Controlled nanoarchitectures for the effective storage of hydrogen

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Storing hydrogen in materials is based on the observation that metals can reversibly absorb hydrogen, however practical application of such a finding has found to be rather challenging especially for vehicular applications. The ideal material should reversibly store a significant amount of hydrogen under moderate conditions of pressures and temperatures. To date, such a material does not exist and the high expectations of achieving the scientific discovery of a suitable material simultaneously with engineering innovations are out of reach. Of course, major breakthroughs have been achieved in the field, but the most promising materials still bind hydrogen too strongly and often suffer from poor hydrogen kinetics and/or lack of reversibility. Clearly, new approaches have to be explored, and the knowledge gained with high-energy ball milling needs to be exploited, i.e. particle size does matter! The properties of nanomaterials are known to be size depend. Such size depend effects could offer powerful means to finally control both the thermodynamic and kinetic properties of hydride materials at the molecular level.

Here, the potential of this new approach[1] as well as the major breakthroughs achieved through nanosizing will be discussed. In particular, the effects of particle size restriction on some of the most promising hydrogen storage materials, i.e. magnesium and borohydrides, will be reported. Hence, through particle size restriction full desorption of hydrogen, i.e. 7.6 mass % of hydrogen, was achieved at 85 °C with colloidal magnesium[1] instead of the usual 400 °C required for bulk magnesium. Similarly, core-shell $NaBH_4$@Ni nanoparticles demonstrated for the first time the possibility of reversibly storing hydrogen under practical conditions with $NaBH_4$,[2] a compound that irreversibly decomposes into its elements at temperatures > 500 °C.

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Effect of the Different Amino Acid Hydrophilic Head in the Adsorption Behavior of Eco-Friendly Glycerol Ether Surfactants at the W/A Interface

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Environmentally friendly surfactants are gaining ground in the last decades. Thus, two novel nonconventional biocompatible and biodegradable glycerol ether surfactants were synthesized. Both molecules have a hydrophobic alkyl chain with 12 carbon atoms, but different amino acids in the hydrophilic head: phenylalanine ($PhGE_{12}$) and tyrosine ($TyrGE_{12}$). The $TyrGE_{12}$ molecule has a phenolic group, viz. a benzene ring with a hydroxyl, instead of a simple benzene ring in $PhGE_{12}$ Measurements of dynamic surface tension by maximum bubble pressure tensiometry and drop profile tensiometry are carried out for alkali aqueous solutions over a wide concentration range and for surface ages spanning from milliseconds to hours. CMC values, standard free energies of adsorption and other physicochemical properties are calculated based on static (equilibrium) surface tension measurements. Interfacial dilatational storage modulus and loss modulus measurements have also been conducted. It is found that $TyrGE_{12}$ not only reduces surface tension to much lower values than $PhGE_{12}$ but it also exhibits much faster interfacial adsorption than $PhGE_{12}$. Thus, different polar heads in glycerol ether surfactants can give appreciable differences to adsorption kinetics comparable to effects commonly expected for surfactants with different alkyl chain length.

Effect of fluid properties on gas-sheared and free interfaces

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The laboratory of Transport Processes at UTh has placed a strong interest in examining phenomena of flows with free surfaces/interfaces or with gas-liquid interfaces in pipes and channels.

The interaction between a gas and a liquid phase moving concurrently in a conduit has been the subject of intense research in the last several decades, due mainly to the importance of such flows in the chemical, nuclear and petroleum industry. Although the flow characteristics such as liquid holdup and pressure drop have been extensively studied, our understanding is still limited regarding the effect of several physical properties of the two phases. The experiments were conducted in a 24-mm i.d., 13-m long transparent pipe at atmospheric pressure. Horizontal and near horizontal (±2°) flows were examined. The physical properties that have been investigated or are being investigated are gas density (by using CO_2 and He), liquid viscosity (glycerol solutions), surface tension (n-butanol and isopropanol solutions) and drag reducing polymers.

Liquid film flows occur in a variety of geophysical and biological situations, and are of central importance in many industrial applications, such as heat/mass transfer equipment and coating processes. The present experiments were performed in two inclined flow facilities of adjustable width, one 800-mm long and 250-mm wide and the other 3000-mm long and 450-mm wide. Inclination angles in the range $\theta = 2$–45° were tested for flat and for periodically corrugated substrates, and the liquids examined were aqueous solutions of glycerol, of isopropanol and of SDS surfactant. The research focused on the modifications of the primary instability of steady flow. It was shown that finite channel width has a significant stabilizing effect, which may be satisfactory correlated in terms of the Kapitsa number and is attributed to three-dimensional effects imposed by the side-walls. Corrugated substrates were shown to have an enormous potential in modifying the characteristics of the flow, prominent among which is the transition from the classical long-wave to a short-wave instability. Finally, soluble surfactants were observed to provide maximum stabilization at concentrations only a few percent of the critical micelle concentration.

Decomposition of MgH_2 films investigated by Ion beam techniques

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Magnesium has been a material widely investigated to store hydrogen[1] because of its cheapness and high gravimetric capacity. However, despite the enormous amount work done, certain problems (high stability and sluggish H-kinetics) continue to preclude its use for transport purposes. In this context, MgH_2 films are an excellent tool to investigate the influence of microstructure or/and the surface state on H-absorption/desorption steps (H_2-dissociation, H-diffusion, ect) and films could be also used in other applications such as the switchable mirrors or H-detectors.

Different techniques have been used to characterize the H-desorption process of Pd-capped MgH_2 films i.e. Glancing-XRD (G-XRD), SEM-FEG, optical and transport measurements, mass-spectrometry, calorimetry. Ion beam techniques (IBT) offers a complementary approach[2,3] to investigate the desorption process giving detailed compositional depth profiles of the films. Among the different available IBT, Rutherford Backscattering (RBS) and Elastic Recoil Detection Analysis (ERDA) were used to determinate the profiles of Mg and Pd as well as hydrogen in the films.

In this work, Mg films of nominal thickness of 300 nm were prepared by e-beam deposition and capped by a 10 nm layer of palladium. Hydrogenation of films was carried out at 100 ºC and 10 b during 20 hours. Hydride films were structurally characterized by G-XRD and FEG. They exhibit MgH_2-crystallites with sizes of 80 ± 30 nm and film thicknesses of 380 ± 20 nm. Thermal desorption was investigated by Mass Spectrometry and "in situ" optical measurements.

MgH_2 films were analysed in detail by RBS and ERDA techniques at different stages during the desorption process. Those results show the evolution of H, Mg and Pd depth profiles in the film during H-desorption. According to obtained data, a brief discussion about the desorption mechanism and the formation and influence of Mg-Pd phases or/and intermixed layer will be given.

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Endoscopic digital holography for application in biomedical flows

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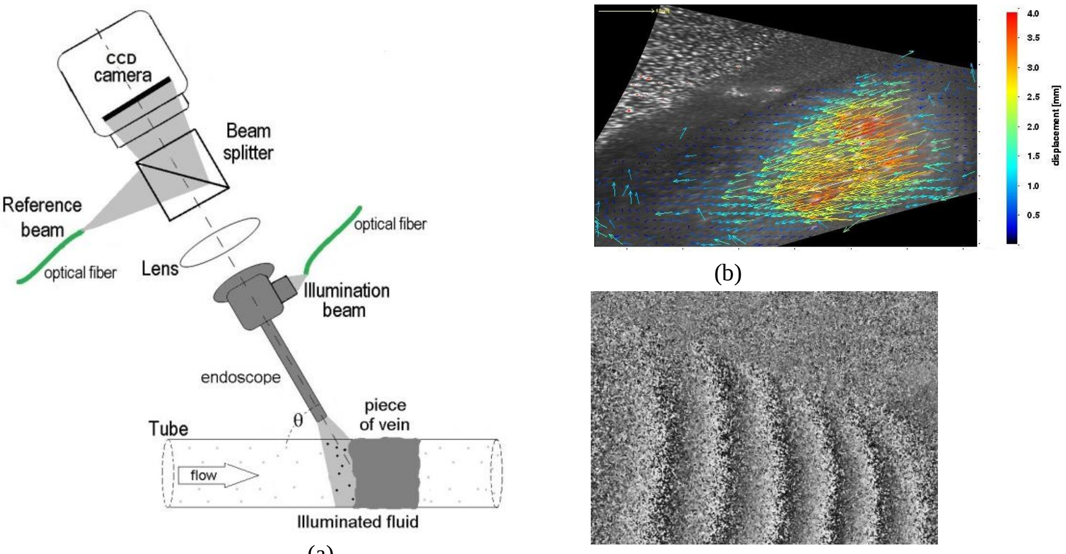
Several approaches for the combination of optical metrology with endoscopes have already been reported[1,2]. On one side, interferometric based techniques have been used for studying the behaviour of cavities both in the medical and in the industrial field. Solid mechanics information (shape, deformation, vibration,…) is obtained and no fluid mechanics is involved in the process. On the other hand, endoscopic PIV has been developed to measure velocity fields on difficult access flows. In this case, the endoscope is used only for illumination while the recording is done through a transparent window.

Our objective is to simultaneously obtain both fluid mechanics (flow velocity field) and solid mechanics (wall deformation) information[3]. We propose to combine endoscopic illumination and imaging with digital holography recording. The reconstructed phase should provide information on the wall deformations while the reconstructed intensity should allow calculating the velocity field. The final goal for the proposed technique is to be used for measuring the fluid-structure interaction in real blood vessels in ex-vivo experiments. This interaction is expected to be related to cardiovascular diseases like atherosclerosis and aneurysms and thus useful information about them could be inferred.



(a)

(b)

(c)

Figure1. a) Endoscopic digital holography setup. Sketch of the off-axis digital holography setup Preliminary results for: b) the flow velocity field inside the vessel; b) the vessel wall deformation.

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On the “very stable” aqueous foams

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Aqueous foams destabilise through different mechanisms: gravity-driven drainage, leading to thinning of films between bubbles, coalescence of bubbles and Ostwald ripening (gas transfer between bubbles). We have shown recently that foams stabilised by partially hydrophobic silica nanoparticles experience drainage, but are fully stable against ripening and coalescence: these foams are “ultrastable”[1]. A similar behavior was observed by Stoyanov and coworkers for foams stabilized by a protein, hydrophobin[2]. We discuss here the case of foams that are much more stable than classical surfactant foams, but that nevertheless destabilise after long times (days) : these are foams stabilized by mixtures of anionic and cationic surfactants (catanionics)[3] and by mixtures of hydrophilic silica nanoparticles and short chain amines[4]. In these cases, drainage is slowed down by bulk aggregates thatcompact in the Plateau borders (junctions between foam films), but ripening and coalescence are not suppressed, they are slowed down due to the rigidity of the surface layer. The difference in behavior between these very stable foams and the ultrastable ones will be discussed.

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Quest for new detection limits in green and smart interface measurements

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There are important metrological issues involved in pushing the limits in both drops and bubble measurements requiring a general reappraisal of specifics in what might be at first sight be considered to be overarching chemical issues. Currie[1] as the chair of the international committee (IUPAC) started to look afresh at long established conventions on limits of detection and limits of quantitations (LO-D&Q). This work is of central importance to metrology and in large part represent the thoughts of the IUPAC; surprisingly this work is not based on rethinking the important metrological issues from statistical fundamentals in determining the LO-D&Q. This determination requires a strict criteria in the formulation of a detection decision by means of a properly defined statistical test. The rigorous statistical survey of such a test method by Liteanu and Rîcă[2] properly addresses this measurement issue and their work is being applied in the research for Drop Technology spectroscopic products. These issues are considered to be very hard work and indeed somewhat of a distraction to many research personnel, whereas for surface science non-collimated spectroscopy (NCS) they are at the core considerations. Here an attempt in revolutionizing the approach to UV-visible measurements is proposed. NCS is clearly a departure in surface science and both bulk and surface spectra of the drop-under-test (DUT) are obtainable on a complex solute offering new measurement possibilities; real time differential analysis have obvious important applications in biochemistry, medical/veterinary and environmental science. The NCS requires a range of measurement protocols to be established that are based on a new surface science which bypass the limitations of the collimated Beer's Law approach of traditional spectroscopy. This new drop science requires that measurement protocols are reframed[3]. The basis of this new quantitative approach illustrates how smart surface science can break through the established protocols and this paper will seek to demonstrate the importance of accuracy and traceability in NCS measurements with NIST standard. Furthermore, a full range of quantitations in these measurements can be delivered to the analyst to assist them develop smart 'flexible and optimized' approaches to measurement that make statistics a live component in laboratory work and not an after-thought that it has unfortunately so often been. This new approach begs the question of using information theory in a more dynamic way that heretofore can be exploited to build an improved measurement platform for smart chemistry and biology. This vital issue is discussed in a general way extrapolating from the specifics of NCS to smart and green surface science in a general way. It is argued that the exact Laplace mathematics defining shapes of drops, bubbles and the meniscus when coupled with advanced numerical methods of computer modeling techniques for optics when applied in the context of best statistical methods can deliver a revolution in spectroscopy.

$LiFePO_4$ cathode – electrolyte interface in lithium ion batteries

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With the increasing demand for improved energy storage technologies, the research in lithium ion battery technology is becoming more and more important. In this work $LiFePO_4$ cathode – electrolyte interface was studied, focusing on the surface of the cathode for $LiFePO_4$/C and $LiFePO_4$/C/graphene bulk material and $LiFePO_4$ thin films. The increase of cathode surface area can improve the rate performance of the cell considerably, thus enable to achieve faster battery charge and discharge times.

$LiFePO_4$/C and $LiFePO_4$/graphene bulk material have been prepared via solid-state reaction. After structural and morphological characterization via X-ray diffraction analysis and scanning electron microscopy an electrochemical test cell with $LiFePO_4$ anode, metallic lithium cathode and $LiPF_6$ electrolyte was assembled. $LiFePO_4$ thin films have been acquired via radio frequency magnetron sputtering.

