

Segregation of inorganic ions at surfaces of polar non-aqueous liquids

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The cover picture shows the surface of 1 M sodium iodide solution in formamide from a molecular dynamics simulation.

Keywords: inorganic ions, surfaces of polar liquids, molecular dynamics, surface selective spectroscopy.

Abstract

We present a short review of recent computational and experimental studies of surfaces of inorganic salt solutions with polar non-aqueous solvents. These investigations complement our knowledge about aqueous interfaces, showing that liquids such as formamide, liquid ammonia, or ethylene glycol can also surface segregate large polarizable anions like iodide, albeit less efficiently than water. For liquids the surface of which is plagued with hydrophobic groups (such as methanol) the surface ion effect all but disappears. Based on the present data a general picture of inorganic ion solvation at the solution/vapor interface of polar liquids is outlined.

Introduction

Segregation of inorganic ions at aqueous surfaces has received considerable attention recently.^[1] Contrary to the traditional view of an essentially ion-free surface layer of aqueous electrolytes molecular dynamics simulations and surface selective spectroscopic experiments showed that certain ions can be present and even enhanced in the top-most layer.^[2-10] This concerns primarily large polarizable anions (e.g., iodide, bromide, thiocyanate, etc.) and the hydronium cation. The importance of this effect has been invoked in surface chemistry at atmospheric aerosols and in other chemical processes invoking small droplets of aqueous electrolytes.^[11-13] A question in the focus of the present paper is whether the surface enhancement observed for certain inorganic ions in water is also present in non-aqueous salt solutions.

Information about the surface structure of inorganic salts in polar solvents can partially be derived from surface tension measurements. Stairs et. al. investigated different alkali halides dissolved in dimethylformamide^[14] and in ammonia.^[15] In all cases an increase of the surface tension upon adding salt was found, similarly as in water.^[16] The slope of the surface tension as a function of the salt concentration is about a few $\text{mNm}^{-1}\text{mol}^{-1}$. This value is similar to the slope found for aqueous alkali halide solutions.^[17] According to the Gibbs equation^[18] increase of the surface tension upon adding salts means that there is an overall depletion of the solute in the interfacial layer, i.e., a negative surface excess. However, the surface excess is an integral quantity and cannot reflect the details of the concentration depth profiles. Thus a negative surface excess does not exclude an enhanced concentration of the solute in the outermost layer of the solution.^[4]

In order to get a more detailed insight into the molecular structure of surfaces of non-aqueous polar liquids and the corresponding salt solutions both experimental and computational methods have been applied. The former concern primarily ion scattering and non-linear optical spectroscopic methods while the latter are molecular dynamics

simulations.^[19-25] In this paper we summarize the most recent advances in this field of research. In particular, we focus on surface segregation of a model anion (iodide) at the surface of methanol and formamide as representatives of non-aqueous polar molecules with and without hydrophobic groups. Our principal aim is to compare segregation of inorganic ions at surfaces of non-aqueous polar liquids to that at water surface and to formulate a general view on this phenomenon.

1. Results

Liquids without hydrophobic groups

Let us first discuss ion segregation at surfaces of polar non-aqueous liquids which do not possess any hydrophobic moieties (such as, e.g., methyl or longer alkyl groups).

Formamide

The surface of salty formamide solutions was investigated by means of neutral impact collision ion scattering spectroscopy (NICISS) and the angular resolved mode of NICISS (ARISS).^[20,21] NICISS is used to probe concentration depth profiles while ARISS enables to investigate the topography around selected atoms in the outermost layer. Solutions of LiI in formamide show a non-monotonous concentration depth profiles of iodide with an enhanced concentration of iodide in the outermost layer^[21] (see Fig. 1). In contrast, an enhanced concentration of chloride in solutions of LiCl in formamide is not supported by the experiments. ARISS shows that the iodide is located in a valley like structure.^[20]

Directly inspired by the above experiments, the liquid/vapor interface of formamide solution of NaI was also studied using molecular dynamics simulations.^[21] The unit cell consisted of 500 formamide molecules with 10 (or 20) sodium cations and iodide anions forming ~0.5 M (or ~1 M) salt solution. Simulations were performed within the NVT

ensemble at 350 K in slab geometry.^[21] A polarizable force field was derived using GAFF parameterization from Amber 8 package^[26,27] and it was verified by comparison with both ab-initio calculations for dimers and radial distribution functions from ab-initio molecular dynamics study of formamide.^[28]

The liquid/vapor interface was analyzed in terms of density profiles which reflect distributions of ions across the slab. Fig. 1a shows a representative snapshot from the MD simulation, while Fig. 1b the iodide and sodium density profiles of 0.5 M solution of NaI in formamide, from the center of slab ($z = 0$) across the interface into the gas phase. The density of solvent (defined as a density of formamide carbon) is also shown. Density profiles are normalized such as to have the same integral under each curve. On the density plots a pronounced iodide surface peak followed by subsurface depletion and a subsurface sodium peak can be observed.

