

In the frame of the present project we investigated biologically or environmentally relevant problems related to (1) fluid (i.e., liquid-vapor and liquid-liquid) interfaces, (2) phospholipids membranes, (3) solid (i.e., solid-gas and solid-liquid) interfaces, (4) room temperature ionic liquids, and (5) other bulk fluid phases, studied by computational methods. The main results are summarized as follows.

1. INVESTIGATION OF PROBLEMS RELATED TO FLUID INTERFACES

1.1. Methodological issues and fundamental problems

1.1.1. Problems related to the calculation of the lateral pressure profile and to the distribution of the surface tension among the particles

The calculation of the lateral pressure profile is hindered by the fact that it requires the localization of a quantity (i.e., the pressure) that is inherently non-local. Namely, the pressure contribution corresponding to the interaction of a given particle pair can be calculated as a contour integral along an open path connecting the two particles. It was shown earlier, however, that several particular choices of the integration contours yield comparable profiles of the lateral pressure. The use, among them, of the Harasima path has several advantages. First, in this way the lateral pressure can be calculated in a computationally feasible and efficient way, and the total lateral pressure can be distributed among the individual particles. Further, unlike other paths, it can be used even if the potential energy of the system is not pairwise additive, such as the long range correction of the electrostatic interaction (i.e. the reciprocal space term occurring in the Ewald summation based methods). In the frame of the project, we presented a method to calculate the long-range contribution of the electrostatic interaction to the local pressure tensor, based on mesh-based algorithms. This way, the lateral pressure contribution of the long range part of the electrostatic interaction can be taken into account when the computationally very efficient PME method is used in combination with the Harasima integration path. As a result of this new method, the regretful practice of calculating the lateral pressure profile a posteriori, by changing the potential between the simulation and the profile calculation, shown to result, in certain cases in systematic error of several hundred bar, can be avoided.

The importance of the calculation of the lateral pressure profile stems from the fact that the difference of the lateral (p_L) and normal (p_N) pressure components (the latter being

constant along the surface normal due to the requirement of mechanical stability) is related to the surface tension as

$$\gamma = \int_{-\infty}^{\infty} (p_N - p_L(X)) dX, \quad (1)$$

where X stands for the position along the surface normal axis. It should be emphasized that in the two bulk phases $p_N = p_L$, thus, the above integrand is different from zero only in the interfacial region. Using the above method, the contribution of the individual molecules to the surface tension can be accessed, allowing us to address the questions (i) how the subsequent subsurface molecular layers contribute to the surface tension at liquid-vapor interfaces, (ii) how the two liquid phases and the two components contribute to the interfacial tension at liquid-liquid interfaces, and (iii) how the different molecules and moieties contribute to the surface tension in aqueous surfactant solutions. In the investigation of these problems we obtained the following results.

(i) We calculated the lateral pressure profile across the liquid-vapor interface of five molecular liquids, i.e., CCl_4 , acetone, acetonitrile, methanol, and water. The results showed that the surface tension is distributed in a 10-20 Å wide range along the interface normal, and at least 85% of its value comes from the first molecular layer of the liquid in every case. The remaining, roughly 10% contribution comes from the second layer, with the exception of methanol, in which the entire surface tension can be accounted for by the first molecular layer.

(ii) The interfacial tension in binary fluids emerges ultimately from the uneven interaction between its two components. To understand its molecular level origin, we calculated the contribution of the two phases to the interfacial tension at the interface of five different organic liquids, i.e., hexane, cyclohexane, hexanol, dichloromethane, and carbon tetrachloride, with water. We found that the organic component contributes 20-30% to the total interfacial tension, and this result is independent from the temperature, pressure, water model used, and also from the type of the organic molecule as long as it does not interact strongly and, consequently, does not mix in a considerable extent with water. Among the chosen organic liquids, hexanol is the only one that exhibits partial miscibility with water to an extent accessible by computer simulation. We found that this partial miscibility is associated to a negative contribution of the hexanol molecules, and also that of the hexanol-rich mixed phase, to the total interfacial tension.

(iii) We investigated how the surface tension is distributed between the water molecules, surfactant tails, surfactant headgroups, and, when present, counterions at the surface of the aqueous solutions of various nonionic and ionic surfactants at the surface densities of $1 \mu\text{mol}/\text{m}^2$ (corresponding to an unsaturated monolayer) and $4 \mu\text{mol}/\text{m}^2$ (corresponding to a saturated monolayer). The most important finding of this study is the key role the counterions play in contributing to the surface tension in the case of the ionic surfactants. This role seems to be related to the “hardness” of these ions according to the Hofmeister series, and hence to their surface affinity. On the other hand, there is a strong compensation between the surface tension contribution of the counterions and ionic surfactant heads. In this compensation, the free energy gain of certain ions for being at the surface comes from the vicinity of the oppositely charged ions in the ion-rich layer beneath the liquid surface. Finally, water molecules contribute to the surface tension in these systems in two different ways. Thus, besides the trivial, positive contribution of the surface water molecules that are in contact with the vapor phase, the water molecules hydrating the ionic headgroups and counterions contribute negatively to the surface tension. The balance between these two contributions depends, besides the surface coverage, on the chemical nature of the headgroups and counterions. To address the role of the soft-hard character of the counterions in this respect, we considered all alkali halogenide solutions with the alkali counterions ranging from Li^+ to Cs^+ , using the KBFF force field of the ions. Unfortunately, with the exception of Na^+ , the surface tension of the solutions turned out to be larger rather than smaller than that of neat water, showing a severe shortcoming of the KBFF force field. We traced back this failure to the unphysically strong attraction of the KBFF counterions, except for Na^+ , to the anionic head of the surfactants. Despite this failure of the model, we observed a clear relation between the soft-hard character (in the sense of the Hofmeister series) and the surface tension contribution of the counterions, which, given the above limitations of the model, can only be regarded as an indicative result.