The electrode – electrolyte interface has been characterized with electrochemical impedance spectroscopy (EIS), determining charge transfer resistance and electric double-layer capacity along with lithium ion diffusion coefficients. It was found that graphene additive increases not only the electron conductivity of the material, but also electrical double layer capacitance, thus indicating larger electrode surface area.

It was found that annealing $LiFePO_4$ thin films promotes grain growth and crystallization, thus improving charge capacity and rate capability. Charge transfer resistance, electrical double layer capacity and lithium ion diffusion coefficients have been determined at various charge and discharge rates. It was determined that charge transfer resistance is smallest at the equilibrium state (3.4 V potential) with electrical double layer capacitance being significantly lower for thin films than for bulk materials.

Deposits from evaporating droplets

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As suspension droplets lose their solvent through evaporation, the particles left behind are deposited into distinctive "dry out" patterns on the surface. Although uncontrolled experiments are simple to perform, there are many parameters to consider and making *a priori* predictions for the shape of these patterns is difficult. Competing effects occur simultaneously and influence the dry-out pattern: a pinned contact line leads to radial solvent flow and formation of the familiar ring-stain; spatial variations in surface tension across the droplet (due to either temperature or concentration gradients) produce Marangoni flow which can redistribute the particles; phase changes within the liquid (e.g gelation, vitrification or crystallization) and external fields (gravitation, electrostatic, magnetic) alter the droplet shape and influence the dry out pattern; changing the evaporation rate alters the relative importance of sedimentation, particle diffusion and heat diffusion…

I will present experimental results from drying droplets of particle suspensions and polymer solutions which highlight some of these effects. Dilute particle suspensions typically form ring-stains, the dimensions of which are found to be robustly predicted by established scaling laws over a wide range of experimental parameters: particle size, concentration, orientation and drying rate. By contrast, the dry out patterns from polymer solutions are seen to be sensitively dependent on the underlying phase behaviour of the polymer, with significant differences observed between semi-crystalline and glass-forming polymers.

The Phypode Project, new advances in Physiopathology of Diving

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Funded by the European Union under the Marie Curie Initial Training Networks initiative, PHYPODE (physiopathology of decompression) is a 4 year project dedicated to the fostering of bubble/diving/oxygen related research by means of a training consortium to build up the future researchers in the field.

This up-to-date integrative and translational approach unites 13 teams with complementary competences from research institutions, industry and clinical practice and supports 14 fellows.

The mechanisms behind the decompression induced formation and growth of intravascular bubbles that can lead to decompression sickness (DCS) are investigated from an epidemiological and physiological approach, using the development of technological devices. It combines Human, Animal, Cellular and Ultracellular Biology as well as Fundamental Physics, Mathematical Modeling and Industrial device development.

The main structure of the program will be briefly presenting, before concentrating on the new results obtained thus far in terms of risk factors and preconditioning, focusing on the effect of vibrating [1] or heating [2] the diver before the dive on the bubble formation observed postdive.

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Flocculation of bacterial suspensions using polyelectrolytes

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Flocculation by polyelectrolytes (PE) is an alternative method for concentration of cellular suspensions, separation and de-watering of biomasses, etc. We have studied the kinetics, laws and mechanisms of flocculation of *E. Coil and B. Thuringiensis israelensis* bacteria suspensions (the latter is increasingly used as ecologically friendly anti-mosquito agent) by cationic and/or anionic polyelectrolytes, as well as polyelectrolyte-surfactant mixtures. It has been shown that *B. Thuringiensis* suspensions can be efficiently flocculated both by cationic and anionic PE, the flocculation activity of polymers can be enhanced (a) if the polymer solution is added to the suspension in two portions, (b) by using polyelectrolyte-oppositely charged surfactant mixtures, and (c) increasing the cell numbers in the system. *E. Coli* suspensions can be efficiency flocculated only using cationic polyelectrolytes. The influence of molecular mass and hydrodynamic dimensions of macromolecules, their charge density and hydrophobicity, pH and ionic strength of the solution, the composition of the medium on the efficiency of flocculation of cells has been determined. Also is shown that for flexible cationic macromolecules, the isoelectric point (IEP) of the cell surfaces is reached at the minimum suspension stability (neutralization mechanism of flocculation), whereas the IEP of suspensions in the presence or rigid-chain polyelectrolytes (chitozan and its derivatives) is reached at much higher concentrations that corresponds to the optimum flocculation. Examples on the efficient phase separation in bacterial suspensions using polyelectrolytes, their binary mixtures and mixtures with surfactants are given.

Alcohol - water mixtures on hydrophobic surfaces

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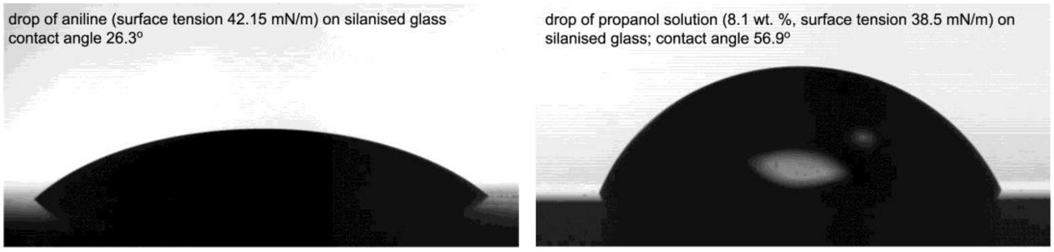
Alcohols along with surface active agents (surfactants) are used in many industrial applications. Aqueous solutions of alcohols or mixtures of alcohols and surfactants exhibit lower surface tension and therefore they influence the wettability of solid surface. Due to the development of new materials and their surfaces, the wettability or nonwettability is a very important material property. These materials are developed as hydrophobic, but a small addition of alcohol or surfactant could change the hydrophobicity into the hydrophilicity. Mixtures of water, alcohols, surfactants and oils are also used for production of micro emulsions. Here, alcohols are used both in low concentrations (as co-surfactants) and in high concentrations (co-solvents). The systems consisting of alcohols and surfactants are studied with a high impact on critical micellar concentration, concentration of alcohols in micelles and bulk liquid, micellar dynamics etc. Together with this research, the study of internal structure of aqueous alcohol mixtures is going on. Hydrogen bonding liquids, such as alcohols, have a rich microstructure that the stronger hydrogen bonding water does not seem to possess. It is found that simple alcohols are micro heterogeneous, since they tend to develop distinct local microstructures, which depend on the geometry of the constitutive molecule, as chainlike structures or micelle like structures. This project was focused on the experimental study of wettability of two hydrophobic surfaces (silanized glass and Teflon) using aqueous solutions of methanol, ethanol and *n*-propanol in full concentration range. The surface energy of both tested materials was examined using Zisman's method. The surface tension of liquids and contact angles were measured. For comparison, wettability of one anionic surfactant was studied too. Based on the experimental data and detailed research study of the internal structure of aqueous solutions of alcohols, we tend to claim that the dominant factor influencing the surface wettability of alcohol-water mixtures on hydrophobic surfaces is the presence of microstructures in these solutions. These mixtures have a higher contact angle when compared with a pure liquid having the same surface tension (Fig. 1).

Fig. 1 Drop of aniline (A) and propanol solution 8.1% (B) on silanized glass.



Study of the three-phase contact line expansion during stationary and dynamic experimental arrangement

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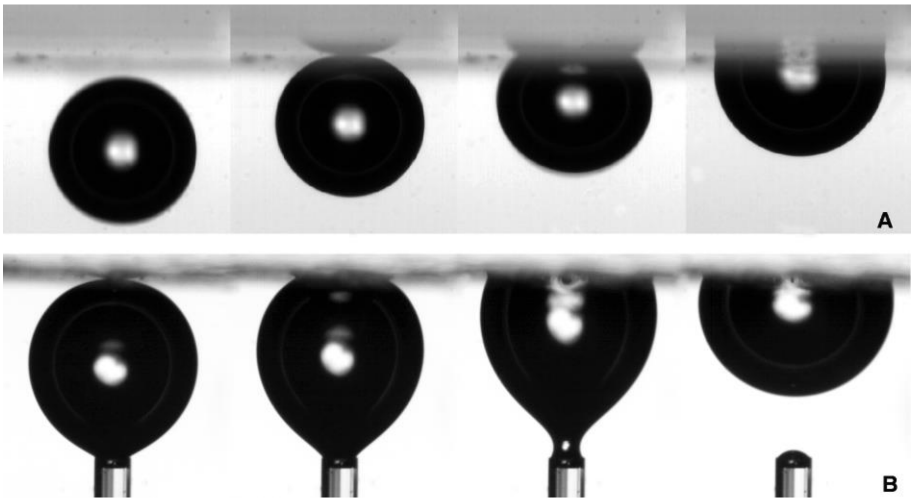
The bubble attachment onto a collecting surface is a common natural phenomenon and the bubble-particle interactions are used in many industrial applications. The adhesion process is usually divided into three independent steps – thinning of the liquid film between the bubble and the particle, rupture of the liquid film and expansion of the three phase contact (TPC) line. The aim of this project is to study the bubble adhesion on a horizontal plane with a special focus on the TPC line expansion under different experimental arrangements. The moving bubble (diameter up to 1 mm, Fig 1A) and stationary bubble (attached on the capillary, Fig 1B) are considered here. Measurements are provided in pure water; therefore the mobile bubble surface was considered. The adhesion process is recorded using the high-speed digital camera and bubble parameters (TPC diameter, contact angle) are evaluated using the image analysis software. The hydrodynamic and molecular-kinetic models[1,2] are used for the mathematical description and parameters of these models are compared for both types of experimental arrangement.

Fig. 1 Buble adhesion during dynamic (A) and stationary (B) experimental arrangement.



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Energy density enhancement of AC/AC capacitors in aqueous electrolyte through hydrogen storage in the negative electrode

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Supercapacitors (or Electric Double-Layer Capacitors – EDLCs) are a relatively new kind of device which is used for quick harvesting and delivery of electricity. They are implemented for electricity management and improving energy efficiency of stationary and mobile systems. Hence, they play a major role for developing cleaner systems.

Most of the current research on supercapacitors is oriented to energy density enhancement, in order to broaden their application spectrum. As given by formula $E = ½CU^2$, energy is highly depending on voltage U, the latter being controlled by the stability window of the electrolyte. Therefore, most of the commercially available systems use organic electrolyte, e.g., NEt_4BF_4 in acetonitrile, allowing 2.7–2.8 V to be reached. Due to the relatively high cost of these devices and environmental unfriendly character of these electrolytes, alternative solutions such as use of protic electrolytes must be investigated.

Until recently, H_2SO_4 and KOH were mainly considered as aqueous electrolytes for supercapacitors, giving voltages of 0.7–0.8 V. By the use of neutral alkali sulfate solutions, we have demonstrated voltages up to ca. 2 V for AC/AC capacitors[1,2]. Such high values are possible owing to the high over-potential for di-hydrogen evolution related to the pH increase in the porosity of the carbon negative electrode[3]. This presentation will show the various steps in the development of a prototype, utilizing safe, cost effective and environmental friendly materials.

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Motion of a spherical particle near a planar fluid-fluid interface: The effect of surface incompressibility

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Hydrodynamic coupling of a spherical particle to an undeformable planar fluid-fluid interface under creeping-flow conditions is discussed [1-2]. The interface can be either surfactant-free or covered with an incompressible surfactant monolayer. In the incompressible surfactant limit, a uniform surfactant concentration is maintained by Marangoni stresses associated with infinitesimal surfactant redistribution. Our detailed numerical calculations show that the effect of surface incompressibility on lateral particle motion is accurately accounted for by the first reflection of the flow from the interface. For small particle-interface distances, the remaining contributions are significant, but they are weakly affected by the surface incompressibility. We show that for small particle-wall gaps, the transverse and lateral particle resistance coefficients can be rescaled onto corresponding universal master curves. The scaling functions depend on a scaling variable that combines the particle-wall gap with the viscosity ratio between fluids on both sides of the interface. A logarithmic dependence of the contact value of the lateral resistance function on the viscosity ratio is derived. Accurate numerical calculations are performed using our Cartesian representation method.

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Environmental and medical technologies:
Link between science and industry

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Secura Nova Ltd. and its Microspun R&D Team is focused on selected environmental and medical technologies which are developed in cooperation with the Faculty of Chemical and Process Engineering at Warsaw University of Technology (FCPE WUT). Depth filtration is used for removing solid or liquid phase particles from liquids and gases by filtering suspended matter against a layer composed of grains or fibers. Fruitful cooperation between the Company and FCPE WUT results in generation of innovative technological solutions, which provide the implementation of new filtration processes and new products [1]. Recent R&D program includes:

- increasing the efficiency and lifetime of absolute filters,
- aerosol filtration,
- developing of the production of nanofibers from different polymers,
- designing filtration materials and cartridges with the nanofibers
- developing technology of producing nanofibers with implemented electrical charge (electret fibers).
- designing coalescers for different applications
- enhancing performance of pleated filter cartridges

The research and production capability of Secura Nova together with the research potential of the Faculty (staff, laboratories, production, etc.) led to the cooperation which brought many custom and unique solutions that were implemented in production[2]. Recently, new filter structures combining nano- and microfibers have been developed. Filter media produced by this method may be used to efficiently remove nano- and submicron particles from liquids and gases.

Another filed of the activity of the Company is focused on optimization of medical devices intended for drug delivery by inhalation of aerosols produced by liquid atomization[3]. The research is also done in cooperation with the FCPE WUT and allows to establish national guidelines in nebulization technology [4].

