Research Networking Programmes

Science Meeting – Scientific Report

Scientific report (one single document in WORD or PDF file) should be submitted online within two months of the event. It should not exceed seven A4 pages.

***Proposal Title**: Liquid/Solid interfaces: Structure and dynamics from spectroscopy and simulations*

Application Reference N°: 4566

1) Summary (up to one page)

The central scope of our workshop was to gain microscopic insight in the processes occurring at solid liquid interfaces, bringing together scientists from computational physics and chemistry and experimentalists of interfaces.
Liquid-solid interfaces play an important role in a number of phenomena encountered in biological, chemical and physical processes. Surface-induced changes of material properties are not only important for the solid support but also for the liquid itself. In particular it has been shown that water at the interface is substantially different from bulk water, even in proximity of apparently inert surface, such as a simple metals.
This workshop aimed to provide the framework for people from both theoretical and experimental
communities to describe the state -of-the-art developments in their respective fields. The underlying motivation was also to give people the possibility to interact and trigger new collaborations, especially between theoreticians and experimentalists. Bringing together communities ranging from solid-state, surface science, liquid-state and biochemistry permitted to exchange ideas and methodologies, with the purpose to create a network of collaborations and therefore provide new advances.

2) **Description of the scientific content of and discussions at the event (up to four pages)**

i) The first key topic included the most recent progresses in vibrational sum frequencies generation, with particular focus on phase sensitive experiments and multidimensional spectroscopy.

Phase sensitive SFG experiments have permitted to unveil the molecule orientation at the interface. For example in case of mineral surfaces they have permitted to address the details of surface including the types of functional groups present, their protonation state and bond orientations, and the nature of near-surface water organization.

YR Shen who is a pioneer of this technique, described the basic theory of SFS with emphasis on how the bulk electric-quadrupole contribution contributes to the SF output. He showed that from transmission and reflection SFS measurements, the surface and bulk contributions can be separately deduced. If the bulk electric-quadrupole contribution is negligible compared to the surface electric-dipole contribution, then the latter can be used to characterize the surface unambiguously.

E. Backus presented some recent expansions into time-resolved (two-dimensional) spectroscopy which provide insight into the energy flow at the interface and into structural dynamics. By using this technique she showed that the water-air interface is structurally heterogeneous, yet highly dynamical. She addressed the timescale on which the heterogeneity decays and revealed the presence of surprisingly rapid inter- and intramolecular energy transfer processes. On the contrary, for the water-lipid interface she found extremely fast structural dynamics (~300 fs).

After the two experimental talks **A. Morita** summarized his recent efforts toward combining the two powerful techniques to obtain microscopic understandings of liquid interfaces. He showed applications including water, ice and other aqueous interfaces, liquid-liquid interfaces, and surfaces of organic molecules. He also addressed some fundamental issues for the surface non linear spectroscopy, such as quadrupolar contribution and local dielectric properties.

In the afternoon session of the first day **J. Lisy** engaged a discussion on the SFG interpretations, focusing on the nature of the interfacial region, how it changes when going from pure water to aqueous salt solutions, and trends within specific types of salts. He presented selective examples from current experimental and theoretical investigations, along with suggestive insights from the gas-phase cluster spectroscopy of solvated cluster ions.

Y. Nagata presented his work on the interplay of the nuclear quantum effects on the aqueous interface and the water bending mode SFG spectra. Through his talk, I tried to demonstrate how direct comparison between simulation and experiment is possible. He was followed by **M.P. Gaigeot** who further pursued the comparison between simulation and experiment. She presented the rganization of water at the interface with silica and alumina oxides. She showed how the interfacial hydrogen bond network can be related to the chemistry of the oxide surfaces. She extracted the vibrational IR spectra at these interfaces from the DFT-MD trajectories in order to give assignments of VSFG experimental signals in terms of interfacial water H-bond donors (“liquid-like”) and water H-bond acceptors (“ice-like”) to the surface silanols/aluminols.

In the case of the liquid water/vapor interface, the VSFG spectrum was computed from DFT-MD trajectories, as well as interfacial IR and Raman spectra. The real and imaginary parts of the VSFG spectrum were found in good agreement with the

experimental data providing an assignment of the VSFG bands according to the dipole orientation of the interfacial water molecules. She also showed how by calculating the Infrared and Raman spectra for interfaces of varying thickness, the bulk signatures appear after a thin layer of 2−3 Å only.

ii) **The second key topics on our program was how can simulation methods and new developments cope with the challenge of interpreting the new experimental results on interfaces.** This points to the new method development aspect of our workshop. On one side is the demand for high accuracy, including electronic structure effects, such as electronic polarization. On the other hand is the need to accumulate the relevant statistics in order to compare the calculated signal to the experimentally recorded one. In this respect we invited scientists from both the quantum mechanics (A. Michaelides, K. Leung, M. Sprik, N. Marzari) and classical mechanics/multiscale modelling (P. Jungwirth, L.C. Ciacchi, M. Salanne, Heinz) communities and experts from non-linear quantum optics (A. Morita, Y.Nagata) to share their view and their solutions to the response functions calculations at interfaces.
In his talk **A. Michaelides** presented some of his recent work in Ft-based molecular dynamics simulations and raised a discussion on the importance of quantum nuclear effects in hydrogen-bonded clusters, crystals, and overlayers as well as for H adsorption on graphene. He also showed some his recent works on the development of improved van der Waals functionals for DFT as well as the their application to problems relating to water adsorption. Also **N. Marzari** presented some recent methodological developments aimed at performing first-principles simulations in realistic electrochemical environments, starting from a proper description of the solvation medium, an electrolyte, and an applied electrochemical potential in a multi-scale electrostatic framework, and discuss applications ranging from vibrational Stark tuning to the equilibrium shape of platinum nanoparticles under hydrogen under-potential deposition. **M. Sprik** provided a review of his work on the TiO2 (rutile)-water interface, also reporting on the first results on the MnO2 (pyrolusite)-water interface.

iii) **A special chapter of our workshop was dedicated to the role of ions at the solid/liquid interfaces.** There has been a huge effort in the discussion of ions location at the water/vapor interface in connection with the Hofmeister series and its impact on a series of phenomena involving interfaces, such as protein binding and folding. Among our participants we had leading experts in the field, such as P. Jungwirth.
P.Jungwirth present recent simulations and experiments characterizing autoionization at the surface of liquid water and at the water/oil interface in an attempt to resolve the existing controversy.
More recently there has been also a lot of debate on the ions influence on the interface vibrational spectra of surface water. Pioneer work of H. Allen has shown how different ions with different surface propensity and different solvation properties can have a quite distinct impact on the water/vapor interface spectroscopy. However not less crucial is the role of ions at solid/liquid interfaces, which has been less characterized, but is fundamental to fields such as geochemistry, but also to the characterization of devices for energy production(photovoltaic, fuel cells,(bio-)sensors). The role of charge distribution at solid/liquid interface is a key step toward the design of new devices living in contact with electrolyte solutions.
J. Kubicki presented a novel mechanism for protonating bridging O atoms (Obr) and dissolving silica that is consistent with experimental data and quantum mechanical simulations of the α-quartz (101)/water interface. He discussed DFT molecular dynamics

simulations and static energy minimizations performed on the α-quartz (101) surface and with pure water, with Cl–, Na+ and Mg2+. The nature of the H-bonding of the surface silanol (SiOH) groups with the solution and with other surface atoms was examined as a test of the dissolution hypothesis. Silica interfaces were also addressed in the contribution of **D. Costa**. She discussed details of the H-bond network for the crystalline and the amorphous models. Moreover she also presented results for the adsorption on the bohemite/water interface.

Among the young investigators, K. Campean and Md. Shafiul Azam presented their first results on the ions behaviour at solid/liquid interfaces. **K. Campean** addressed the alpha alumina (0001) surface under UHV conditions using a molecular beam source and characterizing the resulting dissociated states using vibrational sum frequency spectroscopy. Comparison of the spectral response -- both lineshape and thermal stability -- with plane wave density functional theory calculations and the results of a microkinetic model strongly suggested that it is possible experimentally isolate the two possible, heretofore only theoretically predicted, dissociation pathways. The later challenge was addressed by simultaneous characterization of the vibrational sum frequency OH stretch, interfacial water bending and alpha alumina surface phonon response as the pristine alpha alumina surface reacts with water under ambient conditions. Experimental and computational characterization of all three frequency regimes made possible the unambiguous separation of the spectral response of molecularly and dissociatively adsorbed water and elucidates the mechanism of surface structural change on exposure to water. **Md.S. Azam** utilized surface specific second harmonic generation (SHG) to report on changes in the surface charge density of silica in the presence of ions in real time. He observed that the intrinsic equilibrium constant of the silanol groups is sensitive to the identity of the alkali ion. In contrast, varying the identity of the anion does not affect the intrinsic acidity of the sites but rather their mechanism of deprotonation. Specifically, positive cooperativity is observed in the deprotonation of silanol groups with increasing halide size and polarizability. He also discussed the complementary measurements of the water structure using sum frequency generation spectroscopy.

iv) **Nano- and microparticles** have optical, structural, and chemical properties that differ from both their building blocks and the bulk materials themselves, due to the high surface-to-volume ratio. To understand the properties of nano- and microparticles, it is of fundamental importance to characterize the particle surfaces and their interactions with the surrounding medium. Recent developments of nonlinear light scattering techniques have resulted in a deeper insight of the underlying light-matter interactions. They have shed new light on the molecular mechanism of surface kinetics in solution, properties of interfacial water in contact with hydrophilic and hydrophobic particles and droplets, molecular orientation distribution of molecules at particle surfaces in solution, interfacial structure of surfactants at droplet interfaces, acid-base chemistry on particles in solution, and vesicle structure and transport properties.

S. Roke showed results on the charge and orientation of water at the oil/water interface by combining ζ-potential measurements with sum frequency scattering (SFS) measurements. In these experiments she measured SF scattering spectra of the interface of 300 nm hexadecane droplets dispersed in water. Analysis of the data showed that the average water orientation on a neat oil droplet/water interface is the same as the water orientation on a negatively charged interface. pH dependent experiments show, however, that there is no sign of selective adsorption of hydroxide ions. Molecular dynamics simulations, both with and without inter-molecular charge transfer, showed that the

balance of accepting and donating hydrogen bonds is broken in the interfacial layer, leading to surface charging. This can account for the negative surface charge that is found in experiments.
L. Colombi Ciacchi showed that the contact forces between TiO2 nanoparticles in the presence of adsorbed water layers arise from a superposition of capillary and structural effects. The latter are directly related to the cross-correlation (i.e. the interference pattern) between the water density oscillations in surface proximity. He also presented exemplary studies of proteins and short polypeptides interacting with and adsorbing at metal oxide surfaces.

v) **Finally a few selected talks contributed to our last topic: Not only water.** Water has been the most widely studied liquid due to its universal presence and its very special phase diagram, however solid/liquid interface also involve different liquids, where completely different properties are involved. In the realm of new systems for energy production such as dye-sensitized solar cells and super capacitors, room-temperature ionic liquids are considered the medium of choice. Thus, while the ionic liquid appears to be a promising medium, there is almost no molecular-level information as to their interaction with the solid surfaces. Recent new investigations were able to provide the orientation of room-temperature ionic liquid at the graphene-ionic liquid interface and to describe the nature of an ionic liquid-(solid) salt interface.
In this session **K. Leung** presented his advances in the simulation of interfaces of lithium ion batteries. In lithium ion batteries, the voltage difference between an electrode and the electrolyte governs lithium intercalation into anodes and cathodes as well as the sacrificial decomposition of organic solvent-based electrolyte (i.e., "solid electrolyte interphase" (SEI) formation). While readily controlled in experiments, this quantity has proven challenging to calculate or enforce in Density Functional Theory simulations. He reported ab initio molecular dynamics predictions of voltage drops between the basal planes of model lithium-intercalated graphite electrodes and a liquid ethylene carbonate/lithium ion electrolyte as the net charge on the electrode varies. The results, although somewhat limited by the nanoscale simulation cell size, serve as a calibration guide for other interfaces. The effect of surface spatial inhomogeneity was also discussed.
M. Salanne reported his results on molecular dynamics simulations of realistic electrode structures comparable with carbide-derived carbons with polarization of the electrode atoms by the ionic liquid electrolyte. This original design of an electrochemical cell allows to recover capacitance values in quantitative agreement with experiment and to gain knowledge about the local structure of the ionic liquid inside the pores (local ionic densities, local coordination numbers). Then, from the comparison between planar (graphite) and porous electrodes, he proposed a new mechanism explaining the capacitance enhancement in nanoporous carbons.

3) Assessment of the results and impact of the event on the future directions of the field (up to two pages)

We believe that most of our aims were fully achieved. Indeed we managed to gather together most of the main active scientists investigating the solid-liquid interfaces within different communities. We had live discussions in a friendly atmosphere where questions could be freely asked. We received positive feedback from many of the participants. In particular younger participants enjoyed the discussion and profit from the presentations and discussion.
People from different communities, especially theoretical/computational and experimental could sit together and discuss the different view points.
New collaboration has been started, to name some, D. Costa, M-P Gaigeot, M.Sulpizi and MS Azam have initiated a collaborative activity to advance understanding on absorption of ions at the silica/water interface. M. Sprik and J. Luetzenkirchen will collaborate on electrolyte/mineral interfaces. M-P Gaigeot and M Sulpizi will collaborate with E. Backus on understanding 2D-SFG spectroscopy results at the solitd/liquid interfaces combining experiments and simulations.
We believe that our microscopic understanding of solid-liquid interfaces is advancing and a lot more is now know about it. However the progresses on both the experimental point of view and theoretical raise new questions which will need to be addressed. We aim to organize another workshop on the same topics possibly in 2015. New challenges ahead include:

1. Simulation of spectra in the condensed phase? A difficulty remains in realizing the promise of interface specific spectroscopy to provide a detailed picture of interfacial structure and dynamics has been the interpretation of the spectra – what molecular dynamics produce the spectral signature?

2. New 2D-SFG spectroscopy has opened new questions on structural dynamics of interfacial liquids? What can we understand from experiments and simulations? Multidimentional interface specific spectroscopy poses new challenges for theory/simulations, including how to combine accuracy and statistically relevant sampling of the necessary time-scale.

4) Annexes 4a) and 4b): Programme of the meeting and full list of speakers and participants

Annex 4a: Programme of the meeting

Day 1 - June, 24th 2013

Session I (Spectroscopy, phase sensitive, multidimentional)

- 09:30 to 09:40 - Welcome
- 09:40 to 10:30 - **Yuen Ron Shen**
  Bulk Contribution in Optical Sum-Frequency Spectroscopy
- 10:30 to 11:20 - **E. Backus**
  Structure and dynamics of interfacial water
- 11:20 to 11:40 - Coffee Break
- 11:40 to 12:30 - **A. Morita**
  Theory and Computational Analysis of Sum Frequency Generation Spectroscopy of Liquid Interfaces

Lunch break

- 12:30 to 14:00 - Lunch

Session II (Spectroscopy, phase sensitive, multidimentional)

- 14:00 to 14:50 - **Jim Lisy**
  Interpretations of Vibrational Sum Frequency Interfacial Spectra: How Certain Can We Be?
- 14:50 to 15:20 - **Y. Nagata**
  New Information on aqueous interface from direct comparison of simulation and experiment
- 15:20 to 15:50 - **Marie-Pierre Gaigeot**
  Water interfaces: structure and vibrational spectroscopy from DFT-based MD simulations
- 15:50 to 16:10 - Coffee Break
- 16:10 to 16:40 - **Atsushi Urakawa**
  Probing Solid-Liquid Interfaces by Infrared Spectroscopy
- 16:40 to 17:10 - **J. Luetzenkirchen**
  Some experimental observations at electrolyte/mineral interfaces at more or less controlled laboratory model systems

Session III (Poster Session)

- 17:10 to 18:30 - Poster Session

Day 2 - June, 25th 2013

Session IV (New Methods Developments)

- 09:30 to 10:20 - **Angelos Michaelides**
  Towards accurate and reliable simulations of ice, water at surfaces, and some other things…
- 10:20 to 11:10 - **Michiel Sprik**
  All-atom modelling of transition metal oxide water interfaces
- 11:10 to 11:30 - Coffee Break
- 11:30 to 12:20 - **J. Kubicki**

A New Hypothesis for the Dissolution Mechanism of Silicates

- 12:20 to 12:50 - **Dominique Costa**
  Amorphous silica-water interface studied by DFT-MD

Lunch break

- 12:40 to 14:00 - Lunch

Session V (Interfaces in Nanoparticles)

- 14:00 to 14:50 - **S. Roke**
  The Orientation and Charge of Water at the Hydrophobic Oil Droplet/Water Interface
- 14:50 to 15:40 - **Lucio Colombi Ciacchi**
  Adhesion phenomena mediated by the liquid structure at solid/liquid interfaces
- 15:40 to 16:00 - Coffee Break
- 16:00 to 16:50 - **Nicola Marzari**
  Soggy, swampy, and maybe steamy, but never sloppy: Quantum modelling of electrified interfaces
- 16:50 to 17:40 - **H. Heinz**
  Mechanisms of Molecular Recognition and Shape Control at the Nanoscale: Computation Meets Experiment

Social Dinner Grand Cafe de Montbenon

- 19:30 to 22:30 - Social Dinner

Day 3 - June, 26th 2013

Session VI (Ions at the Interface)

- 09:30 to 10:20 - **P. Jungwirth**
  Can inorganic ions swim on water?
- 10:20 to 11:10 - **Kevin Leung**
  Towards calculating the voltage difference between electrodes and electrolytes in ab initio molecular dynamics and the voltage dependence of electrolyte decomposition in batteries
- 11:10 to 11:30 - Coffee Break
- 11:30 to 12:20 - **Mathieu Salanne**
  Modeling the interface between a room-temperature ionic liquid and a carbon electrode
- 12:20 to 13:10 - **R.K. Campen**
  Understanding Water Dissociation and Surface Reconstruction at the alpha-Al2O3 (0001) surface
- 13:10 to 13:40 - **Md. Shafiul Azam**
  Specific Ion Effects on Acid-Base Equilibria at the Planar Silica/Water Interface

Lunch Break

Annex 4b: Full list of speakers and participants

Australia

- Tiff Walsh *(Deakin University)*

Belgium

- Dan Lis *(National Fund for Scientific Research (FRS- FNRS), Brussels)*

Canada

- Md. Shafiul Azam *(University of Alberta)*

Czech Republic

- P. Jungwirth **(invited speaker)** *(Academy of Sciences of the Czech Republic)*
- Ondrej Kroutil *(PhD student)*
- Babak Minofar *(Institute of Nanobiology and Structural Biology, Academy of Sciences of the Czech Republic)*
- Stanislav Parez *(Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic)*
- Milan Predota *(University of South Bohemia,)*

France

- Álvaro Cimas *(Université d''Evry val d''Essonne)*
- Manuel Corral Valero *(IFP Energies nouvelles)*
- Dominique Costa **(invited speaker)** *(CNRS, Ecole Nationale Supérieure de Chimie, Paris)*
- Laurent Joly *(Lyon)*
- Carine Michel *(CNRS, Ecole Normale Supérieure de Lyon)*
- Morgane Pfeiffer-Laplaud *(Université d'Evry Val d'Essonne)*
- Mathieu Salanne **(invited speaker)** *(Université Pierre & Marie Curie)*

Germany

- E. Backus **(invited speaker)** *(MPI for Polymer Research, Mainz, Germany)*
- R.K. Campen **(invited speaker)** *(Fritz Haber Institute, Berlin,)*
- Lucio Colombi Ciacchi **(invited speaker)** *(University of Bremen)*
- Isidro Geada *(Johannes Gutenberg University Mainz)*
- Nils Hildebrand *(University of Bremen)*
- Gang Huang *(Johannes Gutenberg University Mainz)*
- Remi Khatib *(Condensed Matter Theory Group KOMET 331 - Johannes Gutenberg-UniversitÃ¤t Mainz)*
- Jens Laube *(Hybrid Materials Science Group, Bremen Centre for Computational Materials Science (BCCMS), University of Bremen)*
- J. Luetzenkirchen **(invited speaker)** *(Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Germany)*
- Santosh Meena *(Johannes Gutenberg University Mainz)*
- Robert Meißner *(Fraunhofer IFAM Bremen, University of Bremen)*
- Y. Nagata **(invited speaker)** *(MPI for Polymer Research, Mainz, Germany)*
- Leila Salimi Parvaneh *(Max Planck Institute for Polymer Research, Mainz)*
- Zhen Zhang *(Max-Planck-Institut für Polymerforschung)*

Japan

- A. Morita **(invited speaker)** *(Graduate School of Science, Tohoku University, Japan)*

Norway

- Maarten Beerepoot *(Center for Theoretical and Computational Chemistry, Tromsø)*

Spain

- Atsushi Urakawa **(invited speaker)** *(Institute of Chemical Research of Catalonia (ICIQ))*

Switzerland

- Matthew Brown *(ETH Zurich)*
- Yixing Chen *(LBP, EPFL)*
- Marcella Iannuzzi *(University of Zurich)*
- Nicola Marzari **(invited speaker)** *(Swiss Federal Institute of Technology Lausanne (EPFL))*
- Ratan Mishra *(ETH Zurich)*
- S. Roke **(invited speaker)** *(EPFL Switzerland)*
- Ekaterina Rostova *(EPFL)*
- Rüdiger Scheu *(EPF Lausanne)*
- Ari Paavo Seitsonen *(University of Zurich)*
- Nikolay Smolentsev *(École polytechnique fédérale de Lausanne)*

United Kingdom

- Jasmine Desmond *(University of Warwick)*
- Xiaozhou Li *(Queen's University Belfast)*
- Angelos Michaelides **(invited speaker)** *(University College London)*
- Michiel Sprik **(invited speaker)** *(University of Cambridge)*

USA

- Mark DelloStritto *(The Pennsylvania State University)*
- H. Heinz **(invited speaker)** *(University of Akron, USA)*
- J. Kubicki **(invited speaker)** *(PennState University, USA)*
- Kevin Leung **(invited speaker)** *(Sandia National Laboratories, Alburqerque)*
- Jim Lisy **(invited speaker)** *(University of Illinois at Urbana-Champaign USA)*
- Yuen Ron Shen **(invited speaker)** *(University of California at Berkeley)*