There are recent claims in the literature that the limit of the thermodynamical stability of the liquid phase (liquid-vapor spinodal) can be determined simply as the minimum lateral pressure along the surface normal axis at the corresponding liquid-vapor interface at the given temperature. Having a method of calculating the lateral pressure profile in hand, we were in the position to address this claim. For this purpose, we performed computer simulations of the liquid-vapor interface of the Lennard-Jones fluid and SPC/E water at various temperatures, to compare the minimum of the lateral pressure profile with the spinodal pressure. We found that

the two pressures agree within error bars for water, but only a proportionality of these values were found in the case of the LJ system. These results might offer a novel tool to estimate the spinodal line in situations of practical relevance.

This part of the research is described in the following publications:

1. M. Sega, B. Fábián, and P. Jedlovsky, Pressure Profile Calculation with Mesh Ewald Methods, *J. Chem. Theory Comput.* **12**, 4509 (2016).
2. M. Sega, B. Fábián, G. Horvai, and P. Jedlovsky, How is the Surface Tension of Various Liquids Distributed along the Interface Normal? *J. Phys. Chem. C* **120**, 27486 (2016).
3. M. Sega, B. Fábián, A. R. Imre, and P. Jedlovsky, Relation between the Liquid Spinodal Pressure and the Lateral Pressure Profile at the Liquid-Vapor Interface, *J. Phys. Chem. C* **121**, 12214 (2017).
4. Fábián Balázs, Imre Attila, Horvai György, Jedlovsky Pál, Laterális nyomásprofil számításával összefüggő problémák vizsgálata számítógépes szimulációval, *Magyar Kémiai Folyóirat* **124**, 157 (2018).
5. Gy. Hantal, M. Sega, G. Horvai, and P. Jedlovsky, Contribution of Different Molecules and Moieties to the Surface Tension in Aqueous Surfactant Solutions, *J. Phys. Chem. C* **123**, 16660 (2019).
6. Gy. Hantal, B. Fábián, M. Sega, and P. Jedlovsky, Contribution of the two liquid phases to the interfacial tension at various water-organic liquid-liquid interfaces, *J. Mol. Liquids* **306**, 112872 (2020).
7. Gy. Hantal, M. Sega, G. Horvai, and P. Jedlovsky, Role of the Counterions in the Surface Tension of Aqueous Surfactant Solutions. A Computer Simulation Study of Alkali Dodecyl Sulfate Systems, *Coll. Interfaces* **4**, 15 (2020)

1.1.2. Other fundamental problems and methodological issues

Besides the above problems directly related to the calculation of the lateral pressure profile, we also addressed the problem whether, besides the virial term, there is also a kinetic contribution to the surface tension, the possible calculation of the surface entropy in computer simulations, and the applicability of anisotropic thermostats in nonequilibrium molecular dynamics (MD) simulations. Further, we also developed an open access software package in Python language for detailed interfacial analyses of fluid interfaces. The main results of these studies are as follows.

Surface tension is routinely calculated as the difference between the lateral and normal components of the pressure or, invoking isotropy in momentum space, of the virial tensor. We showed that the anisotropy of the kinetic energy tensor close to a liquid-vapor interface can be responsible for a large part of its surface tension (about 15% for water, independent from temperature). As a consequence, in such system equipartition should be understood as the full energy rather than just its kinetic contribution is distributed evenly along all possible degrees of freedom. As a consequence, calculation of the surface tension through the virial route is affected by a systematic error, which is as large as 15% in the case of water.

In investigating the computational efficiency and accuracy of the calculation of the surface entropy of liquids, we tested three methods for the liquid-vapor interface of water and argon. The surface excess of the entropy at the liquid-vapour interface of argon and water are

calculated in a broad temperature range in three different ways involving the computer simulation determination of the surface tension. The three methods include (i) the calculation of the analytical derivative of a suitably chosen function fitted to the surface tension vs. temperature data, (ii) calculation of the numerical derivative of these data, and (iii) direct determination of the surface entropy through the surface excess of the energy. Our results show that this latter method provides inaccurate results with large error bars, and the calculation of the surface entropy this way with reasonable accuracy would require unfeasibly long simulations. On the other hand, the use of the numerical and the analytical derivatives leads to compatible results that can be obtained in a computationally feasible way in both cases. Thus, our results suggest that instead of determining the surface entropy through the surface excess of the energy, the surface entropy, determined as the derivative of the surface tension vs. temperature data, can be used to calculate the surface excess of the energy in a computationally efficient way.

The connection of the temperature with the kinetic energy tensor in statistical mechanics leaves open the possibility to define a tensorial temperature. This concept has sometimes been used to simulate isothermal conditions in out-of equilibrium systems. We have shown, by studying a sessile water droplet that the use of a tensorial temperature leads to the wrong thermodynamics, or, in other words, the equilibrium isothermal ensemble generated using a tensorial temperature is not the canonical one, with interfacial free energies that can differ up to 40% from the correct ones.

We developed a computer code, named as Pytim, for various analyses of the intrinsic liquid surface in computer simulations. Pytim is a versatile python framework for the analysis of interfacial properties in molecular simulations. The code implements several algorithms for the identification of instantaneous interfaces of arbitrary shape, and analysis tools written specifically for the study of interfacial properties, such as intrinsic profiles. The code is written in the python language, and makes use of the numpy and scipy packages to deliver high computational performances. Pytim relies on the MDAnalysis library to analyze the trajectory file formats of popular simulation packages, and can be used to steer OpenMM simulations. Pytim can write information about surfaces and surface atomic layers to VTK, CUBE, and PDB files for easy visualization. The code is available as open source and is free of charge.

This part of the research is described in the following publications:

1. M. Sega, B. Fábán, and P. Jedlovsky, Nonzero Ideal Gas Contribution to the Surface Tension of Water, *J. Phys. Chem. Letters* **8**, 2608 (2017).