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Description of the bubble shape on an inclined plane

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The bubble-particle interaction is an important process playing the key role in numerous industrial applications, e.g. in flotation or multiphase reactors. The succesful interaction between the bubble and the solid particle is influenced by the approaching of the bubble to a collision distance, in which the bubble-particle contact occurs. The liquid film between the bubble and the particle surface is then formed and due to the affection of intermolecular and interfacial forces it thins to the rupture. The three-phase contact (TPC) is established and expands to the equilibrium state, when the TPC diameter does not change – a stable aggregate of the bubble and the particle is formed. All mathematical models which describe the TPC line expansion utilize the knowledge of dynamic and equilibrium contact angles. The description of a drop or a bubble placed on an inclined plane or curved surface is very complicated. Up to now few methods were published, but these methods are not suitable for the description of sizeable amount of data. The adhering bubble is not symmetric (as in the case of a horizontal plane); therefore contact angles on the right and left side of the bubble differ. The aim of this project is to find out the methodology for relatively simple and fast calculations of contact angles. The special attention was paid on the ability of the model to describe the bubble shape during the adhesion on hydrophobic solid surface.When compared with the liquid drop placed on an inclined plane, the bubble holds nearly a spherical shape and contact angles in the upper and lower bubble end differ only little. The basic idea of our method is to divide the bubble into two parts and describe these parts separately. A set of points around the bubble is obtained and then the ADSA methodology is used. This method utilizes the Laplace equation of the capillarity; the bubble profile and the contact angle are evaluated using the set of experimental points around the edge of the bubble. The comparison of the experimental and calculated bubble profile shows a good agreement, the error in contact angle calculation is comparable with accuracy of the experimental measurement. The process of the adhesion was recorded using high-speed digital camera and images were evaluated using the image analysis software NIS-Elements. Calculations were performed using the MatLab software.

Droplets of pure and complex fluids evaporation: wetting, instabilities and pattern formation

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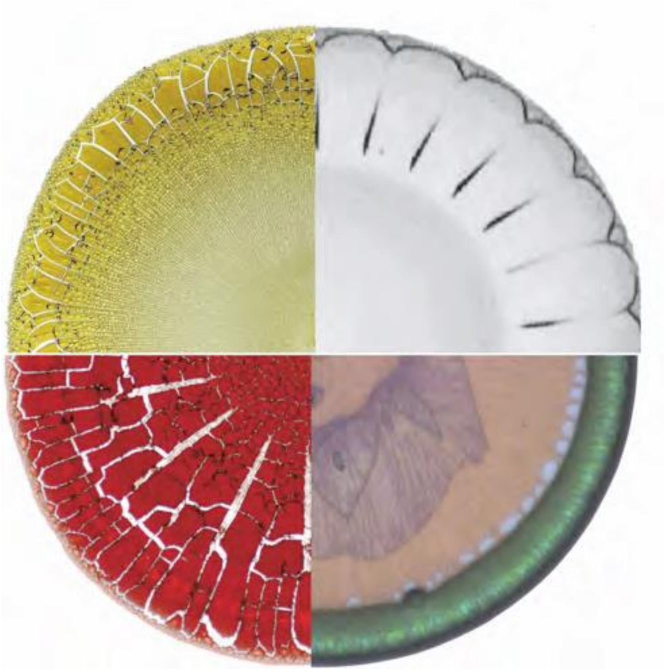
We investigate several aspects of sessile drop evaporation. Pure and complex fluids are studied and cover a wide range of applications. Complex fluids include nanofluids and biological fluids such as human blood[1]. Different tools are used to quantitatively measure the evaporation rate but also to analyze flow instabilities. Experiments performed under microgravity conditions aims to bring new insight thanks to a reduced gravity influence on the evaporation[2]. Thermo-capillary phenomena can develop but also the wetting and spreading is modified. The influence of the triple line dynamics on the evaporation using pure fluids[3] has been demonstrated including the thermal aspects. Now we are looking at the same triple line dynamics with complex fluids also including the heat transfer mechanisms.



Dry-out of different droplets natures [Top left (24 nm polystyrene nanoparticles), Top right (polymer by L. Pauchard) – Bottom left (human blood) – Bottom right (colloids by D. Fairhurst)]

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Multiphase Fluids in Confined Flow

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Microfluidics is the science and technology that process or manipulate small amount of fluids. In this work we show how microfluidic can be useful to quantify droplet deformability and emulsion interfacial properties. Confined droplets flow and deformation in microchannels is a topic of considerable importance because of its industrial implications. To get some insight of a wide range of processes, such as multiphase flow in porous media, process intensification of multiphase fluids, etc., a full comprehension of these phenomena is needed. In our experimental setup a circular cross section glass capillary is placed under the field of view of an optical microscope and the droplet deformation in confined flow is determined by image analysis techniques. Newtonian model system was used to investigate the morphology in transient and steady state flow of droplets having undeformed radius comparable to the capillary size. Drop deformation and velocity as a function of the Capillary number, and of the confinement have been investigated. Stream line inside and outside the drops have also been experimentally determined. Good agreement with theoretical models and numerical simulations available in the literature has been found. A measurement of the transient in the drop deformation, due to extensional flow under convergent-divergent geometry is used to calculate interfacial tension.

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Coalescence of particles with solid core and viscous shell

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Coalescence of particles with solid cores and viscous shell plays an important role in chemical and pharmaceutical industry, in agriculture and in production technology. Coalescence of metal particles, which are partially melted due the laser heating, is an important mechanism responsible for densification of metal powder during selective laser sintering process.

Our model describes coalescence of two or more particles consisting of a solid core and a liquid shell. The flow in the liquid shell is driven by the surface tension. It is assumed that the characteristic Reynolds number is low, so that the creeping flow model can be applied. A two dimensional boundary element model (BEM) is used to solve the governing equations. The numerical model is validated by comparison with available analytical solution for the limiting case of fully viscous particles.

The influence of the liquid properties, the sizes of the particles and the relative sizes of the solid core on the two-phase flow and on the shape evolution of coalescing particles is quantified. In application to the selective laser sintering process densification rate has been defined as an important output parameter. We show that increasing of the solid core radius leads to the decrease of the powder densification rate.

Nanostructure-assisted hydrogen generation by hydro-/thermo-lysis of boranes

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Of the *wheels* of the hydrogen economy, the storage is certainly "the biggest roadblock to the widespread use of hydrogen".[1] Several technologies are investigated but chemical hydrogen storage is particularly attractive owing to high gravimetric hydrogen densities. Typical examples are the boron-based materials, represented by sodium borohydride $NaBH_4$ and ammonia borane NH_3BH_3.[2]

Hydrolytic dehydrogenation of $NaBH_4$ (Eq. 1), NH_3NH_3 (Eq. 2) or hydrazine borane $N_2H_4BH_3$ (Eq. 3) has attracted a great attention:

$$NaBH_4 + 4\ H_2O \rightarrow NaB(OH)_4 + 4\ H_2 \qquad (1)$$

$$NH_3BH_3 + 3\ H_2O \rightarrow NH_3 + B(OH)_3 + 3\ H_2 \qquad (2)$$

$$N_2H_4BH_3 + 3\ H_2O \rightarrow N_2 + B(OH)_3 + 5\ H_2 \qquad (3)$$

The most investigated aspect has been the metal-based catalysts from which It is expected conversion of 100%, selectivity in H_2 of 100% and durability over cycles. An example of nanostructured cobalt catalyst we have developed is shown in Fig. 1.[3] This example as well as others will be presented and discussed during the joint meeting COST.

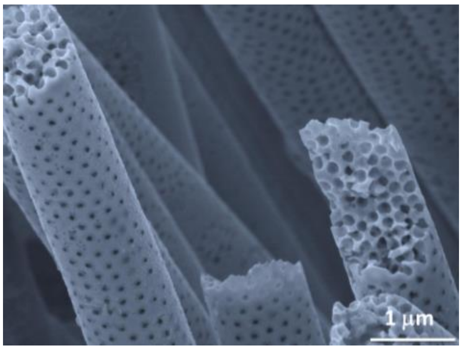

Fig. 1. Cobalt nanowires.[3]

Thermolytic dehydrogenation of NH_3BH_3 is a complex reaction through which 2 equiv. H_2 are released at <200 °C (Eq. 4):

$$NH_3BH_3 \rightarrow [NH_2BH_2] + H_2 \rightarrow [NHBH] + 2\ H_2 \qquad (4)$$

To improve the dehydrogenation properties – the objectives are to decrease the onset of dehydrogenation and avoid the release of unwanted borazine – several strategies have been tested, and one focuses on the hydride nanoconfinement into porous hosts. In this context, we have developed boron nitride hollow spheres (Fig. 2). When NH_3BH_3 is confined within the core of these particles, it dehydrogenates from 50 °C and the generated H_2 is pure.[4] This example will be presented and discussed during the joint meeting COST.

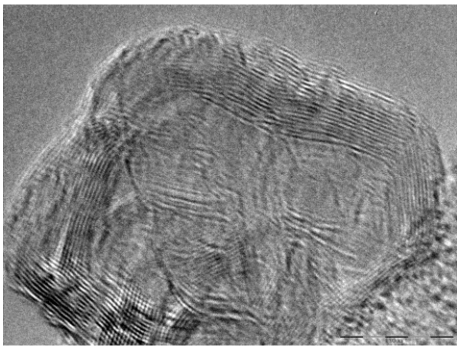

Fig. 2. Boron nitride hollow nanopolyhedrons.[4]

To sum up, nanostructured materials are important in the field of boron-based hydrogen storage materials and our last results will be presented during the joint meeting COST MP1103.

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EURAXESS Initiative and EURAXESS Jobs Portal

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EURAXESS is a European Commission initiative with main goal to strengthen the attractiveness of European countries towards mobile researchers by removing the barriers to free movement of knowledge within Europe, by strengthening cross-border mobility of researchers, students, scientists and academic staff and by providing researchers with better career structures.

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In conclusion, EURAXESS is the most reliable and effective official tool of European Commission for development and further improvement of researchers career in Europe.

Generation of foams in Vancomycin HCl by exposure to laser radiation

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Vancomycin was designed in 1950’s and it is a glycopeptides antibiotic active against most gram-positive organisms, including penicillin-resistant staphylococci[1,2].

UV-Vis absorption spectra of Vancomycin hydrochloride solutions in ultrapure de-ionized water were recorded. The absorption spectra have a broad peak at 280nm and exhibit below 250nm more bands which are partially resolved. Stability studies were performed on Vancomycin hydrochloride 10^{-4}M solutions in ultrapure de-ionized water comparing the absorption spectra recorded at different time intervals after preparation. The samples were stable for at least 24 hours after they were prepared.

The laser – induced fluorescence (LIF) spectra of Vancomycin hydrochloride 2mg/ml (~1.35×10^{-3}M) solutions in ultrapure water were recorded in bulk solutions and in droplets.

The Vancomycin solutions were irradiated with the laser radiation emitted by the forth and second harmonic generation of a Nd:YAG laser (wavelength = 266nm and 532nm). Pulse repetition rate was 10 pps. The average beam energy varied between 1mJ and 20mJ, function of the experimental objectives. The exposure time of each sample also varied. Access of the laser beam to the sample was made via a shutter, computer controlled or manually, so that the LIF emitted by the sample was collected after a known number of laser pulses by the same PC via an Ocean Optics HR4000CG-UV-NIR high-resolution spectrometer. LIF was collected and transmitted to the spectrometer (spectral resolution: 0.75nm) via an optical fiber (inner core: 1mm)[3].

During irradiation foams were obtained. The quantity of foam generated depended on the experimental conditions (exposure time, energy of the laser beam and volume of the solution).

Spectral modifications of the solutions were observed with UV-Vis absorption spectroscopy and LIF spectroscopy.

Laser irradiation induces also structural changes, causing generation of foams in Vancomycin HCl solutions.

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Decompression Algorithms

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Decompression Illness or DCI is the term used for a collection of baurotraumatic symptoms that can arise after a dive, caused by the change in ambient pressure around the body of a scuba diver resurfacing. When resurfacing, a diver must ensure that the dissolved nitrogen is appropriately eliminated through breathing. If the rate of ascent is too fast, the nitrogen precipitates and forms bubbles in tissues or in the blood stream that grow to a size causing damage[1] as they are now too big to pass from the capillaries to the pulmonary alveoli and be expired out of the body. The risk of DCI is usually managed in the scuba diving community by adhering to official guidelines dictating the ascent rate and time to spend at each depth to limit the number and size of bubbles created.

After presenting the basic definitions of scuba diving and different current classifications, the main problems that can arise from decompression failure will be presented, before discussing the different models and bubble dynamics used to prevent them. The Haldane-Bülhmann dissolved gas phase tracking models[2] and the Dual Phase models incorporating bubble dynamics[3] will be discussed, as well as the probabilistic, DCIEM, slab diffusion and exponential-linear models[4,5], focusing on the unknown physics related to bubble generation and growth in vivo and physiological factors that influence them[6-9].

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Drying in porous media

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Drying processes in porous media lead to the removal of water or other liquid from solid materials, in order to reduce the content of residual liquid up to a sufficiently low value. These processes are very common in many industrial manufacturing, typically being the final stage of a sequence of operations. The drying in a porous medium containing a certain percentage of moisture is a thermal process; many materials can be dried by heating to a temperature higher than the liquid boiling point. Typically to remove the moisture from porous solids also involves the transport of the liquid phase through mechanisms that may be different depending on the microstructure of the substrata. A generalized analysis of the drying process applicable to every type of material is not yet available: differences in shape and size of the porous medium, humidity content, matter and heat transport mechanisms, prevent the development of an universal description, although there are some general references. The way in which the temperature changes inside the dryer, for example, depends on the liquid nature and concentration inside the treated product, on the temperature of the heating medium, on the duration of the process and on the final temperature of the bone dried solid.

Novel Materials and Systems for Solid Hydrogen Storage

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Multi-functional complex liquids for coating semi/porous surfaces

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Intensive development of nanotechnology linked with generation of nanostructures and nanomaterials offers great possibilities of creating modern multifunctional materials. Such materials based on semi-porous surfaces, e.g. textile substrates, can have very wide applications due to the new properties and functions rendered to these substrates such as self-cleaning, anti-bacterial, UV protection, flame resistance, super hydrophobicity, electrical conductivity, friction and wear resistance, environmental purification, pH/thermo-responsive hydrophobicity or hydrophilicity[1,2]. The ultimate impact of nanotechnology in the area of textile and other potential application areas will depend on the type and structure of nano-structured functional agents and their coating process[3].

