Soft.Matter@PT 2015

Date: 2-3 July, 2015 Location: FCUL, C6, room C6.2.46

Book of abstracts

Thursday, 2 July 2015 - 9h30

Characterization of enzyme-electrode constructs by surface enhanced vibrational spectro-electrochemistry: relevance for fundamental and applied science.

S. Todorovic

Special emphasis in our research is given to molecular processes at interfaces that involve electron transfer (ET) and catalysis. Interfacial reactions are ubiquitous in biology and also constitute the basis for the functioning of enzyme-supported bioelectronic devices. We employ surface enhanced vibrational spectroscopy (surface enhanced RR, SERR, and IR, SEIRA) coupled to electrochemistry to investigate enzymes immobilized on biocompatible metal electrodes, which can mimic enzymes´ redox partners, i.e. electron donor or acceptor. In this manner we can monitor bioelectrocatalysis in situ, and simultaneously reveal mechanistic and structural properties of immobilized metalloenzymes and even detect their catalytic intermediates. This is crucial for better understanding of functioning of enzyme-electrode constructs for biotechnological applications which rely on direct ET. Moreover, electrode coating can mimic enzyme´s substrate and allow us to probe enzyme/substrate interactions, as it is the case of DNA repair enzyme EndonucleaseIII and DNA-terminated self assembled monolayers (SAMs). Furthermore, immobilization of membrane proteins on biocompatible metal electrodes can reproduce basic features of natural membrane: restricted mobility, influence of strong electric fields and variable dielectric constants on ET. We use surface enhanced vibrational spectro-electrochemistry as a unique tool for investigations of the redox processes of membrane proteins, providing information about the structure of the redox sites, the thermodynamics and kinetics of ET and also protein dynamics under physiological-like conditions.

Thursday, 2 July 2015 - 10h00

Probing the distinctive interactions and structures of ionic liquids and their mixtures using MD simulations and different aggregation analysis tools.

J. Canongia Lopes

In this contribution, we discuss how the relation between interactions and structure in ionic liquids (ILs) can be probed at a molecular level using ab initio and molecular dynamics (MD) methodologies.

The first part of the discussion will focus on the unique and complex properties of ILs as pure substances including the existence of an extended and flexible polar network and the possibility of a second nanosegregated subphase containing the nonpolar residues of the molecular ions that constitute some ILs.

The discussion will then be extended to IL plus molecular species mixtures/solutions. In this context the concept of ILs as charge templates for the electronic make-up of the molecular species will be analyzed at length. Finally, that concept will be extended to ILs adsorbed over solid substrates, at the liquid-air interface or forming solvates with selected molecules.

Thursday, 2 July 2015 - 11h30

Water near ions, hydrophobes and proteins

A. Vilaverde

The ability of biopolymers such as proteins to fulfill their biological function is determined by the balance between their intramolecular interactions, their interactions with natural or artificial ligands, water, free ions and other molecules in solution. Seemingly small changes to the protein or its environment – e.g., fluorinating a single protein alkyl group or sulfating a few amino acids in a ligand - often lead to large alterations in protein properties. In my research group we use molecular simulations to gain fundamental knowledge on various interactions germane to protein structure, stability and function. We investigate: 1) the structure and dynamics of water near extended hydrophobic interfaces (the air-water interface) or small hydrophobic solutes (fluorinated amino acids); 2) the structure and dynamics of water near ions in the bulk and at the air-water interface; 3) the interaction between anionic polymers and proteins.

Thursday, 2 July 2015 - 12h00

How to better understand ordered lipid domains and their function in cell membranes

R. Almeida

The critical role of lipid ordered domains will be demonstrated with biophysical studies of membrane lipid organization in living cells and in model systems, concerning mammalian and fungal membranes. Membrane interactions with different types of bioactive molecules will be briefly presented, including endogenous molecules such as the hormone epinephrine or membrane proteins, as well as drugs, including anticancer and antibacterial compounds. Strategies to tackle the complexity of living cell membranes will be discussed, in an attempt to reach a compromise between lipid lamellar phases in artificial or reconstituted systems and observations in living cells.