2. M. Sega, G. Horvai, and P. Jedlovszky, On the calculation of the surface entropy in computer simulation. *J. Mol. Liquids* **262**, 58 (2018).
3. M. Sega and P. Jedlovszky, The impact of tensorial temperature on equilibrium thermodynamics, *Phys. Chem. Chem. Phys.* **20**, 16910 (2018).
4. M. Sega, Gy. Hantal, B. Fábián, and P. Jedlovszky, Pytim: a Python Package for the Interfacial Analysis of Molecular Simulations, *J. Comp. Chem.* **39**, 2118 (2018).

1.2. Dynamical properties of the molecules at the liquid surface

The identification of the full set of the molecules that constitute the liquid surface at every instant opens also the possibility of studying the dynamical properties of the interfacial molecules, and, in particular, the differences in the dynamical properties of the liquid surface and the bulk liquid phase. In the frame of this project, we studied the single molecule dynamics of five molecular liquids, namely CCl_4 , acetone, acetonitrile, methanol, and water at the intrinsic liquid/vapor interface. In the case of water, several potential models have been considered. Further, we also investigated single particle dynamics of both molecules at the liquid-liquid interface between water and CCl_4 .

After assessing that the characteristic residence times in the surface layer are long enough for a meaningful definition of several transport properties within the layer itself, we characterized the dynamics of the individual molecules at the liquid surface by analyzing their normal and lateral mean square displacements and lateral velocity autocorrelation functions and, in the case of the hydrogen bonding liquids (i.e., water and methanol), also the properties of the hydrogen bonds. The global picture emerging from this analysis is that of a noticeably enhanced dynamics of the molecules at the liquid surface, with diffusion coefficients up to four times larger than in the bulk, and the disappearance of the caging effect at the surface of all liquids but water. The dynamics of water is dominated by the strong hydrogen bonding structure also at the liquid surface.

At the liquid-liquid interface we found that the steric restriction, imposed by the presence of CCl_4 , slows down the dynamics of the surface water molecules, and vice-versa, as compared to the corresponding liquid-vapor interfaces. The presence of CCl_4 , however, restricts also the orientational freedom of the surface water molecules, resulting in fewer in-layer and more out-of-layer hydrogen-bonded neighbors, eventually promoting the exchange of water molecules between the surface layer and the bulk phase. On the contrary, the vicinity of the aqueous phase stabilizes the CCl_4 molecules in the surface layer, resulting in a considerably larger mean surface residence time with respect to the liquid-vapor interface of CCl_4 . All these results consistently show that the interface between the two liquid, in terms of

dynamical properties, is of monomolecular width, as in this respect the second layer already behaves very similarly to the bulk liquid phase.

This part of the research is described in the following publications:

1. B. Fábián, M. V. Senćanski, I. N. Cvijetić, P. Jedlovsky, and G. Horvai, Dynamics of the Water Molecules at the Intrinsic Liquid Surface As Seen from Molecular Dynamics Simulation and Identification of Truly Interfacial Molecules Analysis, *J. Phys. Chem. C* **120**, 8578 (2016).
2. B. Fábián, M. Sega, G. Horvai, and P. Jedlovsky, Single Particle Dynamics at the Intrinsic Surface of Various Apolar, Aprotic Dipolar and Hydrogen Bonding Liquids, As Seen from Computer Simulations, *J. Phys. Chem. B* **121**, 5582 (2017).
3. B. Fábián, G. Horvai, M. Sega, and P. Jedlovsky, Single Particle Dynamics at the Liquid-Liquid Interface. Molecular Dynamics Simulation Study of the Water-CCl₄ System, *J. Phys. Chem. C* **124**, 2039 (2020).

1.3. Surface properties of the aqueous solutions of small particles of relevance in prebiotic evolution or environmental chemistry

In the frame of the project, we studied the structure and dynamics of the surface layer of the aqueous solutions of two small organic molecules, i.e., methylamine and formamide, and of alkali halides, including the surface affinity of these solutes. While the two molecules are of potential relevance in prebiotic evolution (since, given that they can be locally accumulated at high enough concentration, their reactivity might well lead to the formation of several building blocks of biomacromolecules), alkali halide solutions are of relevance in atmospheric chemistry (involving, e.g., aerosols of sea water droplets).

We studied the liquid-vapor interface of water-methylamine mixtures of different compositions up to 30 mol% methylamine. The results showed that methylamine molecules are strongly adsorbed in the first, and somewhat depleted in the second molecular layer, while the composition of the third layer agrees with that of the bulk liquid phase. On the other hand, methylamine does not show considerable self-association within the surface layer. The orientational preferences of the methylamine molecules at the liquid surface are governed by the requirement of maximizing their H-bonding interaction. As a consequence, they point by their apolar CH₃ group straight to the vapor, while by the potential hydrogen bonding directions of the NH₂ group flatly to the liquid phase. Further, within the surface layer, methylamine molecules stay, on average, noticeably farther from the bulk liquid phase than waters. Increasing methylamine mole fraction leads to the gradual breaking up of the lateral percolating H-bonding network of the surface molecules. Finally, methylamine molecules accelerate, while water molecules slow down the exchange of both species between the liquid surface and the bulk liquid phase. Further, methylamine molecules slow down the lateral

diffusion of each other, and even prevent water molecules from showing noticeable lateral diffusion within the surface layer. The reason for this latter effect is that the mean residence time of water at the liquid surface becomes noticeably shorter than the characteristic time of their lateral diffusion in the presence of methylamine.