Among established wet-chemical modifications processes, inkjet printing techniques can be used as a novel approach with high efficiency and low cost to deposit functional agents on fabric surfaces. In our studies, a multi-functional formulations, containing various functional agents which have high affinity to natural and/or synthetic smooth (foils) and semi-porous (textile materials) will be prepared. Semi/porous materials such as polymeric fabrics will be multi-functionalized by the multifunctional formulations including nanoparticles (NPs) with specific properties using wet-chemical and inkjet printing process. The discussed nano-structured functional agents include oxide nanoparticles such as TiO_2, ZnO, Ag as well as artificial and natural nano-clays.

The future studies will be dedicated to semiconductor nanomaterials.

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Dynamic adsorption of dissolved oil compounds in produced water onto air bubbles: Influence of crude oil and water composition

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This study aims at understanding how the surface properties of air bubbles are influenced by adsorption of dissolved hydrocarbons present in produced water. The general aim is to obtain better understanding of mechanisms affecting the oil removal efficiency during flotation processes. Particular focus has been put on determining the influence of crude oil and water composition, both on the characteristics of produced water and on the surface properties of air bubbles. The dynamic surface tension of simulated produced water samples was measured by maximum bubble pressure tensiometry, and the adsorption mechanism of the dissolved hydrocarbons onto air bubbles was predicted based on diffusion controlled adsorption kinetics[1, 2]. The adsorption process deviates from the diffusion-controlled mechanism for a long-time adsorption process. The concentration of dissolved hydrocarbons was smaller in the presence of salts (salting-out effect) [3] and an adsorption barrier appears at short surface ages. The influence of divalent ions (Ca^{2+}, Mg^{2+}) was not very significant. Moreover, the water soluble acidic and basic crude oil compounds exhibit various degrees of surface activity and different adsorption kinetics onto air/water interface was observed for the produced water samples prepared with different crude oils.

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Electrodeposition of Ni-Cu and Ni-Co-Cu porous foams using hydrogen bubble template

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Electrodeposition is a widespread technique for the production of both decorative and functional coatings. During cathodic deposition of most metals from aqueous media, hydrogen evolution is inevitable and commonly viewed as detrimental, reducing the current efficiency of the deposition process and inducing unwanted porosity in dense coatings. On the other hand it is possible to take advantage of hydrogen bubble formation during electrodeposition and use it as a dynamic template for the production of porous 3-dimensional foam-like architectures (Figure 1). This process was described by Shin et al.[1, 2] for the electrodeposition of 3-dimensional porous copper foams, about 100 μm thick, with nanostructured pore walls. Such structures provide a high specific area which is one of the most important characteristics of electrodes for supercapacitors, in order to promote fast electrochemical reactions and charge transfer.

In the present work, Ni-Cu and Ni-Co-Cu foams were produced by electrodeposition using an in-situ dynamic hydrogen bubble template. SEM analysis revealed that they have a nanostructured morphology consisting of micrometric pores with dendritic wall (Figure 2). The morphology and chemical composition of the foams was related to the deposition parameters, namely electrolyte composition, applied current and deposition time. Furthermore, their electrochemical behavior and specific capacitance were studied by cyclic voltammetry and chronopotentiometry in order to assess their application as electrodes for supercapacitors.

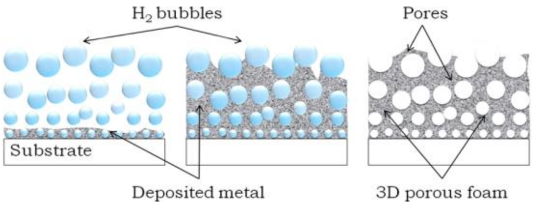

Figure 1.Schematic representation of metal foam formed by electrodeposition using a hydrogen bubble template.

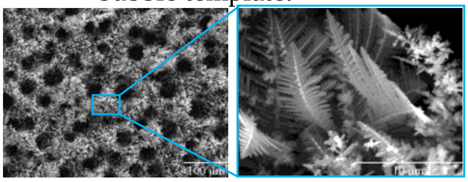

Figure 2. Microstructure of electrodeposited Ni-Cu metal foams.

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An electrical technique for detection of micro-bubbles in living subjects with in-vitro validation

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The objective of the present study is the detection and characterization of micro-bubbles in human bloodstream due to Decompression Sickness (DCS), using an innovative technique that measures with great sensitivity the electrical conductance of human tissues. The focus is on being non-intrusive but yet capable of detecting features far away from vein walls and on attaining high sensitivity even for low gas volumetric concentrations as those encountered during DCS. Work so far includes in-vivo testing of the technique on anesthetized swines and in-vitro validation by making experiments in tubes and mimicking tissues. In both cases, the technique analyzes and processes the electrical footprints of gas volumetric concentration variations in order to provide information about bubbles characteristics in bubbly flows. In-vitro testing concluded having achieved superb measurement sensitivity (~0.00001) that can reliably sense bubble sizes from ~10 μm to ~700 μm for gas volumetric concentrations between ~0.001 and ~0.1. This holds for both static and flow (steady and pulsatile) conditions concerning liquids of variable salinity and viscosity and for liquid velocities from 3 to 30 cm/s. In-vivo tests conducted on anesthetized swines demonstrated that electrical technique's measurement sensitivity is adequate to sense the presence of bubbles ~20 μm in blood flow by placing electrodes over partially conductive tissues & skin and documented ultrasonographically. Additionally, the application of advanced post-processing methods on data collected from both in-vitro and in-vivo tests showed that spectral analysis (such as wavelet, spectrogram and FFT analysis) enhances considerably bubbles detection and characterization. Concluding, the results of the work so far are considered promising for the forthcoming tests on humans, making an effort to sense micro-bubbles generated during DCS in blood flow.

Wide tuning of interfacial viscoelasticity and bulk rheology using thermoresponsive supramolecular assemblies of fatty acids

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Over the last years, the research group at BIA-INRA has designed and studied a simple and sustainable system consisting in a 12 hydroxy stearic acid (12-HSA) in association with an organic counter-ion (such as ethanolamine or hexanolamine): this combination allows us to successfully disperse the - *a priori* highly insoluble - monomers of 12-HSA in water, and to get self-assembled tubes of around 10 µm length and 600 nm diameter. Interestingly, this supramolecular morphology is also temperature-dependent: the tube structural parameters vary with *T*, and the system also exhibit a clear and reversible "tube-micelle" transition.

As a result of a collaboration between the BIA and IPR groups, we report here results on how this thermo-responsivity of the supramolecular morphology has an impact on both interfacial viscoelasticity and bulk dynamical properties. At all scales and as a function of the temperature, we have been able to draw direct correlation between the supramolecular self-organization and the macroscopic properties. In particular, we show that a fine and non-monotonous control of the rheological properties can be found by changing the temperature while remaining within the "tube phase", and that drastic variations on interfaces and bulk are obtained as the "tube-micelle" transition is crossed.

Proteins/nanoparticles interactions in the toxicity of nanomaterials

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The rapid development of nanotechnologies has raised some concerns on the potential effects on human health and on the environment of engineered nanoparticles. At the same time nanoparticles attract intense interest for their potential applications in diagnostic and therapy. The ability to cross biological barriers or the occurrence of specific chemical reactivity makes them very different entities from their micrometric counterparts. Therefore, the behavior of nanoparticles in living organisms is difficult to be predicted.

The fate of particles inside living organisms and their possible adverse effects strongly depend on the early events occurring when they reach the biological fluids. Among these events the interaction of nanoparticles with proteins appears to be a crucial issue.[1,2,3]

The irreversible adsorption of biomolecules to a surface may lead to modification of the biofluid composition. At the same time, surface-driven conformational changes of macromolecules or a selectively oriented adsorption may enhance or inhibit the activity of enzymes or influence the molecular recognition of biomolecules. Oxidative reactions promoted by the surface may impair the biomolecules. Finally, the formation of a stable layer of biomolecules at the interface may modify the surface properties of the materials or the aggregation state in the case of nanoparticles[3].

There are several indications that the occurrence of adverse reactions to a biomaterial depends upon the nature of the surface[4]. However, the comprehension of the processes occurring at the surface/biofluid interface at a molecular level as well as the identification of the determinants driving such processes is still at the early stages.

A big effort has been made in the last years within the scientific community and regulatory agencies to set up protocols suitable for predicting the possible toxicity of nanoparticles. In this perspective, the investigation of the mechanisms of interaction between nanoparticles and proteins is of great importance.

An overview on the experimental approaches to study the chemical and physical interactions between inorganic surfaces and proteins will be here discussed.

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Smart Materials for Additive Manufacturing

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Additive manufacturing is a relatively new and expanding manufacturing strategy that can be used to design sophisticated structures from a host of materials, including metals, ceramics, and polymers with lower cost and less generated waste. Three-dimensional printing provides advantages to traditional molding and metal casting with regards to speed, cost, and ease of production enabling rapid feedback in prototype design and disruptive manufacturing pricing models. Additionally, threedimensional printing enables highly detailed internal and external geometries, creating new paths to complex part manufacturing.

The ExOne ProMetal process utilizes a layer-by-layer technique in which alternating layers of powder and a binding agent are serially assembled. The binder serves to provide intralayer (x,y) binding as well as (z) stitching. The binder is delivered though a piezoelectric printhead and actuated via robotic control. Manufacture involves essentially three phases: 1) printing, 2) curing, and 3) sintering to produce a finished part. We discuss current strategies to optimize the manufacturing process via the use of smart binder systems to decrease defect frequency and increase overall fabrication rate.

Programmable Thermoresponsive Polymers for Interfacial Stabilization

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Stimulus-responsive nanoparticles can be used to exert control on the stability of disperse fluid/fluid systems, however the mechanisms by which this occurs are only partially understood. This is, in part, due to the competition between the dynamic mechanisms interfacial relaxation processes and colloidal aggregation rates – both of which are largely unexplored. Here, we discuss a new class of thermosensitive polymeric materials based on random copolymers of di(ethylene glycol) methyl ether methacrylate (MeO_2MA) and poly(ethylene glycol) methyl ether methacrylate (OEGMA) to investigate the role of hydrophobicity and physicochemical behavior in suspension on the colloidal stability. Gold nanoparticles functionalized with thermosensitive polymer brushes of these copolymers display lower critical solution phenomena (LCST) and switchable aggregation kinetics (k_{11}) that is strongly dependent on the co-polymer ratio, temperature, and ionic strength. Effects of these parameters on the aggregation kinetics were studied by time resolved dynamic light scattering (TR-DLS) experiments. We observe a linear superposition between the critical NaCl coagulation concentration (CCC), temperature, and co-polymer composition resulting in a programmable aggregation that can be exploited for design of thermoresponsive foam and emulsion stability. We also discuss potential applications of these materials for self-cleaning interfaces via thermoresponsive adhesion modulation and interrogating the immunobiology of engineered nanomaterials.

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Acoustic manipulation of rising bubbles at different gravity levels

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Bubbles rising in fluids can easily be found in a wide variety of situations, from simple daily objects (*e.g.* bubbles in a glass of sparkling water) to more sophisticated devices (*e.g.* bubble column reactors). Many of these systems require a certain level of control on bubbles. Acoustic waves have been proved to be an efficient method to control bubble dynamics[1,2], but still further research is required, especially under different gravity levels.

We have carried out an experimental study on the effects of acoustic waves on rising air bubbles at gravity levels ranging from 2g to 19.3g. The experiments were conducted in the frame of the European Space Agency contest "Spin Your Thesis! 2012". Bubbles were injected into the test cell through a 0.15mm (internal diameter) needle by means of a syringe pump. The dynamics of the injected bubbles was modified by the effects of an acoustic standing wave generated by two piezoceramic transducers glued to the walls of the cubic cell (one on one side and one on the bottom) and driven by the amplified signal of a function generator.

The primary Bjerknes force[3] is responsible for the movement of the bubbles towards the pressure nodes. The secondary Bjerknes force[3] takes into account the attraction and repulsion between bubbles. The effects of these forces observed in our experiments are diverse. We have analyzed the bubble size at detachment from the nozzle, the rise path, the levitation, and the attraction or repulsion of bubbles.

We present a preliminary analysis of the results obtained at different gravity levels and compare them with results obtained at 1g. A comparison with results obtained without an acoustic wave is also presented.

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Influence of pseudoplasticity and surface tension on gas volumetric concentration and bubble characteristics in two-phase co-current upward flow

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This work studies the way shear thinning and surface tension affect both gas volumetric concentration and bubble characteristics in upward bubbly flow. In recent years, there has been an increasing recognition of the importance of non-Newtonian flow characteristics displayed by most materials encountered in everyday life, both in nature (gums, proteins etc.) and in technology (polymers and plastics, emulsions, slurries etc.). Blood is a complex multiphase system which in general exhibits non-Newtonian behavior as well. In this study, the influence of Xanthan gum and Triton X-100 in a water/glycerol solution is examined in terms of bubbly flow characteristics. Xanthan gum addition makes the solution pseudoplastic, while Triton X-100 is a surfactant that lowers surface tension of solution when added. The experiments were conducted in a fully automatic flow loop, furnished with basic hydraulic devices, measuring sensors and pressure controllers, capable of generating steady flow conditions of various liquid/gas flow rates. Gas volumetric concentration measurements were conducted using a novel non-intrusive electrical resistance technique capable of detecting micro-bubbles with high accuracy and sensitivity, while bubble characteristics were studied by means of a high resolution camera equipped with proper macro lenses. Data analysis and processing clearly demonstrate the influence of all parameters examined (Xanthan gum and Triton X-100 concentration, gas and liquid flow rate) on gas volumetric concentration and bubble characteristics. It is interesting to notice the presence of voluminous bubble clumps in highly pseudoplastic fluids which, not only generate a strong attenuation of the electric signal, but also cause intense fluctuations that seem to follow a periodic pattern.