The iodide peak gets smaller with increasing concentration (results not shown here) which can be explained by a gradual saturation of adsorption,^[21] similarly to aqueous solutions.^[29] At the same time, extensive ion pairing occurs at higher concentrations. We have also investigated the effect of polarization by comparing the present results to density profiles obtained from simulations employing a non-polarizable force-field. In the latter case, the surface effect of iodide diminishes almost completely which demonstrates that polarization is a key effect responsible for surface propensity of heavier halides. Density profiles presented in Fig. 1b are similar to those in aqueous solutions of NaI,^[3,4] except that the surface propensity of iodide in water is slightly larger than in formamide.

We also analyzed the accessible surface area (ASA) of ions, i.e., the percentage of surface covered by iodide or sodium. Fig. 2 depicts the ASA results along a simulated trajectory for 0.5 M NaI solution. It can be estimated that ~4% of the surface is covered by iodide. According to ASA results for 1 M solution (not shown here) ~7% of the surface is covered by iodide in the more concentrated solution.^[21] These values are about half the ASA

of iodide in aqueous solutions of NaI of corresponding concentrations.^[22] This indicates that the surface exposure of iodide in formamide is smaller than in water.

A local analysis of surface topography of NaI solution in formamide, which allows for a most detailed characterization of the immediate environment of the ions at the interface, was also performed. Within this analysis, only the first solvation shell of each iodide anion was considered with definition based on the iodide-formamide radial distribution function. The difference between the depth of an iodide anion (i.e. its distance from the averaged surface position) and the mean depth of all atoms of formamide in the above defined solvation shell was calculated and denoted as z_{shift} . The value of z_{shift} directly characterizes the surface exposure of an ion with the respect to formamide molecules located in the first solvation shell, and hence gives more detail information than an averaged picture obtained from density profiles and ASA. Namely, three values of z_{shift} are characteristic, as depicted schematically in Fig. 3. For $z_{\text{shift}} = 0$ the considered ion is symmetrically surrounded by solvent atoms which corresponds to the bulk phase environment. $z_{\text{shift}} = z_{\text{under}}$ is the value corresponding to an ion placed just below the averaged surface position (i.e., just touching the surface from the solvent side), while $z_{\text{shift}} = z_{1/2}$ is the value for ions half-exposed above the surface. The concrete values of z_{under} and $z_{1/2}$ depend on the particular ion and solvent.

Fig. 4 depicts values of z_{shift} for the 0.5 M NaI solution in formamide. It can be seen that in the bulk region values of z_{shift} oscillate around zero, as expected for a symmetric solvent environment around iodide. In the subsurface region the density of the z_{shift} points decreases which reflects the subsurface depletion of iodide, observed also at the density profile. Closer to the surface the density of points increases again with the z_{shift} values being scattered mostly between 0.8 and 2.5 Å. This indicates that most of iodide anions in this region can be classified as lying between just touching the surface from the solvent side and being half-exposed. This analysis allows us to conclude that most of surface exposed iodide anions sit in “valley-like” solvent structures, in agreement with the experiment. The average

depth of these valley-like structures can be estimated from Fig. 4 as the difference between the position of the most probable z_{shift} point located in the surface area (13.8 Å) and the position where solvent density reaches half the bulk value (15.3 Å). Thus, the depth of valley-like structures estimated from the simulation is 1.5 (± 0.2) Å.

Liquid ammonia

The surface of NaI solution in liquid ammonia was investigated using molecular dynamics simulations in slab geometry employing polarizable force field, similarly as in the case of formamide. A unit cell containing 760 ammonia molecules with either 10 sodium cations and 10 iodide anions (~ 0.5 M) or 20 sodium cations and 20 iodide anions (~ 1 M) was employed. The polarizable force field was derived using GAFF parametrization from Amber 8 package^[26,27] and it was verified by comparison with both ab-initio calculations for dimers and radial distribution functions from QM/MM study of liquid ammonia.^[30] Simulations were performed in the NVT ensemble at a sub-ambient temperature of 220 K corresponding to liquid phase of ammonia.

