Density profiles are shown in fig. 2.

### 4.3 Formamide and Hexane

molecular parameter				
	name	formular	sites	number
species 1	formamide	$HCONH_2$	5	432
species 2	hexane	$CH_3(CH_2)_4CH_3$	6	128
simulation parameters				
program	computer	knots	Box X,Y,Z [ $\text{\AA}$ ]	timestep [ $f_s$ ]
DL-POLY	CRAY T3E Jülich local workstation	32 1	38.5, 38.5, 120	0.75
run parameter				
simulated time [ $ps$ ]		temperature [ $K$ ]		
3040		290		

Table 2. MD-simulation formamide and hexane, parameters.

The binary system formamide and hexane (HX) is a typical 2-phase system showing macroscopic phase separation. We are interested in properties of the polar / unpolar interface and study what type of molecular features is influenced by the second component.

The simulation reveals that a sharp phase separation does not exist on an atomic level. Both liquids penetrate each other over a distance of  $\sim 10\text{\AA}$  (fig. 3). The FA bulk molecules do not show any preferential orientation but in both interfaces (FA / vacuum and FA / HX) the known tilting of the C-N-backbone is found. This feature is not influenced by the unpolar liquid.

For HX the situation is somewhat different: analysis of the number of trans-configurations per molecule shows that the major part of the unpolar molecules is elongated in the outer surface (HX / vacuum). In the inner interface (HX / FA) the presence of FA leads to an increased amount of HX in coiled conformation (fig. 4).



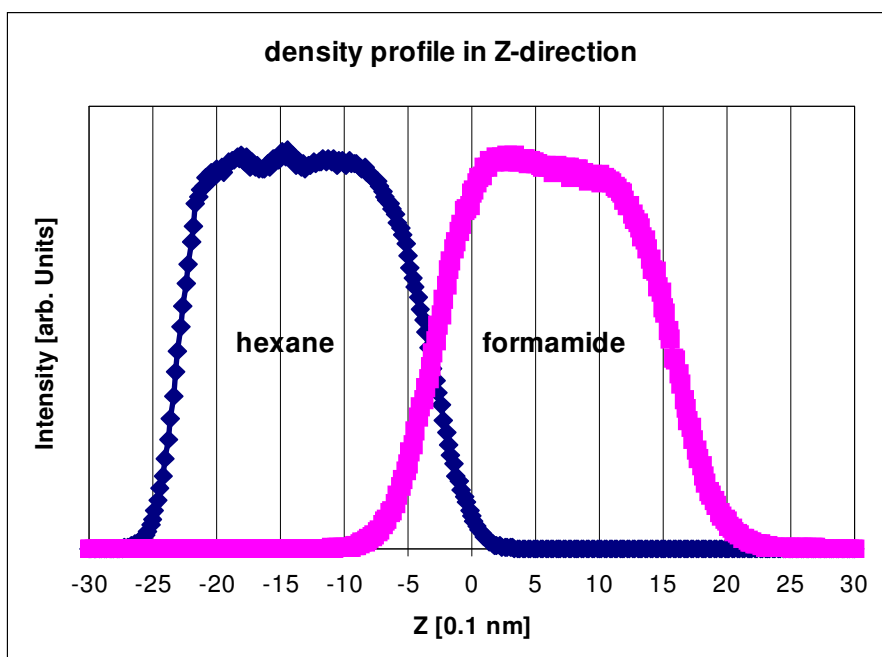


Figure 3. Density profile for the binary system formamide / hexane which shows a miscibility gap.

## 5 General Remarks and Outlook

One general restriction of MD simulations even with nowadays computer power is the limited number of interaction sites and the small time interval accessible.

Experimentally we study segregation processes taking place in *msec* – *sec* depending on the respective surfactant. In contrast classical MD methods cover a time regime of several *100ps* up to a few *ns*. Since this means that diffusion itself can not be simulated we choose a different strategy: A particle ratio  $\frac{\text{surfactant}}{\text{solvent}}$  was taken from the experiment and reproduced in the liquid surface simulated. Afterwards the simulation was used to analyze properties like orientation processes which take place at a much shorter time scale.

In order to extend the simulation time window up to experimental values we plan to use the so called *targeted dynamics* method<sup>6</sup>: movement or conformational changes of a molecule are accelerated by applying an additional constraint force along a given reaction coordinate (for example: distance from an aim point). We have already tested this approach for the adsorption of thiol molecules at a gold surface<sup>7</sup> and for the movement of a single formamide molecule through a slab of benzyl alcohol<sup>8</sup>.

Tracing the total energy of the respective molecule under constrains gives a handle on preferred orientations and positions without the demand of simulating long enough until these situations are reached randomly.

We plan to use this *targeted dynamics* algorithm for the study of concentration depth profiles of different salt solutions and the behaviour of more complex surfactants like phos-

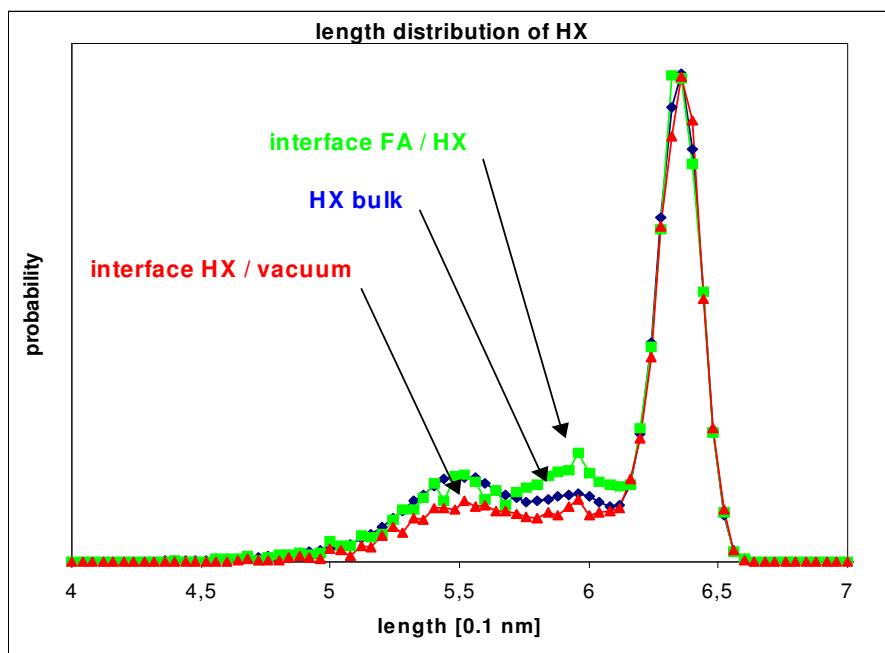


Figure 4. Length distribution of the alkane for different surroundings. The major part of the alkane molecules exhibits an elongated conformation in the interface HX / vacuum. Presence of formamide in the interface HX / FA leads to a higher amount of coiled hexane.

pholipids (lecithin for example).

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