Surface dilatational rheology of triterpenoid and steroid saponins on the air/water interface

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Saponins are a class of natural surfactants found in more than 500 plant species. They consist of flat hydrophobic head group (triterpenoid or steroid) with hydrophilic oligosaccharide chains. Due to their strong surface activity they are good foam stabilizers. To understand and control the properties of saponin-stabilized foams it is essential to have a detailed knowledge of the surface rheological properties of these surfactants. In previous articles [1, 2] we studied the rheological behavior of saponin adsorption layers, subjected to shear deformation. Triterpenoid saponins exhibited high surface modulus (in shear), G, and complex visco-elastic behavior, while steroids had very low modulus and viscous behavior. The subject of the current study is the behavior of various saponins on the air/water interface, subjected to dilatational deformation (steady and oscillatory). We employed capillary pressure tensiometry (CPT). Different factors were studied: (1) Age of the surface, t_A; (2)Amplitude of deformation, A; (3) Frequency of deformation, ν. Generally the triterpenoid saponins had high dilatational modulus, E. The elastic component, E`, was much higher than the viscous one, E``. E increased with t_A and ν, and decreased with A. The value of E for steroid saponins was moderate. A comparison was made between the response of the saponins in dilatational and in shear deformation. We also performed experiments with Langmuir trough (LT). The stress vs. deformation curves obtained with a LT exhibited hysteresis for triterpenoids, and no hysteresis for steroids. We compared results obtained with different methods (CPT and LT). Possible correlations between the structure of the saponins and the respective rheological response are discussed.

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Research activities at the UPC-BarcelonaTech Microgravity Laboratory

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The Microgravity Laboratory of the Universitat Politècnica de Catalunya-BarcelonaTech started its research activities at the end of 2005. Numerous experimental, numerical and analytical studies on multiphase flows have been performed in the laboratory and in different microgravity and hypergravity platforms since then. The common goal of the majority of these studies consists in the management of two-phase flows at different gravity levels.

We present an overview of the achievements carried out in the last years as well as some of the current and future projects in the lab.

Hydrogen bonding in zeolite – experiments and possibility to use for storage

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Growing demands of increase of volume for hydrogen storage, for launching hydrogen industry, leads to new developments in industry and scientific investigation. Due to its structural variety and almost 3 million theoretical structural combinations to create zeolite structures, it is a promising material for hydrogen storage. Economical convenience is a good reason to seek simple and common materials for storage, and natural materials are especially interesting.

Although there are couple of theories about hydrogen's bonding with zeolite, such as adsorption, mainly trough Langmuir equations, spillover effect – thanks to strong catalysts which manipulate hydrogen gas as well as atomic hydrogen, and basic filling of pores, also explained by Langmuir equations, results are not always consistent. While experimenting and using different methods to precise the mechanism of adsorption and measuring efficiency some irregularities has been found. In our work the various experiments using natural zeolite (clinoptilolite) are performed - mass spectroscopy, Sievert type – volumetric method and thermogravimetry. Effects of low pressure, air humidity, temperature on adsorption efficiency are investigated to explain their influence on hydrogen bonding process with zeolite.

Rheology of interfacial layers at different density and degree of entanglement

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This work is focused on the 2D rheological properties of air/ water interfaces covered by proteins or polymer/ surfactant mixtures. Studies are carried out in a Langmuir trough, where the layers are deformed by compression/ expansion, and the surface pressure is measured. It is found that the stress response essentially depends on the extent of association of the molecules, with the $\Gamma_a$concomitant restriction on their degree of freedom. The presence of molecules which can be exchanged reversibly between the interface and the adjacent sub-surface is shown to be related to Gibbs' elasticity, E_G, and apparent viscosity, η_a. An expression is derived[1] to connect η_a with the kinetic coefficient of mass transfer rate, K_r: $\eta_a = E_G/f(\Gamma_r)K_r$, where $f(\Gamma_r)$ depends on the equation of state due to the reversibly adsorbed molecules, whose amount per unit area is Γ_r.

On the other hand, some material can be irreversibly attached to the liquid boundary, so that no exchange with the bulk or the sub-surface is possible. In that case, the respective coverage Γ_{irr} is varied when the layer is shrunk or expanded. Experimentally, one takes the $\Pi(A^{-1})$ isotherm which can be fitted with an appropriate equation of state – see Fig. 1.

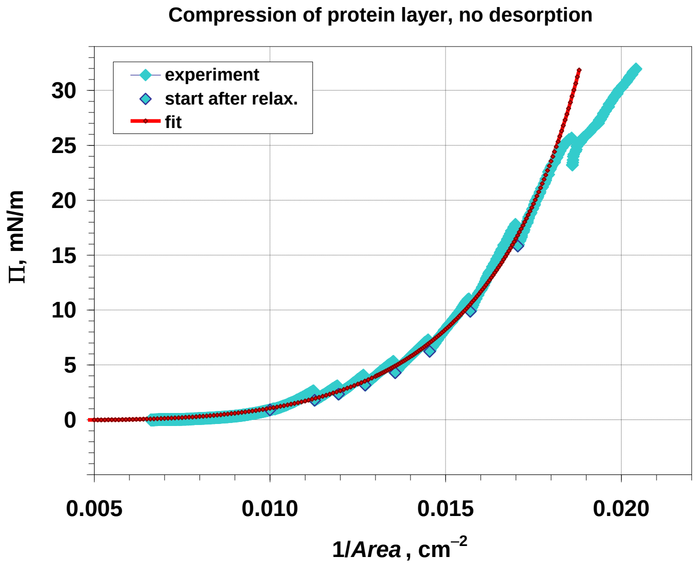

Figure 1. Fit of the stress response to slow compression (10 cm^2/min) with an equation of state for a solute/ solvent binary mixture with an interaction term $\sim\beta\Gamma_{irr}^2$ (two adjustable parameters).

We determine the layer elasticity, E, and discuss its dependence upon the surface pressure, Π. The rheological response is influenced by the distribution of molecules among different states of aggregation (mono-, bi- and multi-layers, lumps, etc.). Some time may be required for the equilibrium distribution to be established. This is usually manifested as relaxation effects in the rheological properties, connected also with the deformation rate and the operational prehistory.

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Interactions of lipopolysaccharides and antennary glycine compounds in aqueous media

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Self-assembly of star-like oligomers results in nanostructures of unusual properties and important applications (medicine, waste water purification, etc.). Some of these oligomers form stable hydrophilic nanoplatforms in aqueous media. These platforms may serve as captive agents for endotoxins. The aim of the present study is to perform systematic investigations on the interactions of one type of lipopolysaccharides from bacteria *Escherichia Coli* with aqueous solutions of antennary glycine compounds. Conditions for fine tuning of lipopolysaccharide capture by the glycine platforms are outlined. The initial results are encouraging and the acquired knowledge may be applied e.g. for controlled purification of contaminated waters.

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Stabilization of aqueous foams using co-surfactants

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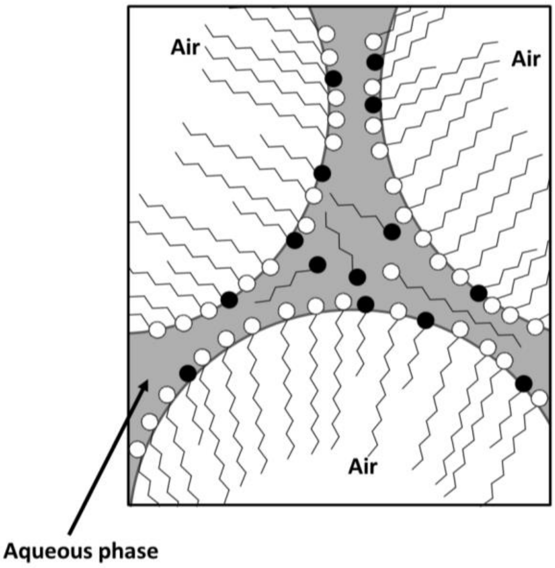
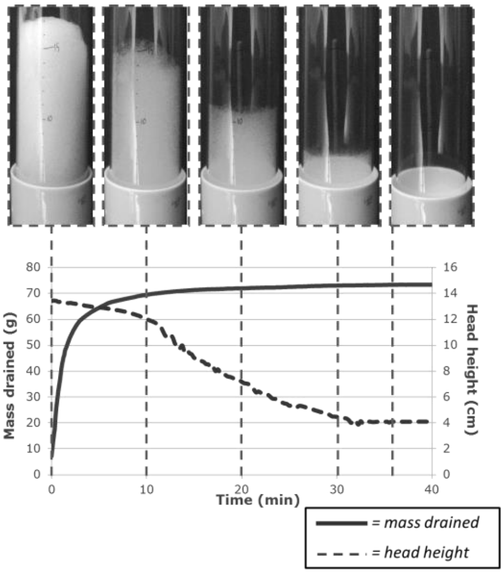
Aqueous foams are a common occurrence in everyday life (e.g. washing up foams) and are stabilized by surfactants assembling at the solution-gas interface. Our work is concerned with investigating the impact of the addition of a secondary surfactant to the surfactant solution on the stability of the resultant foam. This poster presents the setup we use for foam generation and the apparatus used for our stability tests along with preliminary stability experiments carried out on foam generated from an aqueous solution of sodium lauryl ether sulphate (SLES).





Foam processes at VTT

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At the start of the presentation there will be short introduction of VTT (Technical Research Centre of Finland). Then the rest of the talk will concentrate two foam processes that have been studied lately at VTT.

Foam forming method is process where foam instead of water is used to transfer fibers to the actual web former. At former section foam is sucked away and fiber mat is created. The advantage of this process is that is allow wide variety of raw materials (fiber length 0.5 mm – 5 cm) and saving on water consumption. Method also guarantees very even fiber distribution and allows making low density structures. In this method the retention of nano particles is good and it is easy to make layered structures.

Foam coating method is process where foam instead of water is used to transfer coating material to the coater applicator. In this method coating particles are locked inside foam vortices, thus preventing aggregation of the coating particles. It is especially beneficial in nano particle coating, because it allows to make very thin coatings evenly. We have been able to make coating of nano silica particles on paper surface, where coating thickness was 0.5 µm and particles were evenly distributed. Method is suitable for coating of all porous materials that absorb water.

Exploiting the Kubas Interaction in Hydrogen Storage

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The use of the Kubas interaction[1] in hydrogen storage is discussed, with a focus on approaching ideal enthalpies for on-board storage and the synthetic efforts involved in designing an extended solid without organic ligands that adsorbs and desorbs H_2 using this mechanism.[2,3] Thus, titanium(III) hydrazide gels designed for Kubas-type hydrogen storage were synthesized from the reaction between tris(bis(trimethylsilyl)methyl) titanium and anhydrous hydrazine. The materials demonstrate a fully reversible H_2 adsorption capacity of 2.63 wt% and 36.7 kg/m3 at 298 K and 143 bar without saturation. Interaction between the adsorption center and H_2 gas was probed by electron paramagnetic resonance. Computational efforts showed a maximum adsorption of 9.9 wt% rationalized the rising enthalpies and linear isotherms by a new mechanism involving a pressure-induced deformation of the amorphous structure. We also show how porous Ti (III) hydride gels are a promising new hydrogen storage medium, exploiting the first example of a solid state hypervalent metal hydride. This was accomplished using weak chemisorption to a Ti (III) hydride framework with binding enthalpies in the 15-30 kJ/mol range, predicted to be ideal for use in a room temperature hydrogen storage system. These materials use bridging hydride ligands as an ultra-lightweight structural feature to support a microporous network of Ti binding sites for molecular H_2 chemisorption. High-pressure Raman spectroscopy confirmed the first evidence of hypervalent Ti hydride species with Kubas-type dihydrogen ligands. The material with the highest capacity has an excess reversible storage of 3.49 wt % at 140 bar and 298 K without saturation, corresponding to 44.3 kg/m^3 of volumetric density, comparable to the DOE 2017 volumetric system goal of 40 kgH$_2$/m^3. By extrapolation, removal of all hydrocarbon from this material would lead to storage capacities of over 6 wt% at pressures under 150 bar without any kinetic or thermodynamic problems.

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New modules for automised foam characterisation in the FoamScan

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The FoamScan (Teclis), is an automated device to analyse the generation and stability of foams. Since foams are in general turbid media, the determination of the bubble size is difficult. Thus, in most cases, images are taken at the surface of the container. However, it is not clear whether the cell size distribution at the surface is really representative of that in the volume.

To overcome this problem, we are developing two new modules for the FoamScan which allow to obtain information about the evolution of the bubble size. On the hand, this is done via the scattering of white light which relies on the strong link between light transmission, liquid fraction and size of bubbles in a foam. On the other hand, we implement automated investigations of 2D Foams (monolayers of bubbles between plates) using a cell with small plate spacing. This module measures foam conductivity, the height of foam and the size of the bubbles. The two modules extend the possibilities of automated foam characterization and open doors to further foam science.