Fig. 5 depicts the density profiles of Na^+ and I^- ions in a 0.5 M solution (the density profile of nitrogen in ammonia molecule is also presented). A pronounced iodide surface peak is clearly visible together with a sizable subsurface depletion. A complementary subsurface peak of sodium is also present. With increasing concentration (results not shown here) the iodide peak gets smaller.

ASA values for NaI in ammonia were also collected. In the case of 0.5 M solution ASA of iodide anions is about 2%, while in 1 M solution about 4% of the surface is covered by iodide. In the case of ammonia the surface enhancement of iodide deduced from density profiles is slightly stronger than that in formamide, however, ASA values are lower by about a factor of 2. This seeming controversy can be explained using the local topography analysis. This shows that in the case of ammonia the valley-like structures have iodide ions buried

deeper in the solvent surface than in the case of formamide. In ammonia the calculated average valley depth for the 0.5 M system reaches 1.9 (± 0.2) Å, hence iodide anions are less exposed at the surface than in the case of formamide solutions.

Hydrogen fluoride

Molecular dynamics simulations of hydrogen fluoride are somewhat tricky due to the necessity to describe properly the higher multipole moments (quadrupole) of the HF molecule. In order to investigate NaI solutions in HF we used a polarizable force field developed recently,^[31] with minor modifications to comply with the force field format requirements in the Amber program. The employed force field was then verified against ab-initio energies and geometries of dimers, as well as radial distribution functions from ab initio molecular dynamics study of hydrogen fluoride.^[32] We performed simulations of NaI in HF in the slab geometry with a unit cell of 892 HF molecules with 20 sodium cations and 20 iodide anions (~ 1 M NaI concentration). The simulations were performed in the NVT ensemble at 273 K.

In the bulk of hydrogen fluoride, due to the tendency to form two strong hydrogen bonds, HF dimers and both linear and ring oligomers are prevalent. We also observed such dimers and oligomers at the surface of hydrogen fluoride. The presence of these strongly bound complexes is the reason for a significant surface coarseness and dynamical instabilities. For this reason, collection of well equilibrated data from the simulation of the surface of hydrogen fluoride was very difficult. Preliminary results yield not completely converged density profiles of ions in 1 M NaI solution in hydrogen fluoride with no appreciable surface peak of iodide. Rather, subsurface peaks of both iodide and sodium can be identified. The almost complete absence of iodide from the surface is likely a consequence of the fact that the outer regions of the hydrogen fluoride surface consist mainly from dynamically changing

bended oligomers or rings of HF molecules. This is different from the well defined (albeit rough) surface of liquids like water or formamide, which surface segregate iodide.

2. Liquids with hydrophobic groups

In this section we discuss ion segregation at surfaces of polar non-aqueous liquids containing hydrophobic (e.g., alkyl) groups.

Methanol

Surface of amorphous solid methanol (which is a structural proxy to the corresponding liquid) containing alkali halides has been investigated by means of metastable impact electron spectroscopy (MIES) recently.^[22] MIES is known as an almost ideally surface sensitive spectroscopic technique.^[33,34] CsI was evaporated on amorphous solid methanol and the change of the surface composition was followed by monitoring MIES and photoelectron spectra (the latter probing a thicker interfacial region). It was found that the iodide MIES signal disappears upon heating of the amorphous solid methanol before methanol desorbs. This finding is different to amorphous water.^[22] A conclusion drawn from this finding and supporting molecular dynamics calculations is that iodide strongly segregates to the surface of water while this is not the case for liquid methanol. Such interpretation of the MIES experiments is based on the assumption that both solid amorphous methanol and solid amorphous water reflect the properties of the respective liquids.^[35]

Molecular dynamics simulations provide computational evidence for the lack of substantial surface segregation of large polarizable ions such as iodide at the surface of liquid methanol.^[22,25] We discuss here in detail the results of these calculations performed in a similar setup (slab geometry) as those described in previous sections. The number of

dissolved species ranged from a single iodide ion for free energy (potential of mean force) calculations to molar concentrations of NaI for straightforward MD runs.