We also studied the liquid-vapor interface of water-formamide mixtures of different compositions, spanning the entire composition range. The obtained results reveal the strong lateral hydrogen bonding ability of the surface molecules, which form a percolating lateral hydrogen bonding network in every case, making the surface layer more compact than the subsequent subsurface molecular layers. Neither strong adsorption, nor lateral self-association of any of the components in the surface layer has been observed. Further, in contrast with the percolating lateral hydrogen bonding mixed network of the surface water and formamide molecules, no such network of the like molecules is observed, even in the case of their large excess at the surface of the mixed systems. The orientational preferences at the surface are also governed by the requirement of maximizing the hydrogen bonds. The main preference of both molecules is found to be the parallel alignment with the macroscopic plane of the liquid surface. The dynamics of the surface molecules is also dominated by the hydrogen bonding of unlike pairs. Thus, water stabilizes the stay of the formamide molecules at the liquid surface, while formamide immobilizes water molecules within the surface layer, preventing them from lateral diffusion during their entire stay at the liquid surface.

We studied the interfacial structure of various aqueous alkali chloride and sodium halide solutions, considering all ions from Li^+ to Cs^+ and from F^- to I^- . The surface tension of all alkali halide solutions is higher than that of pure water. According to the Gibbs equation, this indicates a net depletion of the ions in the interfacial region. However, simulations and experiments show that large, soft ions, such as I^- , can accumulate at the liquid/vapor interface. We showed that to resolve this contradiction, a clear distinction has to be made between adsorption in its thermodynamic sense (as described in terms of the surface excess and the change of the surface tension) and its structural sense, discussed in terms of surface enrichment. Thus, besides the positive contribution of the first layer, the subsequent layers give negative contributions to the surface excess of the I^- ion, and this depletion overcompensates the enrichment of the surface layer. We also showed that negative ions are more strongly hydrated than positive ions of the same size, because of the charge asymmetry of the water molecules. However, this stronger hydration can be accompanied by an increase rather than a decrease in the surface excess of large anions, simply because the same but opposite effect is stronger on the smaller cations. This result points out that it is not possible

to rationalize the surface affinity of ions in solutions in terms of the properties of anions and cations separately. Further, the surface excess is generally dominated by the smaller of the two ions.

This part of the research is described in the following publications:

1. B. Kiss, B. Fábián, A. Idrissi, M. Szőri, and P. Jedlovsky, Investigation of the Liquid-Vapor Interface of Water-Formamide Mixtures by Computer Simulation and Intrinsic Surface Analysis, *J. Phys. Chem. C* **122**, 19639 (2018).
2. R. A. Horváth, B. Fábián, M. Szőri, and P. Jedlovsky, Investigation of the liquid-vapour interface of aqueous methylamine solutions by computer simulation methods, *J. Mol. Liquids* **288**, 110978 (2019).
3. Gy. Hantal, R. A. Horváth, J. Kolafa, M. Sega, and P. Jedlovsky, Surface Affinity of Alkali and Halide Ions in Their Aqueous Solution: Insight from Intrinsic Density Analysis, *J. Phys. Chem. B* **124**, 9884 (2020).

2. INVESTIGATION OF PHOSPHOLIPID MEMBRANE RELATED PROBLEMS

In this part of the project, we investigated the effect of several general anesthetics on the properties of lipid membranes of various compositions. We were seeking for membrane properties that are potentially related to the molecular mechanism of anesthesia and its pressure reversal, namely that they change in the same way in any membrane with any anesthetics, and change oppositely with increasing pressure. For this purpose, we always simulated (i) the anesthetic-free membrane at atmospheric pressure, (ii) membranes containing anesthetics at atmospheric pressure, and (iii) membranes containing anesthetics at elevated pressures. Thus, we simulated four general anesthetics, i.e., chloroform, halothane, enflurane, and diethyl ether in a fully hydrated DPPC membrane both at 1 bar and 1000 bar, and also diethylether and sevoflurane in neat DPPC and PSM membranes as well as their equimolar mixtures with cholesterol both at 1 bar and 600 bar. The picture emerging from these studies, in accordance with the increasing body of evidence seen from similar investigations, is the following. Anesthetics are accumulated at the boundary of the polar and apolar parts of the lipid membrane. Although they might also have a preference for staying in the middle of the membrane, this preference is not always present and only the former preference seems to be related to anesthesia. The anesthetic molecules push the lipid molecules, among which they are located, farther apart from each other, leading thus to the increase of the area per lipid headgroup. The decreased lateral density induces higher mobility of the lipid tails and an increase of the free volume at the outer edge of the hydrocarbon phase, where anesthetics prefer to stay in every case. This latter change triggers a decrease of the lateral pressure in the nearby region of the lipid ester groups, where the anesthetics do not

penetrate. All these changes, occurring upon introducing anesthetics in the membrane, are reverted by the increase of the global pressure. The observed systematic change in the lateral pressure profile, hypothesized earlier by Cantor, can explain anesthesia through conformational changes, induced by this decrease of the lateral pressure, in channel proteins embedded in the membrane. Our results also suggest that if anesthesia is indeed caused by conformational changes of certain membrane-bound proteins, induced by changes in the lateral pressure profile, the relevant conformational changes are expected to occur in the membrane region where the ester groups are located.

This part of the research is described in the following publications:

1. B. Fábián, M. Sega, V. P. Voloshin, N. N. Medvedev, and P. Jedlovsky, Lateral Pressure Profile and Free Volume Properties in Phospholipid Membranes Containing Anesthetics, *J. Phys. Chem. B* **121**, 2814 (2017).
2. Gy. Hantal, B. Fábián, M. Sega, B. Jójárt, and P. Jedlovsky, Effect of general anesthetics on the properties of lipid membranes of various compositions, *BBA – Biomembranes* **1861**, 594 (2019).
3. P. Jedlovsky, Simulation of Membranes Containing General Anesthetics, in: *Biomembrane Simulations. Computational Studies of Biological Membranes*, ed. M. L. Berkowitz (Taylor and Francis: New York, 2019), pp. 177-198.