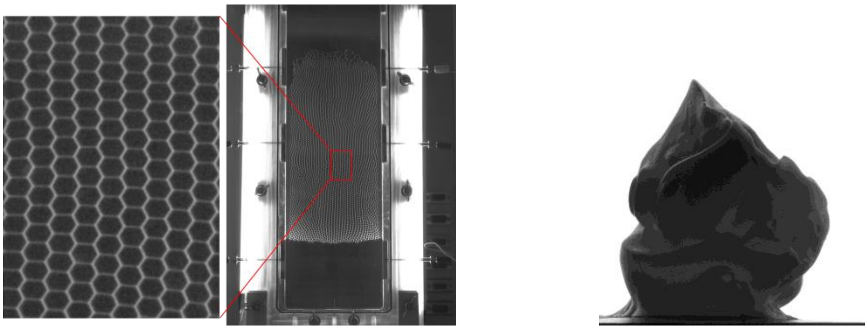

Figure 1: Left: 2D foams module; Right: shaving foam by white light scattering

Nanoparticles characterization by a non-intrusive measurement technique

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Because of the large interest in nanoparticles and nanoparticles flows, there is a strong need for online submicron particle characterization techniques. In this framework the Multi Wavelength Light Extinction (MWLE) technique, which is a non-intrusive optical technique for nanoparticles size and concentration measurement, is developed. Its operation relies on the measurement of the spectral transmittance of a light beam. The transmittance spectrum depends on the size and concentration of the investigated particles. Therefore, the underlying particle size distribution and concentration can be retrieved after the inversion of an appropriate light scattering model. The inverse light scattering problem turns out to be a highly ill-conditioned problem, hence requiring a specific regularized inversion algorithm for the retrieval of the underlying Particle Size Distribution function from the measurement data. In this presentation the most appropriate regularization method to solve the inversion problem will be discussed [1]. An experimental apparatus, allowing simultaneous measurements with the MWLE technique and a Scanning Mobility Particle Sizer (intrusive probe), has also been built for the purpose of validation. Measurements are performed with a Potassium Chloride (KCl) solid particles aerosol. It is shown that, in typical experimental conditions, the measurement of the particle size with the two instruments is in satisfactory agreement with a maximum discrepancy of 10% [2]. The development of this technique gives rise to a large amount of applications, going from the measurement of nanoparticles in plasmas or in more complex environments, to the measure of self-assembled structures which are formed on the surface of a thin evaporating liquid film containing nanoparticles. For the latter application, the presence of the liquid-gas interface is expected to influence the accuracy of the MWLE measurements and a light scattering model, which is capable to account for the presence of an interface, is currently in development.

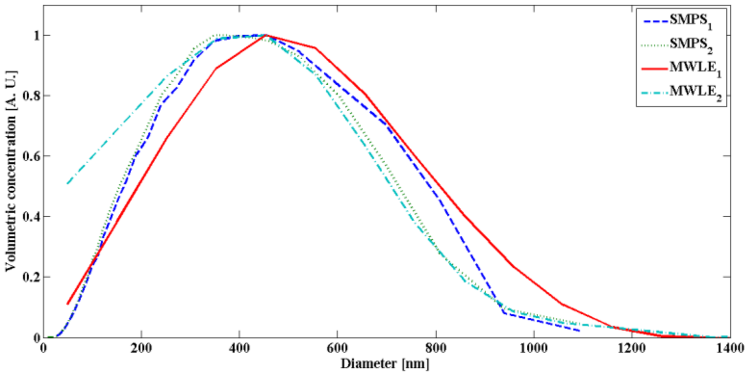

Figure 1 Comparison of SMPS and MWLE distribution obtained for a KCl nanoparticles flow

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A Front-Tracking Method for Computational Modeling of Viscoelastic Two-Phase System

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A front-tracking method has been developed for direct numerical simulations of viscoelastic two-phase systems including motion of Newtonian droplets/bubbles in a viscoelastic fluid, viscoelastic droplets in a Newtonian fluid, viscoelastic droplet in a viscoelastic fluid and Newtonian droplets/bubbles in a Newtonian fluid. Following Unverdi and Tryggvason[1], one set of governing equations is written for the whole computational domain and different phases are treated as a single fluid with variable material and rheological properties. The interface is tracked explicitly using a Lagrangian grid while the flow equations are solved on a fixed Eulerian grid. The surface tension is computed at the interface using the Lagrangian grid and included into the momentum equation as a body force. The FENE-CR model of Chilcott and Rallison[2,3] is employed to model the viscoelasticity. The FENE-CR model equations are solved coupled with the flow equations using an explicit scheme suggested by Sarkar and Schowalter[4].

The numerical algorithm is first tested for a single-phase viscoelastic fluid flow through an abrupt axisymmetric 4:1 contraction and the results are compared with the computational simulations of Coates et al. [2]. It is found that the present results are in a very good agreement with computational simulations of Coates et al.[2] both qualitatively in terms of streamline patterns and quantitatively for all flow variables including the mean velocity and the extra stress components at various cross sections. The method is then applied to study fluid dynamics of buoyancy-driven viscoelastic two-phase systems in a capillary tube. This problem was recently studied computationally by You et al.[5]. Extensive computations are performed to examine the effects of confinement, material properties, and rheological properties of the two phases on drop mobility and deformation. Sample preliminary simulation results are plotted in Fig. 1 for Newtonian drop in a viscoelastic fluid and a viscoelastic drop in a Newtonain fluid. The preliminary results show that a Newtonian drop immersed in a viscoelastic fluid experiences an extending trailing edge, while a viscoelastic drop in a Newtonian fluid develops an indentation around the rear stagnation point. These preliminary results are consistent with the computational simulations of You et al.[5].

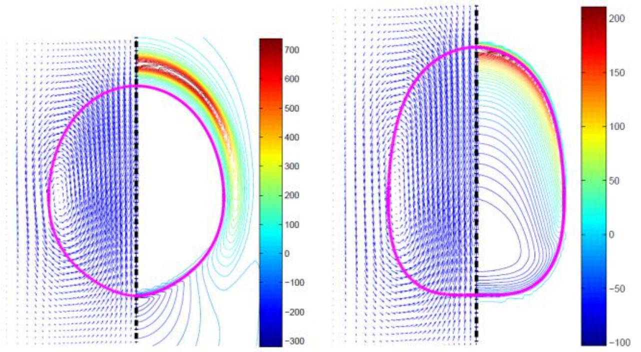

Fig. 1: Steady drop shapes with the velocity vectors (left side) and the contours of extra stress tensor component $\tau_{\theta\theta}$ (right side) in the vicinity of a buoyancy-driven droplet. (a) A Newtonian droplet rising in a viscoelastic fluid. (b) A viscoelastic droplet rising in a Newtonian fluid.

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Nanostructuring of bulk Mg and its alloys via severe plastic deformation

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Equal channel angular pressing (ECAP) has been shown to be an effective tool for grain refinement in bulk Mg and various Mg alloys resulting in improved properties. In most investigations, however, the processing temperature was at or above 200°C to avoid cracking that, in turn, suppress refinement due to grain growth.

In this work, magnesium and selected binary magnesium alloys were processed by equal channel angular pressing with back pressure (ECAP-BP) at room temperature (RT) in order to obtain a material with excess of defects and/or fine-grained microstructure. Microstructure was examined by scanning electron microscope (SEM), electron backscatter diffraction (EBSD), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Microstructural stability was investigated by dilatometry and static annealing. It is shown that multiple ECAP passes with back pressure at room temperature results in crack-free structure with ultra-fine grains and with abundant concentration of defects.

The aim of this presentation is to show current possibilities of microstructural refinement of bulk magnesium and its alloys via severe plastic deformation (ECAP-BP) at RT.

Metal droplet detachment regimes in ring cross-section conical laser beam droplet generation

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Metal droplets can be applied in various manufacturing applications related to droplet joining and 3D structuring. The core process of these applications is a novel laser droplet generation process where the tip of the vertically fed metal wire is melted by a ring cross-section conical laser beam. The critical phase in laser droplet generation is droplet detachment. It has been observed that beside the numerous process variables, the droplet formation process and droplet detachment are governed by the interaction between the laser pulse frequency and the dynamics of pendent droplet. Depending on the laser pulse frequency, three different detachment regimes accompanied by different dynamics have been identified: a) spontaneous dripping, caused by the force of gravity alone, b) resonant detachment, caused by a combination of the gravity force and the laser induced oscillation modes of the pendant droplet, and c) break-up caused by the Rayleigh-Plateau instability.

On the identification of liquid surface properties using liquid bridges

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The term liquid bridge refers to the specific silhouette of a liquid volume when it is placed between two solid surfaces. Liquid bridges have been studied extensively both theoretically and experimentally during the last century due to their significance in many technological applications. It is worth noticing that even today new technological applications based on liquid bridges continue to appear. A liquid bridge has a well-defined surface configuration dictated by a rigid theoretical foundation so the potential of its utilization as a tool to study surface properties of liquids is apparent. However, it is very scarce in literature that the use of liquid bridges is suggested as an alternative to the other well-established drop techniques. The present work presents the theoretical background to setting up the liquid-bridge based surface property estimation problem, describes the required experimental equipment and performs a thorough literature review on the subject. A case with particular interest is that of liquid bridges made of conducting liquids that connect two conducting solids; such a liquid bridge presents electrical conductance which is sensitive to the specific silhouette of the bridge. This enables the use of their conductance as shape descriptor instead of the conventional image processing techniques. Several attempts in the literature for the estimation of the liquid surface tension, liquid-solid contact angle and surfactant induced surface elasticity for conducting or non/conducting liquids are presented and the prospects of the technique are discussed.

Deposition of solid particles at streamlined surface in turbulent flow

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Deposition of corundum 12 and 23 µm particles onto horizontal flat plate within the laminar boundary layer in the free-stream moderate turbulent flow was studied. The presented numerical model considered the deposition onto the surface to be probabilistic process determined both by hydrodynamics and the adhesive behavior of particles and surface.

Numerical simulation was realized under the conditions of the laminar boundary layer. The two fluid approach was used for writing Euler-Euler equations for carrier gas and particulate phase.

Effects of gravity and lift forces on particles velocities and mass concentration, occurring within the boundary layer, and deposition were studied separately for various particle sizes.

It was revealed that gravity and lift forces have decisive influence on behavior of solid particles taken place within the laminar boundary layer and on their deposition, that is expressed via the distributions of the particles transversal velocity and mass concentration. These effects become more pronounced for the larger 23 µm particles.

The given study is the attempt to combine the hydrodynamic and adhesive aspects of the particles deposition for its more accurate estimate, that is suitable for various practical devices.

Turbulent particulate pipe flow at constant Reynolds number

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Effect of the pipe diameter was numerically investigated in the particulate turbulent cylindrical pipe flows at constant Reynolds numbers. The method used is based on 2D Reynolds-averaged Navier-Stokes equations. This approach is supplied with closure equations allowing all pertinent forces and effects: particle-particle, particle-wall, particle-turbulence interactions, gravitation, viscous drag and lift forces and turbulence modulation. Finite volume technique was applied for numerical solution of governing equations.

Results show the effect of the pipe diameter, flow mass loading and particles size on the radial distributions of the velocity lag, turbulence modulation and particles concentration. In particular, increase of the pipe diameter at constant Reynolds number results in decrease of the relative velocity lag and flattening of the radial distributions of particles velocity and mass concentration as well as decrease of a turbulence attenuation rate.

The present model with applying of minimum number of assumptions represents a more contemporary computational approach in turbulent particulate flow.

Emulsification of oil in a shear-thickening fluid

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Emulsification of oil in a shear-thickening continuous phase was investigated. The continuous phase was a mixture of 0.7% w/w hydroxypropylmethyl cellulose (HPMC), a nonionic derivative of cellulose, and 0.00-2.00% w/w of sodium dodecylsulfate (SDS), an anionic surfactant. HPMC-SDS complex formation takes place in the continuous phase when SDS concentration is higher than the critical association concentration (cac=0.15%) [1, 2]. SDS concentration influences rheological behavior of the continuous phases. When SDS concentration is between 0.35-1.25% w/w a characteristic shear thinning viscosity profile is disrupted at shear rates exceeding a critical one. Above the critical shear rate, which depends on SDS concentration, shear thickening is observed, indicating shear-induced structure formation in the system. Emulsions of paraffin oil (5% v/v) in continuous phases of different HPMC/SDS composition were prepared by microfluidzer (M-5000, Microfluidics, USA). Dispersion and rheological properties of the emulsions were tested and were found to be influenced by HPMC/SDS interaction. Emulsions with submicron droplet sizes were obtained when SDS concentration was >0.35% w/w i.e. when shear-induced structure formation took place in the continuous phase of an emulsion. Viscosity of emulsions was found to be lower than that of corresponding continuous phases.

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Uniform, adhesive, robust Cu/TiO_2 films inducing eco-friendly bacterial/viral inactivation under low intensity solar light

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This study reports the sputtering of Cu[1-3] and TiO_2/Cu[4-5] films on textile by conventional pulsed direct current magnetron sputtering (DCP) and highly ionized pulsed plasma magnetron sputtering to inactivate *E. coli* (Gram-negative) and *methicillin resistant staphylococcus aureus* (MRSA, Gram-positive) within short times. Uniform films were obtained with suitable adhesion to the substrate and can be used in a repetitive way to inactivate bacteria at the solid-air interface. Low intensity sunlight with an intensity of 0.5-1% AM1 and actinic light (400-700 nm, with light dose < 1 mW/cm^2) accelerate the bacterial inactivation. This is important when precluding the formation of biofilms pumping infectious bacteria in hospitals, schools and other public places since they are active for long time as a source of pathogens. Surface characterization of the films is presented using X-ray fluorescence (XRF), profilometry, electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS). By highly ionized pulsed plasma magnetron sputtering (HIPIMS) due to the increased M^+-ions energy and the high charge density of $\sim 10^{18\text{-}19}$ $e\text{-}/m^3$, a coating ~38 nm thick inactivated *E. coli* within 10 minutes when using a TiO_2 60/Cu 40 atomic percent target. DCP sputtering inactivated bacteria within similar times but a coating ~ 600 nm thick was required to attain similar bacterial inactivation kinetics.

Using a TiO_2 60/ Cu 40 atomic percentage target in the dark samples sputtered by HIPIMS for 150s induce a slow bacterial inactivation within 120 min showing the Cu-inactivation properties. Under actinic light radiation, samples deposited by pulsed magnetron sputtering time of 150s induced short inactivation times of ~10 min. This sample presents the most suitable structure-reactivity for the Cu-clusters on the TiO_2. The bactericide action under light is due to a synergic effect in the TiO_2/Cu layers since longer inactivation times were observed when sputtering TiO_2 or Cu separately. The HIPIMS sputtered TiO_2/Cu film presenting a thickness of ~38 nm required ~10 min to inactivate *E. coli*. By comparison DCP films with a thickness of 600 nm required ~6 min to inactivate bacteria.