Molecular dynamics simulations of a 2.2 M NaI methanol liquid/vapor interface have been performed.^[25] In Figure 6 we present the density profiles of the methanol center-of-mass, iodide, and sodium ions obtained from averaged over 3 ns of MD simulations. Simulations in liquid methanol suffer somewhat from slow dynamics/equilibration processes of ions. Nevertheless, we can conclude from these computed density profiles that the iodide anions do not exhibit a strong surface peak, although they can be found nearer to the interface than sodium cations. Note that similar behavior has been observed in simulations of a slab of ~ 1 M CsI in methanol.^[22]

Figure 7 shows the free energy profile for transferring a single iodide anion across the methanol liquid/vapor interface at 298 K as a function of its distance to the interface. The free energy profile decreased marginally as the iodide anion approaches the Gibbs dividing surface from the bulk and then starts rising sharply as the ion starts to be removed from the liquid. Before the iodide anion reaches the dividing interface and eventually moves to the vapor phase with a significant free energy of solvation, a very small minimum free energy of the order of kT (-0.6 kcal/mol) was observed. This observation was confirmed by performing reverse simulations (from vapor to liquid phase) to compute the free energy profile of inserting an iodide anion from the vapor phase to the liquid phase. The minimum position was found to be further inside the dividing surface when compared to our previous study of an iodide anion at the liquid water interface. These results can be qualitatively rationalized as follows - because the majority of hydroxyl groups of methanol are oriented toward the bulk liquid and the surface is plagued with hydrophobic methyl groups, the iodide anions do not show a strong propensity to the surface. Instead, they are present below the interface, which allows to optimize the hydrogen-bonding network and to retain the first solvation shell. This

is very different from water and other polar liquids not containing hydrophobic groups, where iodide exhibits a surface peak.

Glycerol

Molecular beam experiments have been carried out investigating sodium iodide solutions in glycerol.^[19] This technique is used to investigate the uptake and solvation of gas molecules into the surface and adjacent regions of liquids^[36] and the composition of the outermost layer. The argon scattering results show that both the inelastic scattered Ar and thermal desorbed Ar atoms shift to higher kinetic energies. The result implies that the effective mass of the species at the surface increases and thus that iodide is present at the surface. Whether the salt concentration is enhanced cannot be determined. The DCI scattering experiments shows an increase in the immediate DCI desorption and DCI → HCl exchange while the entry of the DCI into the bulk is suppressed. The authors explain the results with a strong interaction of the Na⁺ and I⁻ with the OH groups. As a consequence the stronger bound OH groups of the glycerol molecules are not anymore available to bind DCI and initiate their ionization. Moreover the hydrogen bond network of the glycerol molecules could be disrupted.

Molecular dynamics simulations complementing the above experimental observations would be highly desirable. However, the very large viscosity is likely to make equilibrated simulations computationally prohibitive.

Ethylene glycol

Surface of NaI solution in ethylene glycol was investigated by molecular dynamics simulations employing a polarizable force field derived using the GAFF parameterization from Amber 8 package.^[26,27] Simulations were performed in NVT ensemble at 350 K for a

slab system with a unit cell of 432 ethylene glycol molecules with 12 sodium cations and 12 iodide anions (~ 0.5 M solution).

Fig. 6 shows density profiles of ions and solvent molecules collected along the simulation trajectory after equilibration. An iodide peak in the surface area accompanied by subsurface depletion of iodide is visible, while the complementary sodium peak occurs in the subsurface area. According to the results of ASA analysis about 3% of the surface is covered by iodide anions. In order to further investigate the liquid/vapor interface the local topology analysis was also performed. It shows that iodide in the surface region is placed in valley-like structures of average depth $1.5 (\pm 0.2)$ Å formed by solvent molecules, similarly as in formamide or liquid ammonia. It is also worth noting that the CH₂ groups of the ethylene glycol solvent are slightly more surface exposed than the hydrophilic OH groups (Fig. 6).

3. Discussion and Conclusions

We have summarized recent computational and experimental results concerning the propensity of soft inorganic ions (e.g., iodide) for the surface of polar non-aqueous liquids. Most recently, ion segregation at surfaces of mixtures of aqueous and non-aqueous polar liquids (e.g., butanol) started to be studied as well, with interesting behavior (suppression of surface propensity) of inorganic anions such as iodide being observed [37]. Both molecular dynamics simulations and surface sensitive spectroscopic techniques provide structural information about the solution/vapor interface with molecular detail. We have recently reviewed elsewhere the new findings for aqueous surfaces,^[3,4] here we concentrated on inorganic ions at surfaces of non-aqueous liquids. We showed that in solutions with polar liquids such as formamide or liquid ammonia there is an enhanced concentration of ions like iodide in the outermost layer, albeit less pronounced than in water. Simple alcohols such as methanol, however, show almost no surface enrichment of ions, since their surface is plagued with hydrophobic methyl groups. It would be tempting to formulate a hypothesis that polar

liquids in general surface segregate large polarizable anions such as iodide except for solvents where hydrophobic groups protrude from the surface. However, we have already observed exceptions to this rule. For example, hydrogen fluoride does not surface segregate iodide due to its very rugged and dynamical surface, while iodide shows propensity for the surface of ethylene glycol, despite the presence two hydrophobic CH₂ groups (which do not, however, plague the surface).