3. INVESTIGATION OF PROBLEMS RELATED TO SOLID INTERFACES

3.1. Adsorption of small molecules on solid atmospheric particles

3.1.1. Adsorption of halogenated hydrocarbon molecules at the surface of ice

In the frame of the project we investigated the adsorption of all the fluorinated and chlorinated methane derivatives at the surface of crystalline (I_h) ice under tropospheric conditions. Solid water surfaces in ice clouds and snowflakes are now recognized to play important roles in a variety of atmospheric phenomena, among others, in the catalytic ozone destruction due to halogen activation in the polar stratosphere. Small halogenated hydrocarbons are atmospheric pollutants, emitted in a large amount from anthropogenic sources. Some of these compounds may also act as atmospheric greenhouse gases.

Concerning the adsorption of the fluorinated and chlorinated methane derivatives, we found that the shape of the adsorption isotherms is determined by the interplay of adhesive and cohesive interactions. It is found that in cases when the former of the two interaction is clearly the stronger one, multilayer adsorption occurs; when the latter interactions is the dominant one, no considerable adsorption is observed; while in cases when the two interactions are of roughly the same strength, the formation of a saturated monolayer occurs.

The isotherms exhibit the Langmuir shape, at least up to the pressures where multilayer adsorption starts to occur, given that the cohesion acting between the adsorbate molecules is only moderately strong. Too strong cohesion, on the other hand, leads to the deviation of the isotherm from the Langmuir shape. While the strength of the cohesion depends on the properties of the adsorbate molecules (e.g., their mass and dipole moment); that of the adhesion is determined by the hydrogen bond formation between the adsorbed molecules and surface waters. Our results show that while CH₃F and CH₃Cl form several weak, C-H donated hydrogen bonds with the surface molecules of the ice phase, the adsorbates with more than one halogen atoms form only one, though strong, O-H donated hydrogen bond with them.

This part of the research is described in the following publications:

1. I. Sumi, B. Fábrián, S. Picaud, and P. Jedlovsky, Adsorption of Fluorinated Methane Derivatives at the Surface of Ice under Tropospheric Conditions, As Seen from Grand Canonical monte Carlo Simulations, *J. Phys. Chem. C* **120**, 17386 (2016).
2. I. Sumi, S. Picaud, and P. Jedlovsky, Adsorption of Chlorinated Methane Derivatives at the Ice Surface. A Grand Canonical Monte Carlo Simulation Study, *J. Phys. Chem. C* **121**, 7782 (2017).
3. I. Sumi, S. Picaud, and P. Jedlovsky, Dependence of the adsorption of halogenated methane derivatives at the ice surface on their chemical structure, *J. Mol. Liquids* **245**, 17 (2017).

3.1.2. Other atmosphere-related adsorptions

Besides the adsorption of halogenated methane derivatives, we also studied the adsorption of methylamine at the surface of I_h ice, and that of water at aerosols formed by mixtures of formic and acetic acid, under tropospheric conditions. Both methylamine and small acid molecules are abundant atmospheric pollutants, emitted from a variety of sources.

Concerning the adsorption of methylamine, we found that the adsorption isotherm exhibits a plateau, corresponding to the saturated adsorption monolayer, in a broad range of chemical potentials and pressures. However, even this part of the adsorption isotherm deviates noticeably from the Langmuir shape. Shortly before condensation of methylamine occurs outer molecular layers also start building up. The remarkable stability of the adsorption monolayer is caused by the interplay of hydrogen bonding interaction between the adsorbed methylamine and surface water molecules and dipolar interaction between neighboring adsorbed methylamines. As a consequence, the adsorbed methylamine molecules exhibit a rich orientational distribution relative to the ice surface and the adsorption is accompanied by rather large energy variations.

The studies of water adsorption on mixed aggregates of formic and acetic acid did not show any significant effect of the formic acid–acetic acid interactions on the behavior of the

mixed systems, indicating that the adsorption properties of such mixed aerosols can be readily predicted from those of the neat ones.

This part of the research is described in the following publications:

1. V. Szentirmai, M. Szőri, S. Picaud, and P. Jedlovsky, Adsorption of Methylamine at the Surface of Ice. A Grand Canonical Monte Carlo Simulation Study, *J. Phys. Chem. C* **120**, 23480 (2016).
2. B. Radola, S. Picaud, D. Vardanega, P. Jedlovsky, Analysis of Mixed Formic and Acetic Acid Aggregates Interacting with Water. A Molecular Dynamics Simulation Study, *J. Phys. Chem. C* **121**, 13863 (2017).
3. S. Picaud and P. Jedlovsky, Molecular-scale simulations of organic compounds on ice: application to atmospheric and interstellar sciences, *Mol. Simul.* **45**, 403 (2019).

3.2. Adsorption of small molecules on amorphous ice under interstellar conditions

In this part of the project, the adsorption of a set of small molecules, namely methylamine, formamide, cyanamide, and propylene oxide have been investigated at the surface of low density amorphous (LDA) ice at temperatures characteristic of the interstellar medium. These molecules are all known to be present in the interstellar medium, their reactivity under interstellar conditions is thus of great astrochemical relevance. The reactivity of some of these molecules (e.g., methylamine, cyanamide) in the interstellar medium is also of potential relevance in the respect of prebiotic evolution. On the other hand, a large fraction of the solid surfaces in the interstellar medium (comets, interstellar dust, etc.) is covered by LDA ice. Possible adsorption of these molecules on LDA, providing their local concentration enhancement, might thus be a key factor in their reactivity in the interstellar medium. It should be emphasized that this part of the project is closely related to point 3.1 (adsorption of small molecules on I_h ice under tropospheric conditions), partly because the same methodology (i.e., grand canonical Monte Carlo simulation) is used, but also because some of these molecules (e.g., methylamine, formamide) are also present in the atmosphere as pollutants, and their adsorption on I_h ice under tropospheric conditions is also addressed in the frame of this project.