DCP sputtering leads to M^+ ionization >>5% and a charge density $\sim 10^{16}$ $e\text{-}/m^3$ But HIPIMS leads to Cu ionization of ca. 70% with a charge density $\sim 10^{18\text{-}19}$ $e\text{-}/m^3$ and with a power per pulse of 1750 W/100 microseconds compared to the DCP power per pulse of 62.3 W/pulse. The effective antibacterial thin film action by the HIPIMS films were possible due to the applied higher applied since a higher V increases the transition $M \rightarrow M^+$.

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Research of materials for hydrogen generation in electrolysis and photoelectrolysis processes

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Surface modification of steel electrode is investigated to enhance electrolysis process for hydrogen production. Different surface modification methods are compared. Electrode aging process is achieved with prolonged direct current polarization of electrode, electrode cycling with high voltage pulses, and thermal treatment in reducing atmosphere. Raney nickel coating is used to protect steel electrode from corrosion and activate hydrogen evolution reaction on it. Analysis of volt-amperic curves is used to compare electrode suitability for water splitting in electrolysis process. Nanosize powder materials and coatings are tested for application in photo-activated water splitting. Transition metal nitrides and titanium tetrabutoxide are used to obtain thin films of ferrite, titania and mixed ferrite/titania films in spray pyrolysis method. Photo-electrochemical methods are used to investigate photo-activity of sintered powders and thin films, structure and morphology are tested with XRD and microscopically.

Influence of n-octanol on the bubble bouncing and coalescence time at solution surface

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Bubble motion, collision with liquid/gas interface and coalescence are important processes in many industrial applications, i.e. foam formation, froth flotation, aeration of water tanks etc. Outcome of the bubble collisions depends on many mutually interconnected factors such as: bubble size, the bubble impact velocity and shape deformations, the collision contact time, presence and state of adsorption layer at the interacting surfaces, size and stability of the liquid film formed, surfactant adsorption kinetics and drainage velocity of the liquid films formed, etc. It was showed earlier[1,2] that even in the case of pure liquids the coalescence of a bubble at free surface does not have to take place during the first collision because of the bubble bouncing, which occurs when the collision contact time is shorter than the time needed for the film formed to drain to its critical thickness of rupture.

In the present work, influence of n-octanol concentration on the bubble impact velocity, bouncing at the solution surface and stability of the films formed by the colliding bubble is investigated using a high-speed camera (1040 frames per second). The bubble impact velocity, number of the bouncing and the bouncing amplitudes were measured as a function of n-octanol concentration. As the entire lifetime of the colliding bubble consists of the time of bouncing (t_b) and lifetime of the film formed (t_{film}), so these both components of the bubble coalescence time ($t_c=t_b+t_{film}$) were measured. At low n-octanol concentration the bubble impact velocity (U_{imp}) decreases rapidly, but at $c \geq 3\cdot10^{-5}$ M starts to be practically constant (ca. 15 cm/s), what indicates that at concentrations of $3\cdot10^{-5}$ M and higher the fluidity of the bubble surface was completely retarded[3]. In distilled water (U_{imp}= 34.7 cm/s), where the bubble bounced 3 times and ruptured during the 4th collision the bubble bouncing time, the t_b, was equal 72 ms, while the film lifetime, t_{film}, was only ca. 2-3 ms, i.e. the bubble coalescence time was determined by the bubble bouncing. With increasing n-octanol concentration the film lifetime increases rapidly and therefore starts to be the parameter determining the bubble coalescence time. For example, at very low n-octanol concentration $6\cdot10^{-6}$ M (U_{imp}= 24.8 cm/s) the bouncing time was similar as in water (t_b=76 ms) but the coalescence time was immensely prolonged - to ca. 1100 ms. In $1\cdot10^{-3}$ M n-octanol solution the bubble coalescence time was of an order $3\cdot10^{4}$ ms (30 s), while the bouncing time was shortened to 13 ms only - lower bubble impact velocity, U_{imp}= 15 cm/s. These data also show clearly that stability of the liquid film formed determines process of the foam layer formation - the foam layer can be formed when the film lifetime is longer than the time interval between subsequent bubbles arriving at the solution surface.

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Rheology of particle–polymer gels subjected to compression by centrifugation

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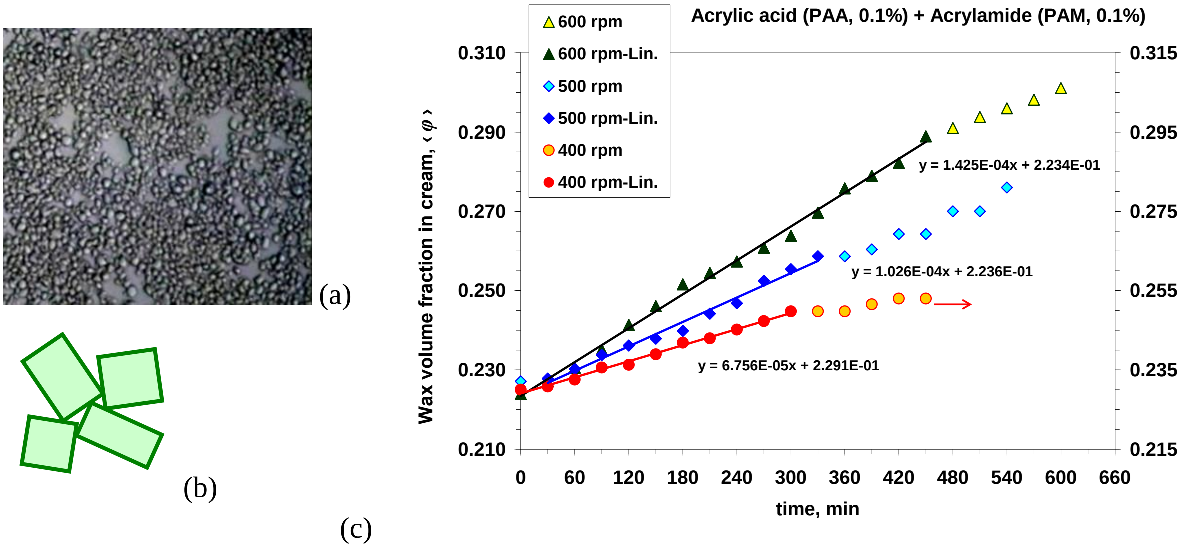
We study the creaming stability of aqueous dispersions whose particles consist of solid fatty alcohols, and have sizes of a few μm. High stability against thickening is provided by polymers (polyacrylamide, PAM, and polyacrylic acid, PAA). Centrifugation is performed in multiple steps, each one with fixed time duration, in two ways: either with increasing rotation speed, or at one and the same rotation speed. The (average) volume fraction of particles in the cream, φ, is determined from the amount of separated cream. The pressure dependence of φ gives information about the structure of the compressed dispersion[1] – specifically, the density, degree of homogeneity, size of voids. The change of φ as a function of time, at fixed acceleration, shows a typical linear dependence (Fig. 1). The latter is related to a viscous-type drainage of liquid from the structure. The slope of the φ(*t*) plot increases with the rotation speed, in agreement with the expected trend, $d\varphi/dt \propto \omega^2$. We discuss the influence of different factors on the creaming stability, such as the concentration of the polymers, the ratio between PAM and PAA, presence of small hydrophilic particles (Bentonite), etc. The interparticle contacts are much stronger with PAA, as compared to the case with PAM.


(a)

(b)

(c)

Figure 1. Structure of dispersions: (a), (b); Cream compaction at low rotation speed: (c).

Information about the extent of irreversible flocculation is gained from experiments with redispersion of the cream and subsequent centrifugation, combined with microscopic observations. When stiff aggregates cannot repack tightly, the volume fraction ‹φ› remains quite low.

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Mechanical Properties of films of self-crosslinked latexes based on copolymers BA/MMA/DAAM or BA/MMA/VEOVA-10/DAAM with adipic acid dihydrazide

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The MFFT (Minimum Film Forming Temperature) and the mechanical properties of self-crosslinked latexes based on copolymers butyl acrylate (BA)/ methyl methacrylate (MMA)/ diacetone acrylamide (DAAM) and BA/MMA / vinyl neo-decanoate (VEOVA-10)/DAAM were measured using the adipic acid dihydrazide (ADH) as crosslinking agent inside the latex.

The surface hardness and the static tensile strength of films were improved in all cases by the addition of the crosslinking agent ADH. Also the use of polymerizable emulsifier during the preparation of the latexes caused an impressive improvement of mechanical properties of the films, in comparison with mechanical properties of the films of latexes which prepared without polymerizable emulsifiers. In the majority of the experiments the addition of ADH caused also clear reduction of the MFFT.

Over and above in our previous publication[1] we found also that the films of the self-crosslinked latexes prepared with the polymerizable emulsifier and ADH showed very good performance in measurements of gloss, water absorption, swelling in butanone. This makes them ideal binder for 1K high performance green coatings that are friendly to the environment and safe to use. The surface tensions of these latexes are relative high due to the fact that most of the surfactant copolymerizes with the monomers. We intent to study the influence of several additives in interfacial tension measurements and measurements of interfacial viscosity and elasticity in a broad range of conditions as close as possible to those met in practice.

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Poly(ethylene oxide)-based structures self-assembled on surfaces after evaporation from aqueous solutions

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Polyethylene oxide (PEO)-based thin films and structures have important biomedical applications as PEO is biocompatible and exhibits protein resistance[1]. One of the unique attractions of PEO (which is related to its biomedical properties) is its water solubility[2] which provides opportunities for environmentally-friendly fabrication, based on self-assembly, of advanced (and potentially 'smart') thin films and structures at several scales.

Firstly, we present an atomic force microscopy (AFM) study of the nano/microstructure morphology of pure PEO thin films spin cast on mica from aqueous solutions. Then, we continue with a comprehensive investigation of a series of amphiphilic poly(isoprene-b-ethylene oxide) diblock copolymer thin films (with various block fractions) fabricated in the same manner. We show the crucial effect of the PEO crystallization in determining the morphology of the self-assembled structures. We also give examples of potential 'smart' use of these nano/microstructures as responsive surfaces to environmental conditions.

In the second part of the presentation, we concentrate on the fabrication of larger (mm-sized) PEO structures. We used drying droplets of PEO solutions (several molecular weights of PEO) to study in some depth the pinning/de-pinning transition which is a determining factor for the final morphology of the deposit (this process can lead to pillar formation[3,4] under specific conditions). The nano/microscopic contact line phenomena are presented and discussed.

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Dynamic interactions of selected mineral nanoparticles with the pulmonary surfactant at the air/water interface

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Mineral nanoparticles (NPs) may be extensively inhaled in different environments, also in the workplace (e.g., production of nanocomposites where NPs are used as fillers to novel polymers). Following inhalation, NPs are deposited inside the lungs on the surface of alveolar liquid where the pulmonary surfactant (PS) forms a barrier between external environment and lung tissue. Interactions between these nanoparticles and the surfactant may be responsible for adverse health effects as it is well recognized that dynamic surface activity of PS is important for the vital lung functions[1].

In this study we evaluate the impact of selected mineral NPs on dynamic surface activity of animal-derived PS (Survanta) at the air/water interface by application of bubble pressure method (BP2 tensiometer, Krüss). Measurements were done at physiological temperature for NPs of natural aluminosilicates (halloysite and bentonite) and of three types of surface-modified montmorillonites (SMM). Particle properties (size, morphology and surface area) were tested during our earlier works[2,3]. Concentrations of nanoparticles in the surfactant solution were estimated from calculations of deposited particle mass after breathing with dust-contaminated air[3]. It was found that all tested nanoparticles change the dynamics profiles of the surface tension at the air/water interface, but the effect is strongly dependent on particles properties and their concentration (Fig.1 & 2). For surface-modified NPs there is an initial increase in the dynamic surface activity, and this effect well corresponds to our previous findings from the measurements with oscillating bubble technique[3]. The results indicate that mineral NPs change the dynamic surface tension of the pulmonary surfactant and this effect may be related to certain health effects in the respiratory system after inhalation of NPs.

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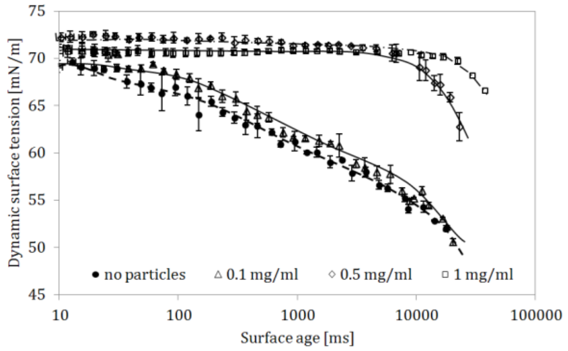

Fig. 1. Dynamic surface tension of pulmonary surfactant (Survanta) in the presence of bentonite nanoparticles.

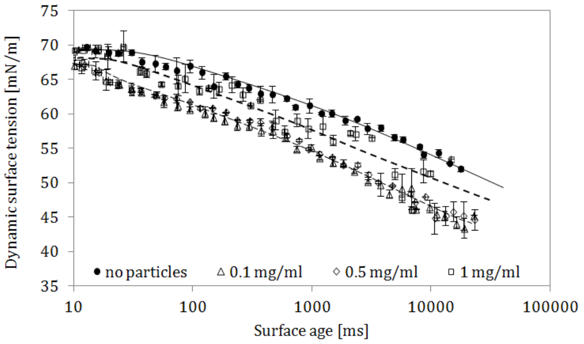

Fig.2. Dynamic surface tension of pulmonary surfactant (Survanta) in the presence of SMM nanoparticles.

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Effect of operating pressure and electrode surface roughness on gas-liquid flow patterns in thin-gap electrochemical microreactor

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Application of a thin-gap electrochemical microreactor (EMR) for intensification of the electro-organic synthesis has been recently investigated by our group[1,2]. In the studied thin-gap EMR, the inter-electrode gap is only 0.1 mm while the microchannel width is 10 mm, so the microchannel has an extremely low aspect ratio of 0.01. This arrangement is particularly interesting for the applications with the low-conductivity electrolytes as it minimizes the ohmic drop between the electrodes.