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Figure legends:

Fig. 1: a) A typical snapshot and b) density profiles (i.e., distributions of sodium and iodide ions, as well as carbon atoms of formamide, from the center of the slab across the solution/vapor interface into the vapor phase) from MD simulation of a 0.5 M NaI solution in formamide, c) concentration depth profile of iodide determined by means of NICISS.

Fig. 2: Accessible surface area, i.e., percentage of the surface covered by iodide or sodium ions during a simulation of 0.5 M NaI solution in formamide.

Fig. 3: A schematic picture showing the ion (brown) with the first solvation shell (green) at different distances from the surface of a liquid (blue), with the corresponding values of z_{shift} .

Fig. 4: Values of z_{shift} (depicted as scattered dots) as a function of the z -coordinate (depth) for all iodide ions averaged along the MD trajectory of the 0.5 M NaI solution in formamide. Water and iodide density profiles, as well as horizontal lines marking the z_{under} and $z_{1/2}$ values of z_{shift} are also shown.

Fig. 5: Density profiles, i.e., distributions of sodium and iodide ions, as well as nitrogen atoms of ammonia, from the center of the slab across the solution/vapor interface into the vapor phase for 0.5 M NaI solution in ammonia.

Fig. 6: Density profiles, i.e., distributions of sodium and iodide ions, as well as methanol (center of mass), from the center of the slab across the solution/vapor interface into the vapor phase for a 2.2 M NaI solution in methanol.

Fig. 7: Free energy profile (potential of mean force) of moving a single iodide atom from the center of the slab across the liquid/vapor interface. Results in methanol are compared to those in water.

Fig. 8: Density profiles, i.e., distributions of sodium and iodide ions, as well as carbon, oxygen and hydroxyl hydrogen atoms of ethylene glycol, from the center of the slab across the solution/vapor interface into the vapor phase for 0.5 M NaI solution in ethylene glycol.

Fig. 1a:

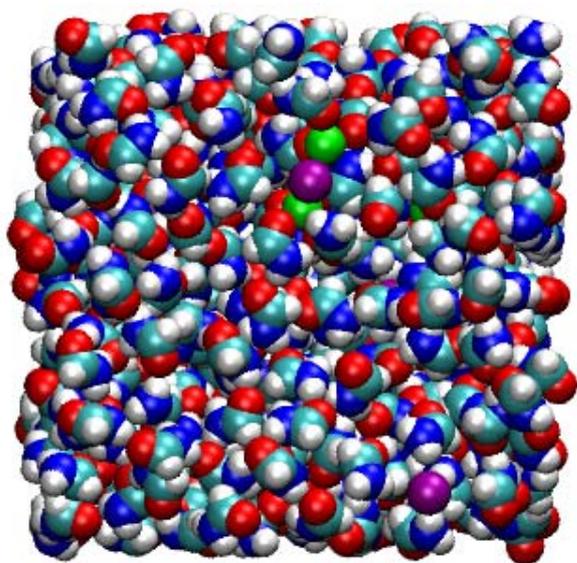


Fig. 1b:

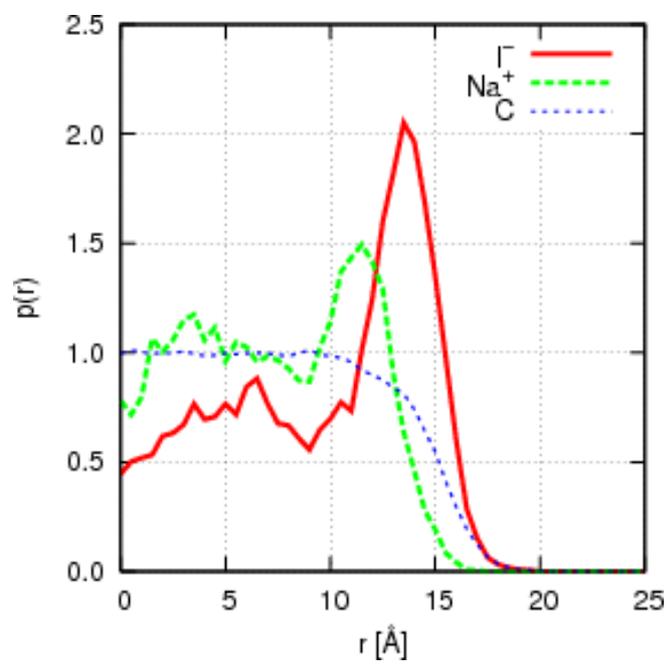


Fig. 1 c:

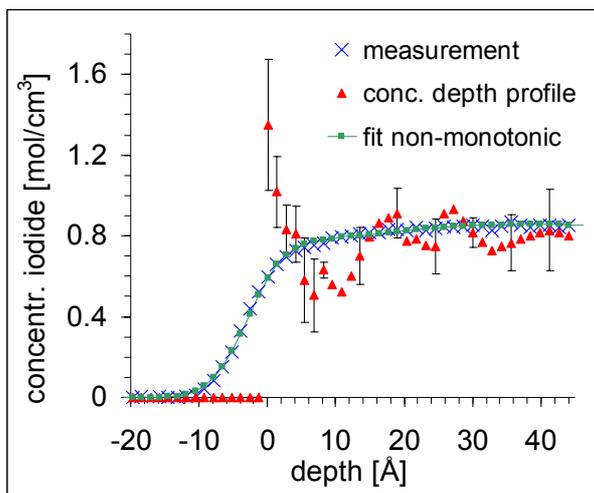


Fig. 2:

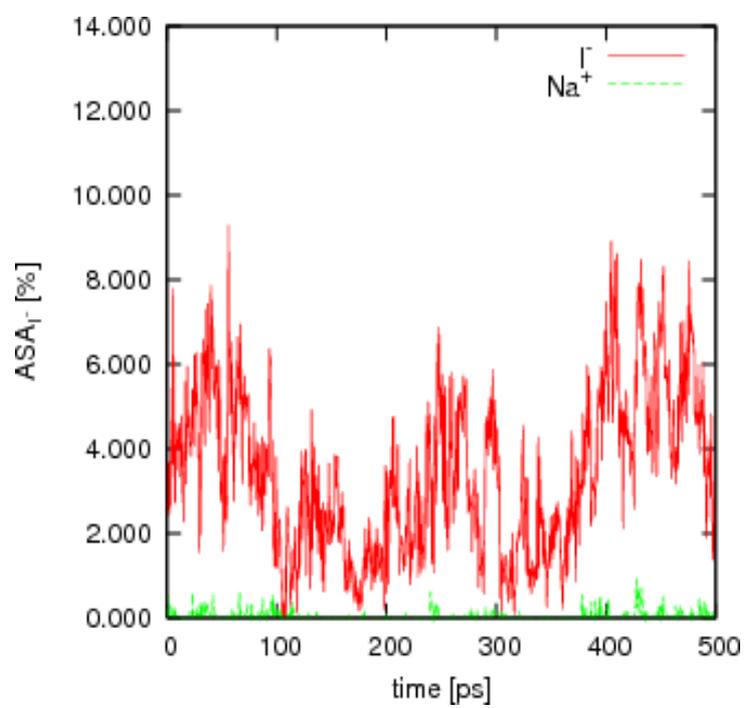
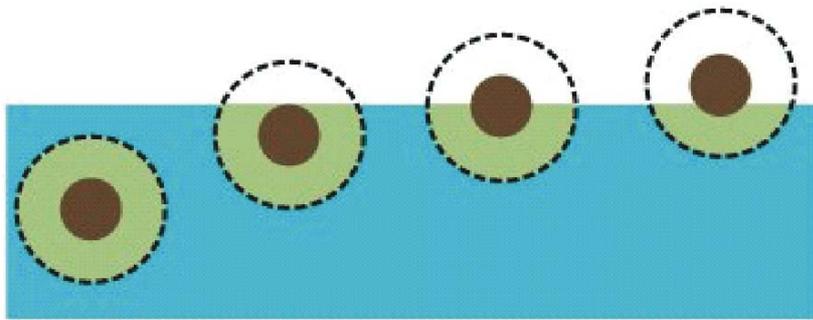