Thursday, 2 July 2015 - 14h00

A Cellulosic Liquid Crystal under shear: Rheo-NMR study

C. Echevarria

Since long ago cellulosic lyotropic liquid crystals were thought as potential systems to produce fibers competitive with spiderwebs or Kevlar, yet the processing of high modulus materials from cellulose-based systems was hampered by their complex rheological behaviour. Cellulose and its derivatives such as hydroxypropylcellulose (HPC) can form networks similar to elastomers when produced from liquid crystalline (LC) solutions, that can be manipulated in order to produce helicoidal structures and spirals that respond to external stimuli producing bending, unbending and torsion motions similar to movements found in plants. The main objective of this work is to understand the structure-properties relationship and the mechanism behind the motion by means of a deep study

of the cholesteric liquid crystal HPC/water system using Rotational rheology and Rheo-NMR in order to determine the structural changes induced by shear flow. [1]

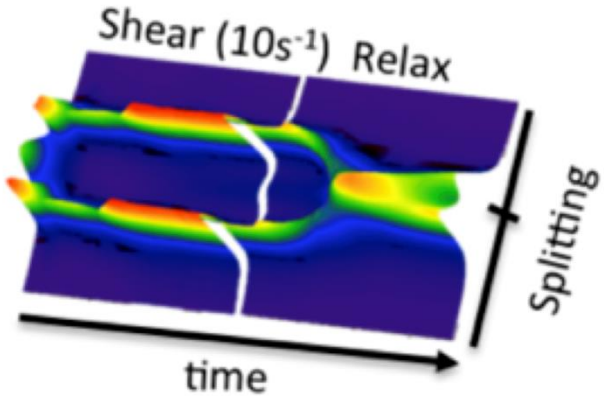

Figure 1 – Evolution with time of DNMR spectra of LC-HPC during shear and relaxation process.

[1] C. Echeverria, P.L. Almedia, G. Feio, J. L. Figueirinhas, A.D. Rey and M.H. Godinho., Rheo-NMR study of Water-Based Cellulose Liquid Crystal System at High Shear Rates, Polymer, DOI: 10.1016/j.polymer.2015.03.050 (2015).

Thursday, 2 July 2015 - 14h30

Microfluidics with in-situ SAXS: from manipulation of soft materials to the study of out-of-equilibrium phenomena

B. Silva

Soft materials encompass a wide variety of nano- and meso-structured materials, and by definition are deformable by thermal stresses and fluctuations. These materials are ubiquitous in biology (e.g. in the membranes and cytoskeleton of cells) and technological applications (e.g. in drug delivery formulations and liquid crystal displays). Nevertheless, despite their equilibrium properties having been the subject of considerable attention, much remains unknown about their out-of-equilibrium behavior and dynamics. In this talk, I will show how microfluidic chips (devices that involve precise control and manipulation of fluids under sub-millimeter confinement), can be used to manipulate soft materials at the nano-scale. This allows us to study fundamental out-of-equilibrium processes (e.g. coupling of structure and flow, dissipation), as well as control and build complex out-of-equilibrium structures of technological interest.

In a first example, we use this manipulation ability to create well-defined flowing interfaces to study the interplay between shear-flow forces and the structure of liquid crystals and surfactant monolayers. By use of a microfocused x-ray beam applied *in-situ* on the microfluidic device we are

able to determine the orientation field of the liquid crystal molecules, and how this orientation is influenced by the flow conditions and chemical nature of the interfaces. In a second example, I will show how microfluidics with *in-situ* SAXS can be used to study the kinetic evolution of phase transitions, more specifically, the lamellar-to-microemulsion transition in surfactant-oil-water systems.

Thursday, 2 July 2015 - 15h00

Liquid crystals at CFTC: an overview

N. Silvestre

In the last decade CFTC has contributed significantly to the study of liquid crystals in a large variety of systems that are important from both the fundamental and the applications points of view. Here we will give a brief account of the major achievements, from interfacial phenomena to liquid crystal colloids, and confined systems. Finally, we will discuss future perspectives.

Thursday, 2 July 2015 - 16h30

Building structures with colloids

N. Araújo

With a typical size in the micron down to the nanometer scale, colloidal particles are considered ideal candidates to produce materials with enhanced physical properties. The state-of-the-art techniques for synthesizing them provide high control over shape, size, and directionality of interactions. In spite of these advances, there is still a huge gap between the synthesis of individual components and the manipulation of their spontaneous organization towards the desired structures. I will give an overview of our ongoing efforts to tackle this problem.

Thursday, 2 July 2015 - 17h00

Smart Hydrogels in Tissue engineering and Regenerative Medicine

Joaquim Miguel Oliveira

“Smart” hydrogels, also variously referred as “intelligent”, “stimuli-responsive”, “stimuli-sensitive” or “environmentally-sensitive” hydrogels, are 3D hydrophilic network structures of polymer chains that are able to change their properties in response to environmental stimuli such as temperature, pH, light, magnetic and electric fields, and ionic strength or enzymatic environment. Systems with multiple responsive properties have also been developed combining two or more stimulus. Rapid and significant responses to changes to external stimuli are critical for the versatility of such “smart”

hydrogels. That stimuli-responsive hydrogels are potentially beneficial for a diverse range of applications because the properties can be changed by the stimulus at the desired point and time. We will present our most recent and relevant reports dealing with the development, applications and processing of “smart” hydrogels, mainly in the context of tissue engineering and regenerative medicine.

Thursday, 2 July 2015 - 17h30

Microfluidic flows of complex fluids

M. Alves

An overview of the research topics investigated at the Transport Phenomena Research Group (CEFT – Centro de Estudos de Fenómenos de Transporte; FEUP – Faculdade de Engenharia da Universidade do Porto) will be presented, with focus on complex flow of non-Newtonian fluids in microfluidic devices.

Key-words: Microfluidics; Viscoelastic fluids; Flow instability; Computational rheology; Elastic turbulence.

Friday, 3 July 2015 – 9h00

Sarspec: o desenvolvimento de instrumentação para espectroscopia em Portugal

R. Silva

Conhecer a Sarspec - a primeira empresa portuguesa dedicada ao desenvolvimento de instrumentação em espectroscopia em Portugal. Apresentação do primeiro espectrómetro, das suas características, componentes e configurações. Aplicações tipo para as soluções Sarspec: Absorvância e Fluorescência.

Friday, 3 July 2015 – 9h30

Spectroscopy Techniques for Research and Industry

J. Cascalheira

Bióptica, Lda was starting on 1987 as a distributor company of Melles Griot (lasers/photonics) and Jobin Yvon (now Horiba Scientific) leader on spectroscopy field research.

Bióptica is committed to providing after sales service and support since the beginning.

In our communication we will present the companies profiles that we represent, showing different application using spectroscopy techniques as Fluorescence, Photoluminescence, Raman, Ellipsometery, SPRi, Vacuum UV spectroscopy, Plasma Profiling TOFMS, different techniques using pulsed and CW lasers, Enhanced darkfield optical microscopy & hyperspectral imaging, Spectroradiometry and photometry, and much more ……

Friday, 3 July 2015 – 10h00

Luminescent nanothermometry. Nanothermometers and nanoheaters get closer

L. Carlos

Friday, 3 July 2015 – 11h30

Weak Power Rheology of Cells

P. Patrício

We describe the weak power law rheology of cells, making a review of recent experimental results and theoretical approaches.

Friday, 3 July 2015 – 12h00

Quantifying and modeling patterned cell fate determination

Filipa Alves

During embryo development, the cells that build the new organism will be differentiated in the right place at the right time, giving rise to different tissues and organs. How do cells "know" where they are? How is gene expression regulation coordinated in space and time? How are gene expression patterns reliably shaped in the presence of molecular fluctuations, genetic variability and environmental perturbations?

To address these questions, we are using theoretical modeling approaches, developed in close relation with the experimental work from our collaborators.

As an example of patterned cell differentiation, I will present ongoing work on the formation of pigmentation patterns on butterfly wings. We are studying how these patterns are formed and why they vary within the same species and between different species.

Furthermore, as the models' validation is strongly dependent on quantifying and estimating the biological parameters involved, we are also developing dedicated image acquisition systems, together with quantitative image analysis methods and databases.

Our results provide testable hypotheses for how the observed variation in the pigmentation patterns may depend on subtle changes on specific biophysical parameters, opening interesting perspectives to understand the development and evolution of these mechanisms.

Friday, 3 July 2015 – 14h00

Living cell rheology

C. Leal

The population growth of a bacterial culture, an active colloidal system of spherical cells, was followed by classical rheological measurements, under steady-state and oscillatory shear flows, allowing us to observe an extremely complex mechanical behavior, not accessible via optical techniques commonly used in biology/medical laboratories. To understand the observed rich viscoelastic behavior we propose a model in which the bacteria develop percolated structures based on cell-to-cell density-dependent interactions.

This field of work opened a new and promising interdisciplinary field of research bringing together biologists, material scientists and physicist.

Friday, 3 July 2015 – 14h30

Surfactant and polymers as non-covalent dispersants of carbon nanotubes: experiments and insight

E. Marques

Carbon nanotubes (CNTs) have great potential *inter alia* in composite reinforcement and molecular electronics. Due to strong van der Waals cohesive forces, CNTs are subject to bundling and entanglement, and yet most applications require individualized tubes. Non-covalent dispersion of CNTs in water using amphiphiles is essential to many applications but still poorly understood at molecular level. The dispersion mechanism and configuration of the dispersant on the nanotube surface still awaits consensus. In this talk, we will present results from two studies: (i) an investigation of the exchange dynamics of a dispersing polymer between the CNT surface and water as probed by ^{1}H self-diffusion NMR; (ii) a study on the role of surfactant molecular properties on the effectiveness and efficiency of CNT dispersability in water. In study (i), we will show that at any instant, only a small fraction of polymers are adsorbed on the nanotubes, with polydisperse residence times in the range of 100−400 ms. Significantly, we provide an estimate of $D = (3–8) \times 10^{-12}$ m^2 s^{-1} for the coefficient of lateral diffusion of the polymer along the CNT surface, consistent with an nonwrapping picture for interaction. In study (ii), we will present and rationalize recent accurate data on the effect of surfactant chain length, charge, concentration and nanotube curvature (single-walled vs. multi-walled) on the dispersability of CNTs.

Friday, 3 July 2015 – 15h00

Fluorinated chains @ interfaces

E. Filipe

Highly fluorinated compounds have become key fluids in a number of fields, due to their chemical inertness, biocompatibility and peculiar physical properties. Some of their most significant applications (liquid ventilation formulations, as oxygen carriers in blood substitutes) involve interfaces.

Perfluorinated chains ($-CF_2CF_2CF_2-$) are not only highly hydrophobic but also lyophobic, i.e. they segregate hydrogenated chains. Mixtures of alkanes and perfluoroalkanes are known to be highly non-ideal systems, exhibiting large regions of liquid–liquid immiscibility and large positive excess properties.

In the last few years we have been studying the interfacial behavior of fluorinated substances and mixtures of hydrogenated and fluorinated substances. Different types of compounds and interfaces have been addressed, such as semifluorinated alkanes, mixtures of hydrogenated and fluorinated alcohols at liquid-vapour, liquid-liquid and air-water interfaces. Very often, the structure of the corresponding bulk liquids has also been examined. Molecular dynamics simulations are also performed in addition to experimental measurements.

The investigated systems display a number of less common phenomena such as aneotropes (minima in the surface tension vs composition curves) and the formation of nano patterned films.

The ultimate aim of the studies is to understand, and thus control, how the simultaneous presence of mutually phobic hydrogenated and perfluorinated chains induces organization.

Friday, 3 July 2015 – 15h30

A small-scale experimental set-up for processing-related materials characterization

L. Hilliou

As polymers progressively meet more stringent requirements in terms of processing and performance, it is often necessary to develop complex material systems while minimizing costs and time-to-market. Thus, it seems useful to make available fast response characterization tools that although using small amounts of sample, are still capable of conveying adequate data on the correlations between rheological response, process-induced material structure and product properties. For this purpose, a prototype small-scale single / twin-screw extrusion system of modular construction, with outputs in the range 30-300 g/h, was coupled to a rheo-optical slit die designed to be able to measure shear viscosity and normal-stress differences, as well as performing rheo-optical experiments, namely small angle light scattering (SALS) and polarized optical microscopy (POM). The extruder is equipped with ports that allow sample collection, in order to subsequently evaluate the evolution of melting and mixing, morphology, or chemical conversion, whichever relevant. Also, downstream equipment is available, so that the engineering properties of the extrudate can be evaluated. As an example, processing of an industrial polymer blend and the properties of extruded sheets will be studied. The morphological evolution along the extruder, the flow-induced structures developed and the corresponding rheological characteristics are presented, together with the mechanical and structural characteristics of the sheets. Also application of this experimental set-up to other topics in soft matter will be reviewed, thus introducing the different lines of research available in our group.