In analyzing the adsorption of methylamine on amorphous ice we found a strong adsorption ability of the methylamine molecules, involving also multilayer adsorption. The decrease of the temperature leads to a substantial increase of this adsorption ability, thus, considerable adsorption is seen at 20-50 K even at bulk gas phase concentrations that are comparable with that of the interstellar medium. Methylamine molecules can also be dissolved in the bulk amorphous ice phase. Both the adsorption capacity of amorphous ice and

the strength of the adsorption on it are clearly larger than those corresponding to crystalline (I_h) ice, due to the molecular scale roughness of the amorphous ice surface as well as to the lack of clear orientational preferences of the water molecules at this surface. The surface density of the saturated adsorption monolayer is estimated to be $12.6 \pm 0.4 \mu\text{mol}/\text{m}^2$, 20% larger than the value of $10.35 \mu\text{mol}/\text{m}^2$, obtained earlier for I_h ice, and at low enough surface coverages the adsorbed methylamine molecules are found to easily form up to three hydrogen bonds with the surface water molecules. The estimated heat of adsorption at infinitely low surface coverage is calculated to be $-69 \pm 5 \text{ kJ}/\text{mol}$, being rather close to the estimated heat of solvation in the bulk amorphous ice phase of $-74 \pm 7 \text{ kJ}/\text{mol}$, indicating that there are at least a few positions at the surface where the adsorbed methylamine molecules experience a bulk-like local environment.

Concerning the adsorption of formamide, our results revealed that, while no considerable amount of formamide is dissolved in the bulk ice phase, adsorption at the LDA and I_h surfaces under these conditions is a very strongly preferred process, which has to be taken into account when studying the chemical reactivity in the respective environments. The adsorption was found to lead to the formation of multimolecular adsorption layer, the occurrence of which somewhat precedes the saturation of the first molecular layer. Due to the strong lateral interaction acting between the adsorbed formamide molecules, the adsorption isotherm does not follow the Langmuir shape. Adsorption is found to be slightly stronger on LDA than I_h ice under identical thermodynamic conditions, due to the larger surface area exposed to the adsorption. Indeed, the monomolecular adsorption capacity of the LDA and I_h ice surfaces was found to be $10.5 \pm 0.7 \mu\text{mol}/\text{m}^2$ and $9.4 \mu\text{mol}/\text{m}^2$, respectively. The first layer formamide molecules are very strongly bound to the ice surface, forming typically four hydrogen bonds with each other and the surface water molecules. The heat of adsorption at infinitely low surface coverage was found to be $-105.6 \text{ kJ}/\text{mol}$ on I_h ice at 200 K.

We found that the adsorption of cyanamide is strictly monomolecular, moreover, condensation well precedes the saturation of the adsorption monolayer. Adsorbed cyanamide molecules are found to form altogether 3-4 hydrogen bonds with each other and with the surface water molecules at every surface concentration. As a consequence, their adsorption is strongly exothermic, and hence becomes progressively more pronounced with decreasing temperature. Lateral H-bonding between the adsorbed cyanamide molecules leads to their noticeable clustering, evidenced also by the non-Langmuir character of the adsorption isotherm, becoming more pronounced at lower temperatures. Besides adsorption, cyanamide

molecules are also found to be able to dissolve in the bulk LDA phase in a noticeable extent. However, contrary to the surface adsorption, dissolution turns out to be an entropy-driven, endothermic process, and hence becomes more pronounced at higher rather than at lower temperatures. The surface concentration of the saturated monolayer, estimated from that of the first layer of the condensed phase, and the heat of adsorption at infinitely low surface coverage turned out to be about $11.0 \pm 0.8 \mu\text{mol}/\text{m}^2$ and $-86.7 \pm 1.8 \text{ kJ}/\text{mol}$, respectively. We found that the formation of the adsorption layer of cyanamide of non-negligible (i.e., $0.5 - 2 \mu\text{mol}/\text{m}^2$) surface concentration and, due to the strong tendency for lateral self-association, the occurrence of H-bonded cyanamide dimers and small clusters at the surface of LDA ice is thermodynamically preferred at least in some parts of the interstellar medium.

Propylene oxide, on the other hand, can form a saturated monolayer at the LDA surface; the occurrence of traces of a second layer precedes condensation in the entire temperature range, and even multilayer adsorption occurs at 200 K. The adsorption isotherms exhibit again non-Langmuir shape due to the considerable lateral interaction. The surface concentration of the saturated monolayer was estimated to be $6.75 \pm 0.15 \mu\text{mol}/\text{m}^2$. Adsorbed molecules of the first layer were found to preferentially align in such a way that their three-member ring lays parallel with the surface plane, and they typically form one H-bond with the surface water molecules. The heat of adsorption at infinitely low surface coverage was found to be $-51.0 \pm 3.7 \text{ kJ}/\text{mol}$. However, the adsorption of propylene oxide on LDA ice can only be expected to occur in the lowest temperature domains of the interstellar medium, and involves a highly unsaturated adsorption layer.

This part of the research is described in the following publications:

1. R. A. Horváth, Gy. Hantal, S. Picaud, M. Szőri, and P. Jedlovsky, Adsorption of Methylamine on Amorphous Ice under Interstellar Conditions. A Grand Canonical Monte Carlo Simulation Study, *J. Phys. Chem. A* **122**, 3398 (2018).
2. B. Kiss, S. Picaud, M. Szőri, and P. Jedlovsky, Adsorption of Formamide at the Surface of Amorphous and Crystalline Ices under Interstellar and Tropospheric Conditions. A Grand Canonical Monte Carlo Simulation Study, *J. Phys. Chem. A* **123**, 2935 (2019).
3. P. Jedlovsky, R. A. Horváth, and M. Szőri, Computer Simulation Investigation of the Adsorption of Cyanamide on Amorphous Ice at Low Temperature, *J. Phys. Chem. C* **124**, 10615 (2020).
4. B. Kiss, M. Szőri, and P. Jedlovsky, Adsorption of Propylene Oxide on Amorphous Ice under Interstellar Conditions. A Grand Canonical Monte Carlo Simulation Study, *J. Phys. Chem. C* **124**, 16402 (2020).