Fig. 3:



$$Z_{\text{shift}} = 0 \quad = Z_{\text{under}} \quad = Z_{1/2}$$

Fig. 4:

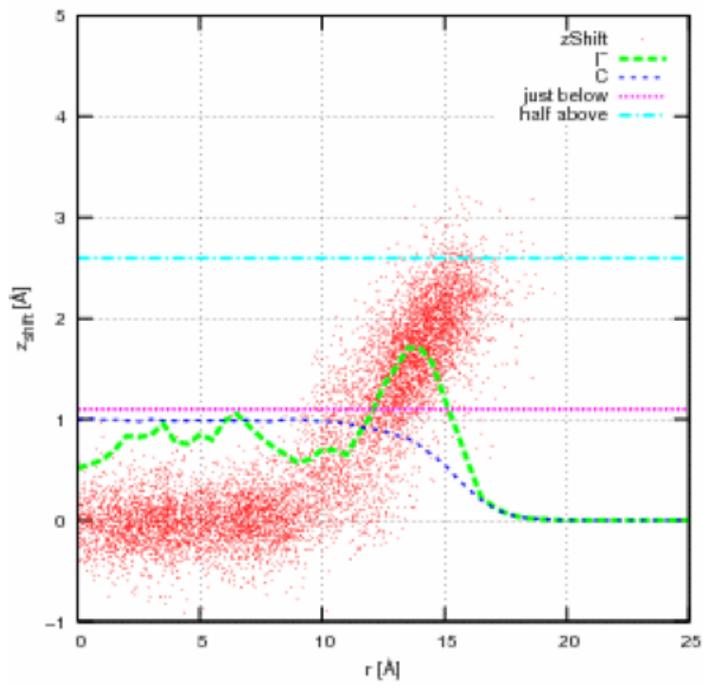


Fig. 5:

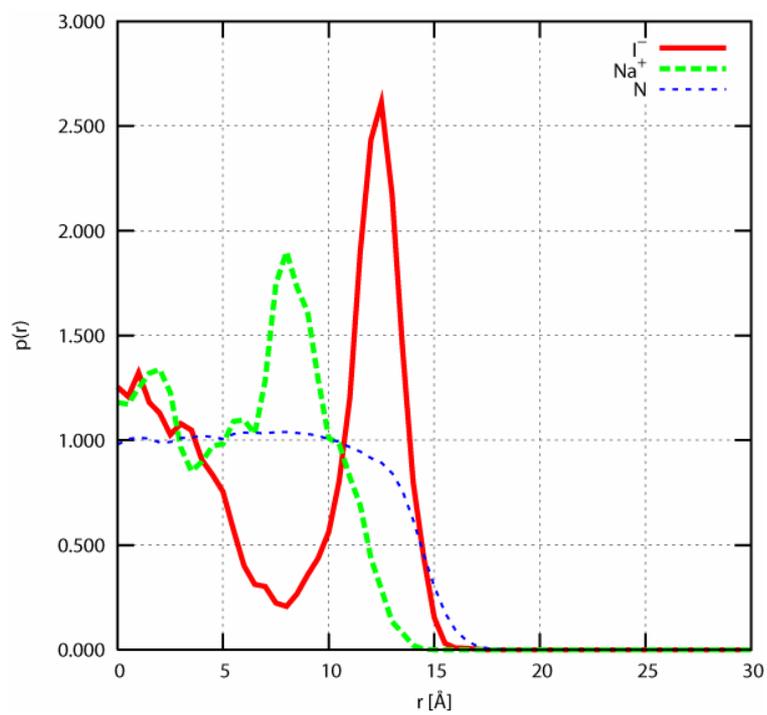


Fig. 6:

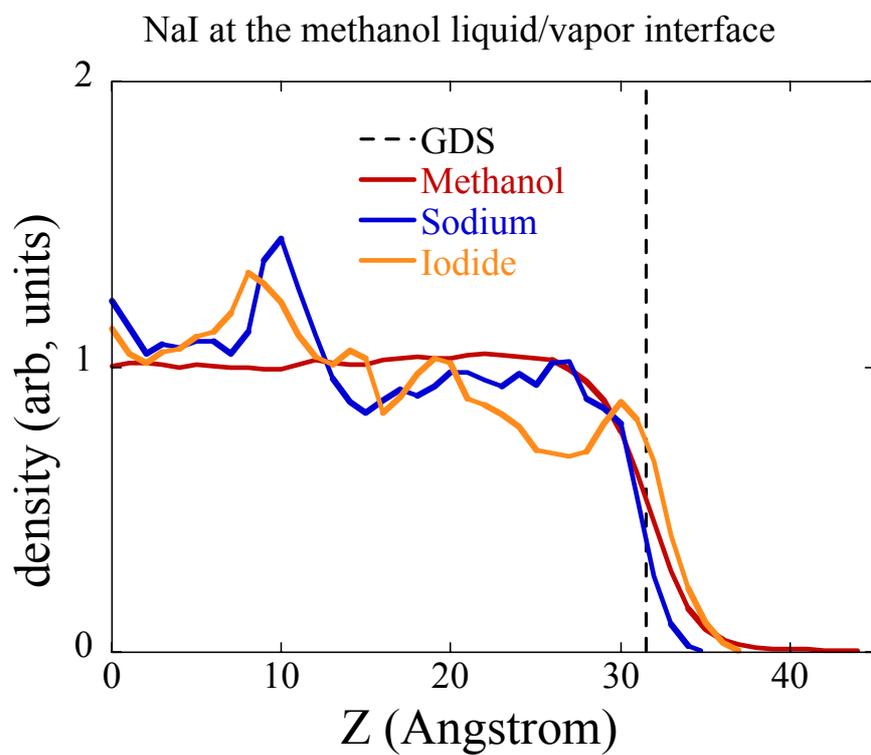


Fig. 7:

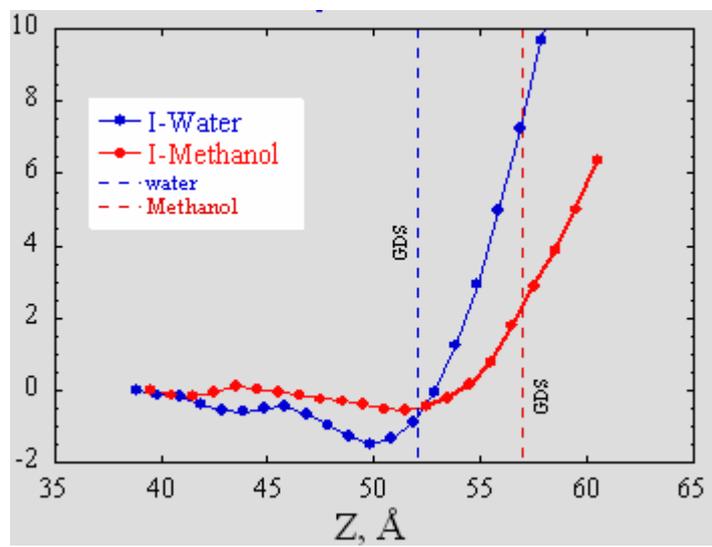
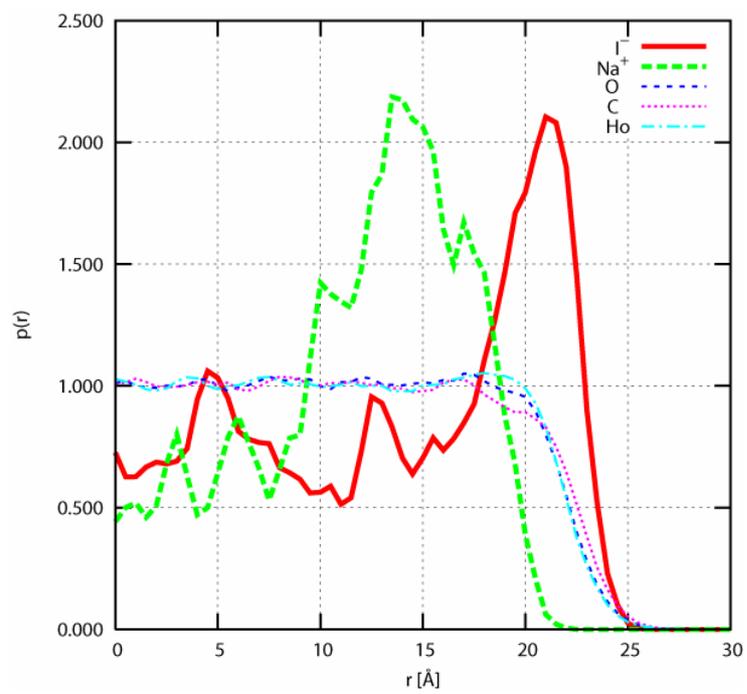


Fig. 8:



Cover picture:

