CFCAM Sponsored Event

Proposed title:

Modeling Oxide/Water Interfaces and Reactivity

Location : Paris

Proposed date: September 2013

Proposed duration: 2 days

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1 *Proposal*

1 Introduction and motivation

Oxide surface reactivity is exploited in many industrial processes and is fundamental to environmental chemistry and geochemistry. Understanding chemical reactions occurring at metal oxide-aqueous solution interfaces has importance in a variety of fields, including atmospheric chemistry, heterogeneous catalysis and photocatalysis, chemical sensing, corrosion science, environmental chemistry and geochemistry, metallurgy and ore beneficiation, metal oxide crystal growth, soil science, semiconductor manufacturing and cleaning, and tribology [1]. The metal oxide-aqueous solution interface is reactive due to acid-base, ligand exchange, and/or redox chemistry involving protons (hydronium ions), hydroxyl groups, aqueous metal ions, aqueous organic species and also complexes among these species. Interfacial localization of those species (adsorption) may result from electrostatic, chemical complexation, and hydrophobic interactions between surface and sorbate. One very important, but only partly understood, aspect of oxide-aqueous solution interfaces is the nature of the interfacial solvent, in which the structure and properties of interfacial water are perturbed relative to bulk water. Recently, a deeper insight has been gained thanks to major advances in both experimental techniques and computer simulations.

2 State of the art

On the experimental side, surface specific techniques, such as non-linear optical spectroscopy (Sum Frequency Generation Spectroscopy (SFG) and Second Harmonic Generation (SHG)), surface sensitive X-ray scattering, in situ Scanning tunneling microscopy (STM) and infrared reflection absorption spectroscopy have permitted to gain information on layers of nanometric thickness at the interface.[2]. On the other hand it is quite clear that the experiments require theoretical modelling in order to dissect the results and to rationalize the different factors that contribute to the interfacial properties. In this respect molecular dynamics simulations can prove a major tool to accurately describe both structure and reactivity in a consistent way. Oxides/water interfaces have been described by means of classical molecular dynamics (MD) simulations: Goethite FeOOH,[3] TiO_2,[4] SiO_2,[5], CaO,[6] SnO_2,[4a, 4c, 7,] ZrO_2,[4c] clays,[8] alumina polymorphs, [9] Fe_2O_3,[10] CeO_2,[9e] MnO_2,[9e] ZnO [11], copper oxide[12] are examples of materials of interest. The organization of water at the surface, and adsorption of inorganic ions have been investigated. However, classical MD suffers from the difficulty to model the acid-base character of hydroxyl groups and to model proton transfers at the oxide-liquid interface, all properties that determine the surface reactivity.[13] Recent works go beyond these limitations, using reactive force fields (Reax FF).[4g, 5g, 6, 9g, 11b, c, 12, 14]

Progresses in first principles MD simulations in the past 3-5 years have been enormous. In particular efficient treatment of basis set and long range interactions have permitted to extend the simulation to hundred-thousand atoms, which now allows to tackle realistic models for interfaces, maintaining first principles quality. Those methods have indeed been successfully used in the past decade to describe bulk liquids,[15] and solutes in liquids.[16] Spectroscopic properties are for instance derived from such simulations with very good agreements with experiments[16], and properties such as proton transfers in water,[17] and pKa of acid-base are described in the solution and at interfaces with a

remarkable accuracy.[18]. Recently, oxide/water interfaces [19] have been modeled by means of DFT based MD.

3 Objectives

The objectives of the proposed workshop is to gather french researchers from the field in order to try to set up an active collaboration group that could a) define research directions of pivotal interest in the field, b) carry out collaborative projects, c) respond to french/international ANR proposals on this specific field within a 2 years period of time.

Key events occuring at the interface are, eg. (1) the water density and organisation near the surface (2) the effect of water on the structure, composition, and reactivity of surface sites including defect sites; (3) the organization of adsorbed charged species (cations and anions), i.e. the speciation of metal ions in solution and how they are modified when they react with the solid surface (4) how many protons are released from the metal oxide surface during the sorption process (5) how complexes bond to the surface; (6) the effects of sorption on surface atomic and electronic structure; (7) the effects of electron-transfer reactions between sorbate and surface.
Methods (theoretical and experimental), codes and strategies will be exposed and compared.

4 Participant List

A possible list of key actors and participants might be the following, where we have also included a few foreigners (either experimentalists or theoreticians) for their pivotal contribution to the field of interest.

Name	Speciality	Affiliation	*Email*
S. Parker	MD simulations	U. Bath (to be invited)	*chsscp@bath.ac.uk*
J. Lutzenkirchen	Zetametry	KIT (to be invited)	*johannes luetzenkirchen∂kit edu*
J. Gibbs Davis	SFG	Alberta (CA) (to be invited)	*gibbsdavis@ualberta.ca*
M. Bonn, E. Backus	Molecular Spectroscopy	MPIPR Mainz (to be invited)	*bonn@mpip-mainz.mpg.de*
M.L. Sulpizi	MD simulations	CMTG Mainz (to be invited)	*sulpizi@uni-mainz.de*
O. Durupthy	RMN	CMCP	*Lovier.durupthy(at)upmc.fr*
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4000 euros are requested to CFCAM for the invitations of some of the foreigner speakers proposed here and two lunches for the participants.

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