3.3. Selective incorporation of ammonia within clathrate hydrates

We studied the trapping of ammonia molecules into a clathrate structure at three temperatures, namely at 100, 150 and 180 K, that are relevant for astrophysical environments. We found that the ammonia clathrate of structure I is stable at partial filling, irrespective of the temperature investigated here. It could also be metastable in a chemical potential (pressure) range that corresponds to a maximum of 8 ammonia molecules per unit cell, *i.e.*, to the full occupancy of the clathrate structure at very low temperature. However, at higher chemical potential values, partial dissolution of the clathrate is evidenced, concomitant with its transformation to low-density amorphous ice at 150 and 180 K. In the clathrate stability regime, we found that ammonia molecules can also displace water and become incorporated into the water lattice, which results in the progressive destabilization of the clathrate lattice with increasing number of trapped ammonia molecules. The obtained results point out the subtle interplay between the various environmental conditions (temperature, partial pressure of ammonia) on the stability of the clathrate phase in various planetary environments.

This part of the research is described in the following publication:

1. Ammonia Clathrate Hydrate As Seen from Grand Canonical Monte Carlo Simulations
B. Fábián, S. Picaud, P. Jedlovský, A. Guilbert-Lepoutre, and O. Moussis
ACS Earth Space Chem. **2**, 521 (2018).

3.4. Multiscale modeling of the reactivity of an atmospheric self-assembled monolayer

We analyzed the first few elementary steps of the reactions of a C=C terminated self-assembled monolayer with various reactive oxygen species using multiscale modeling. Such monolayers are occurring in atmospheric aerosols, where reactive oxygen species are also present, this analysis is therefore of relevance in atmospheric reactivity. Ab initio calculations were performed on a cluster taken out from MD simulations. The energetics of the reactions was compared with the analogous gas phase results, in order to characterize the energetic consequences of the presence of the surrounding alkene chains. We found that the relative energies of the interface reactions became lower by the average value of 11.5 ± 6.1 kJ/mol than the corresponding gas phase values. Due to this effect, interfacial H-abstractions by OH• on both allylic and vinylic positions have submerged barriers. Also, the relative energy of the transition state of the C-C bond scission reaction started from the non-terminal adduct become negative. Such lowering of the energy barriers might enhance the overall oxidation rate, and

change the branching ratio of the atmospheric oxidation of the unsaturated compound by OH• at the interface.

This part of the research is described in the following publication:

1. K. Korcsok, M. Szőri, B. Fábián, S. Picaud, P. Jedlovsky, and B. Viskolcz, Multiscale Modeling of Interfacial Oxidation Mechanism at Air/ Organic Interface: Reactions of CH₂=CH- Terminated Self-Assembled Monolayer with OH•, O₃, and HO₂•, *J. Phys. Chem. C* **122**, 9886 (2018).

3.6. Coating of magnetite nanoparticles in aqueous environment.

In this part of the project, we have only reached preliminary results. *Ab initio* calculations concerning the adsorption of six consecutive water molecules at the (100) surface of a magnetite unit cell were performed. The results indicate that six water molecules per unit cell can be chemisorbed on magnetite, some of which are chemisorbed in a dissociative way. Several H-bonding patterns of the six chemisorbed molecules correspond to rather similar energies, indicating that a H-hopping mechanism among these chemisorbed waters can occur. When developing a classical force field of these chemisorbed water molecules and OH groups, to be used in large scale simulations, besides the torsional rotation of the OH groups this proton transfer is also needed to be taken into account. Work in this direction is in progress.

At the experimental side of this project, micro-XRF (X-ray fluorescence) and micro-Raman spectroscopy measurements have been performed. These measurements, which will be repeated on freshly synthesized samples, confirmed the purity of the sample that will be investigated by HR-TEM measurements, to provide an experimental control of the above discussed *ab initio* calculations.

4. INVESTIGATION OF PROBLEMS RELATED TO ROOM TEMPERATURE IONIC LIQUIDS AND THEIR SURFACES

In the frame of this project, we also studied room temperature ionic liquids and their mixtures with polar molecular co-solvents, as potential green solvents. Concerning the bulk liquid phase of such mixtures, first we studied the role of the used charge distribution on the hydrogen bonding in mixtures of ionic and molecular liquids. Here we found that a

composition dependent charge distribution of the ionic liquids, proposed by several authors, perform worse than the unscaled one concerning the hydrogen bonding in mixtures of ionic and molecular liquids. For this reason, we used the unscaled charge distribution in the subsequent studies.

Then, we studied the changes in the local interionic and ion-solvent structure in mixtures of imidazolium-based ionic liquids, consisting of various anions (i.e., BF_4^- , trifluoromethylsulfonate, PF_6^-) and polar aprotic molecular solvents (i.e., acetonitrile, γ -butyrolactone, and propylene carbonate), occurring with increasing mole fraction of the polar solvent. Our results showed that, in the case of BF_4^- or trifluoromethylsulfonate anions, the anion moves from the above/below position (with respect to the imidazolium ring plane) to a position that is nearly linearly aligned with the C-H bond located between the two N atoms of the imidazolium ring, and hinders the possible interaction between this group and the solvent molecules. On the other hand, in the presence of PF_6^- anions the results are compatible with the direct interaction between the solvent and this CH group. The obtained results are in accordance with the experimentally observed ^1H chemical shift of this CH group and red shift of its vibrational mode. We also found that the ring H atoms are mainly solvated by the anions, while the methyl and butyl terminal H atoms are self-associated. The extent of this self-association is not very large: clusters of up to four H atoms were found, and such clusters occur only with low probability.

We also studied the liquid-liquid interface of the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (Bmim NTf₂) and the simplest aromatic liquid, benzene. This choice was dictated by the high miscibility of benzene and the virtually zero miscibility of the ionic liquid. The low miscibility of the ionic liquid results in a well defined interface, while the high miscibility of benzene provided a challenge, as the equilibrium concentrations are very close to each other in the two phases, and the interface between the high and low benzene concentration regions is difficult to locate. We presented a computational approach that is able to tell apart molecules belonging to different phases in solutions with high mutual solubility.

This part of the research is described in the following publication:

1. M. Sega, Gy. Hantal, Phase and interface determination in computer simulations of liquid mixtures with high partial miscibility, *Phys. Chem. Chem. Phys.* **19**, 18968 (2017).
2. V. Koverga, O. N. Kalugin, F. A. Miannay, Y. Smortsova, K. Golviznina, B. Marekha, P. Jedlovsky, A. Idrissi, The local structure in BmimPF₆/acetonitrile mixture: The charge distribution effect, *Phys. Chem. Chem. Phys.* **20**, 21890 (2018).

3. V. A. Koverga, Y. Smortsova, F. A. Miannay, O. N. Kalugin, T. Takamuku, P. Jedlovszky, B. Marekha, M. N. D. S. Cordeiro, A. Idrissi, Distance Angle Descriptors of the Interionic and Ion-Solvent Interactions in Imidazolium-based Ionic Liquids Mixtures with Aprotic Solvents: a Molecular Dynamics Simulation Study, *J. Phys. Chem. B* **123**, 6065 (2019).
4. V. Koverga, N. Maity, F. A. Miannay, O. N. Kalugin, Á. Juhász, A. Świątek, K. Polok, T. Takamuku, P. Jedlovszky, and A. Idrissi, Voronoi Polyhedra as a Tool for the Characterization of Inhomogeneous Distribution in 1-Butyl-methylimidazolium Cation-Based Ionic Liquids, *J. Phys. Chem. B* **124**, 10419 (2020).

5. INVESTIGATION OF PROBLEMS RELATED TO OTHER BULK FLUID PHASES

In the frame of this project, we studied the changes occurring with the composition in the local structure of aqueous dimethyl sulfoxide (DMSO) solutions at relatively low DMSO mole fractions. The aim of this study was to better understand the cryoprotective properties of such systems as well as the solvation process of proteins and amino acids. Significant changes in the local structure around the DMSO molecules were observed around the DMSO mole fraction of 0.1. These changes were associated with the simultaneous increase of the number of DMSO-water and decrease of water-water hydrogen bonds with increasing DMSO concentration. In other words, below the DMSO mole fraction of 0.1, DMSO molecules are mainly solvated by water molecules, while above it, their solvation shell consists of a mixture of water and DMSO. Adding DMSO was not found not affect the H-bonding between a reference water molecule and its first neighbor hydrogen bonded water molecules, while it increased the bent hydrogen bond geometry involving the second ones. The H-bonding between water and their first, second, and third DMSO neighbors were found to be stronger than those with the corresponding water neighbors. We also found that water molecules are more ordered in the vicinity of the hydrophilic group while their structure is close-packed near the hydrophobic group of DMSO.

We also studied the changes of various extensive thermodynamic quantities occurring upon mixing formamide as well as primary alkanolamines with water (at 298 K), and liquid methanol with supercritical CO₂ (at 313 K) in the entire composition range. These investigations mainly serve as preliminary studies for further investigations (which, in the case of formamide-water mixtures, have also be completed in the frame of this project, see points 1.3 and 3.2). The results obtained for formamide-water mixtures showed that the mixing of these two components is close to the ideal mixing, as both the energy and entropy of mixing turned out to be rather close to the ideal term in the entire composition range. Concerning the requirements of the full miscibility of the two components and the

reproduction of the experimental energy of mixing, the combination of the CHARMM formamide and SPC/E water models turned out to be the most reliable one. Concerning the alkanolamine-water mixtures, the free energy of mixing is found to be negative for all alkanolamines at every composition. This free energy decrease occurring upon mixing is found to be clearly of energetic origin. The obtained results suggest that alkanolamines form, on average, stronger hydrogen bonds with water than what is formed by two water molecules. In the case of CO₂-methanol mixtures, the transition of the system from liquid to supercritical state was found to occur at the studied temperature of 313 K around the CO₂ mole fraction value of 0.95. This liquid to supercritical transition is always accompanied by positive Helmholtz free energy of mixing and, consequently, by the non-miscibility of the two components. Further, both this non-miscibility around the liquid to supercritical transition and also the miscibility of the two components below this transition were found to be primarily of energetic rather than entropic origin. We also found that the methanol expansion coefficient is insensitive to the details of the potential models, and it is always in an excellent agreement with experimental data. On the other hand, both the volume and the energy of mixing depend strongly on the molar volume of neat CO₂ in the model being used, and in this respect the TraPPE model of CO₂ is superior over that of Zhang and Duan.

This part of the research is described in the following publication:

1. A. Idrissi, B. A. Marekha, M. Barj, F. A. Miannay, T. Takamuku, V. Raptis, J. Samios, P. Jedlovszky, Local Structure of Dilute Aqueous DMSO Solutions, as Seen From Molecular Dynamics Simulations, *J. Chem. Phys.* **146**, 234507 (2017).
2. B. Kiss, B. Fábián, A. Idrissi, M. Szőri, and P. Jedlovszky, Miscibility and Thermodynamics of Mixing of Different Models of Formamide and Water in Computer Simulation, *J. Phys. Chem. B* **121**, 7147 (2017), Erratum: *J. Phys. Chem. B* **121**, 9319 (2017).
3. A. Idrissi and P. Jedlovszky, Thermodynamics of Mixing Primary Alkanolamines with Water, *J. Phys. Chem. B* **122**, 6251 (2018).
4. R. A. Horváth, G. Horvai, A. Idrissi, and Jedlovszky, Thermodynamics of mixing methanol with supercritical CO₂ as seen from computer simulations and thermodynamic integration, *Phys. Chem. Chem. Phys.* **22**, 11652 (2020).