This contribution reports on the experimental investigation of the effect of the operating pressure and electrodes surface roughness on gas-liquid flow in the thin-gap electrochemical microreactor. For description of gas-liquid flow in the microreactor two hydrodynamic characteristics were selected: flow pattern and bubble size distribution. Experimental data obtained by visualization of gas-liquid flow in microreactor were evaluated by image processing using Matlab Image Processing Toolbox. Our results show that in a thin-gap microreactor the four distinct flow patterns may exist. Namely, the flow without bubbles, dispersed bubbly flow, bubbly flow and churn flow were observed. Presented flow maps indicate the conditions for the respective flow pattern. Results of bubble size distribution confirmed the expected trends; with increasing liquid flow rates the bubble size decreases, and with increasing current density, bigger bubbles are generated. Utilization of the electrodes with lower surface roughness resulted in bigger bubbles, whereas coarser electrodes generated more uniform flow of smaller bubbles. Operating pressure had a dominant effect on bubble size. Already at operating pressure of 1 bar, the electrochemically preferred dispersed bubbly flow was observed for wider range of operating conditions when compared to the atmospheric operation. The effect of operating pressure was significantly stronger than the effect of electrode surface roughness, and appears very promising from the application point of view.

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Local particle–free-surface interaction causes global particle accumulation

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Surface-tension-driven flows are characterized by very high flow velocities near the interface. When the flow is laden with finite-size particles which easily follow the fluid motion in the bulk these are transported to the close vicinity of the interface owing to the interfacial streamline crowding. Due to the high velocity and shear the particles can no longer perfectly follow the fluid motion near the free surface and the interaction of the particle with the interface becomes important.

Considering the system of a thermocapillary liquid bridge[1] it is shown that a simple particle—free-surface interaction model[2] can lead to a de-mixing of initially randomly distributed spherical particles into so-called Particle Accumulation Structures (PAS)[3]. We show that the topology of the flow in form of chaotic and regular streamlines (figure 1) is of crucial importance for the de-mixing process. The model can explain the extremely rapid formation of PAS as observed in experiments[4].

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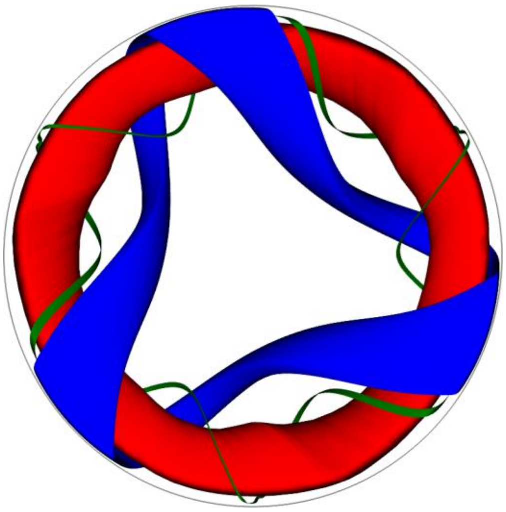

Fig. 1: KAM tori in the surface-tension driven flow in a liquid bridge.

Arching structures in granular sedimentary deposits

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Experimental results on arching structures formed in sedimentary deposits are presented. Polydisperse mixtures of non-spherical rough natural calcite particles (ground limestone) settled collectively in a liquid (water) and formed the deposit beneath. The morphology of the deposit layer was studied with help of visualization and image analysis. Families of interconnected arching patterns in form of voids or cavities were identified, of highly complex geometry[1,2]. Such geometry is quantified by measuring of *total voidage* and qualified by measuring of *void fraction* in sedimentary vessel height. The ratio of *total voidage* and *maximal void fraction* determine degree of cavity accumulation. The effect of the mixture composition (fraction size, volume fraction) and effect of the liquid viscosity on the deposit structure was investigated. Simultaneously was visualised grain size distribution and fraction size localisation. For instance, it was found, that cavities tend to form under specific conditions, and that the large and small grains promote the void formation while the medium grains inhibit the voiding.

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Ethane 1,2-di-amineborane as a new derivative of ammonia borane for hydrogen storage: desorption and relaxational properties

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Ethane 1,2-di-amineborane ($BH_3NH_2CH_2CH_2NH_2BH_3$) (EDAB hereafter) has been recently considered as an interesting material for hydrogen storage applications [1]. This compound releases *ca.* 10 wt% of pure hydrogen in a two step process taking place at moderate temperatures.

Here, we present novel results on the dehydrogenation properties of EDAB by means of combined thermogravimetry (TG), differential thermal analysis (DTA) and mass spectrometry (MS) measurements both under vacuum and under an inert gas flow. These measurements show a clear influence of the surrounding atmosphere (vacuum or inert gas) on the decomposition pathway of EDAB. In addition, we analyze the internal relaxation processes of EDAB by means of Anelastic Spectroscopy measurements. An elastic energy loss peak has been observed at about 220 K, which is related to a relaxation process in the bulk of EDAB. These results will be discussed and compared with those previously obtained with its parent compound ammonia borane [2].

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Drainage dynamics of water/surfactant droplets in paraffin oil

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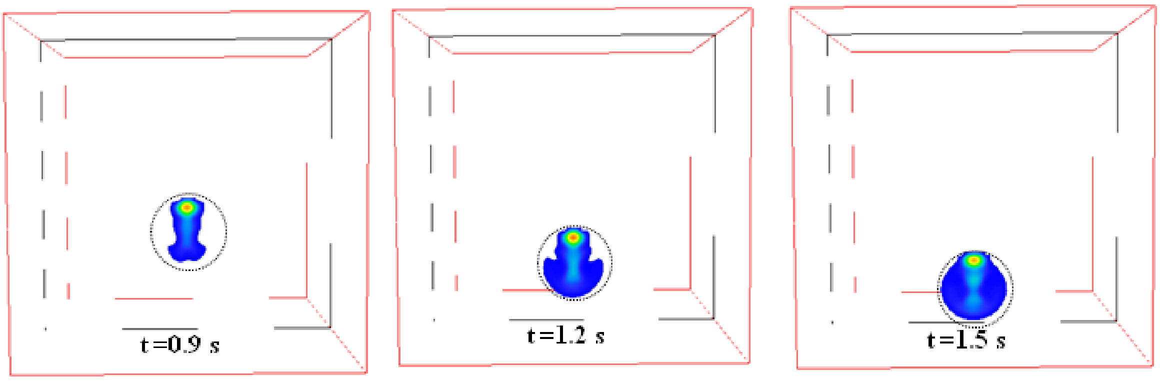
This work reports on numerical simulations of the unsteady hydrodynamics in a system consisting of a single water droplet in a continuous paraffin oil phase. The considered droplets have varying radius and are confined in a 1cm × 1cm square simulation domain. The model is two-dimensional, droplets are submitted to gravity and capillary effects are accounted for[1]. Such systems are typical examples of two phases, unsteady, free interface problems. The Navier-Stokes equation for incompressible fluids is solved with the PHOENICS Software and a volume of fluids (VOF) technique without interface reconstruction is used.

From the numerical point of view, as a droplet moves in a continuous medium, its interface 'disappears' upstream and is 'created' downstream. This simple propagation problem is still open and raises important numerical precision and stability difficulties. When including capillary effects, the Navier-Stokes equation is modified by a coupling term that includes the water-paraffin oil interface curvature and surface tension[2]. The structure of the velocity field is shown to depend on the droplet radius, average velocity, initial position and on the working temperature.

The effect of a soluble surfactant is also investigated[3]. Initially its concentration is assumed to be uniform and small enough for the surfactant to be located only on the water-paraffin oil interface. Due to the droplets motion, this distribution evolves with time. Surfactant is first transported towards the apex of the droplets and, as it is assumed to be water soluble, it is then transported inside the droplets as illustrated in the figure below. The main effect of this time evolution is a slowing down of the overall drainage velocity.

Besides single droplet dynamics, this work also aims to propose a numerical description of flocculation and coalescence phenomena. It is conducted within the framework of the ISS/FSL/FASES project and, from this point of view, can be seen as a step in the direction of numerical studies devoted to the simulation of emulsions.



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Preparation and characterization of electrophoretic Fe-TiO_2 films

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TiO_2, both in the form of powdered material or thin film, has been increasingly used as photocatalyst in diverse environmental applications and solar cell manufacture due to its unique physico-chemical properties. The use of TiO_2 thin films for heterogeneous photocatalysis significantly reduces several drawbacks of practical application, such as the need of powder separation or agglomeration of the particles. Traditionally, the photoactive coatings on flat substrates are deposited by sol-gel, spin coating, chemical vapor deposition, sputtering or electron beam evaporation. For coating of irregular conductive surfaces the electrochemical methods are most eligible. The advantages of electrophoresis over other coating methods are the homogenity of deposition for complex shapes, reduction of material usage, low contamination level and high production rates.

However, the use of TiO_2 as photocatalyst also is limited because of its large band (~ 3.2 eV). Therefore, it is necessary to prepare modified TiO_2 films to improve its photoactivity under visible light irradiation. Transition metal ion Fe^{3+} has been considered as an appropriate option because its radius is similar to that of Ti^{4+} hence Fe^{3+} ions might easily incorporate into crystal lattice of TiO_2 and act as electron/hole traps.

The purpose of current work is the optimization of parameters for the sol-electrophoretic deposition process to produce nanostructured Fe-TiO_2 thin films. Obtained films were characterized by phase composition, morphology and their microstructures using X-ray diffraction and fluorescence, Raman spectroscopy, as well as scanning electron microscopy (SEM). The open-circuit voltage and photocurrent density of Fe-TiO_2 films were measured in order to obtain the influence of Fe^{3+} doping content on the photoactivity of Fe-TiO_2 films.

The results show that Fe^{3+} ions have been successfully doped into TiO_2 crystal lattice by substituting Ti^{4+}, thus inducing absorption shift toward visible region compared with the un-doped TiO_2 films. The highest photoactivity under visible light is demonstrated by 0.5-1.0 % Fe-TiO_2 films.

Effects of carbonaceous nanoparticle on the surface properties of model lung surfactant layers.

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The potential toxicity and the health hazard associated with the exposition to engineered nanoparticles and to nanoparticulate produced by the anthropic activities is a controversial subject, limiting the use of nanotechnologies in sensitive fields, such as nanomedicine or food technologies, and the assessment of the impact of specific productions, such as mining or energy from combustion.

Investigating the basic physico-chemical interactions of NPs with cell tissues and body fluids is an important step to rationalize the results from classical toxicological in vitro or in vivo assays, develop new screening methods, or design biocompatible NPs for biomedical applications .

Among the various body entry points, lungs represent probably the most important for NPs dispersed in the environment. The physicochemical aspects of the interaction of NPs with the pulmonary surfactant (PS) layer, composed by a mixture of lipids and some specific proteins, can be effectively studied by a surface science approach [1, 2].

Here we report the results of the investigation on the interaction of carbonaceous nanoparticles with monolayers of 1,2-Dipalmitoyl-sn-glycerol-3-phosphocholine (DPPC, the main component of PS), performed by means of a Langmuir trough equipped with a Wilhelmy plate tensiometer. The study has pointed out that the modifications induced by these NPs to both the equilibrium and rheological features of the lipid layer are essentially driven by the hydrophobic interactions between particles and lipid molecules which, combined with the change of the free surface area available per DPPC molecule, affect the packing and the molecular cohesion in the monolayer.

To better understand the potential toxicological effects, specific tests have been performed to asses the changes induced in the functional features of the monolayer, such as the Surface Pressure – Area isotherms, the collapse pressure, the dilational elasticity, the linearity of the surface pressure response. The functionality during simulated respiratory cycles has also been quantified, by the help of classical (normalized Hysteresis Area - HA, Stability Index - SI) or newly defined (Total Harmonic Distorsion – THD) cumulative indexes.

The study shows that already a relatively simple approach, based only on tensiometric measurements, can produce a number of useful information about the NP interaction with lung surfactants.

Some of these results can be extended to biological membranes, DPPC also being their major component. The application of other techniques, such as Brewster Angle Microscopy, Ellipsometry, AFM amplifies enormously the possibility of investigating in more details the features of these lipid-NP monolayers.

Acknowledgements: IIT-Italian Institute of Technology, Project Seed2009 "NIPS-Nanoparticle Impact on Pulmonary Surfactant Interfacial Properties"

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Changes in the morphology of emulsion droplets stabilized by surfactant modified particles

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By optical tomographic technique it has been determined that under certain surfactant/silica particle mixing ratios, instead of spherical oil droplets, the dispersed oil droplets in the aqueous solution have a polymorphous shape[1]. The transition range from spherical to polymorphous droplet shapes has been confirmed by bulk rheological measurements[2] and scanning electron microscopy[3].

In the present contribution a systematic study on different mixed systems of silica particle-CTAB//paraffin oil-Span 80 has been performed using optical tomographic microscopy, Cryo-SEM and interfacial shear rheology. It has been obtained that the presence of an oil soluble surfactant has a strong influence on the emulsion's properties. At a certain threshold concentration of Span 80 in the oil phase the spherical shape of dispersed oil droplets are recovered. These findings have been confirmed by step changes in interfacial shear rheological properties and are discussed in more detail.

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Effect of gravity on heat and mass transfer phenomena during the immersion of a water saturated porous matrix in hot oil.

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The effective enhancement in boiling heat transfer provided by porous-layer coatings is mainly attributed to combinations of an extended surface area effect, an increased nucleation site density effect and the bubble dynamics at the top of the layer adjacent to the liquid pool. However, up to now, no model has been proposed putting forward the above concepts in order to describe the heat transfer coefficient on such porous surfaces.

In order to provide original experimental evidence to support such modeling efforts, an experiment is conceived, where a ceramic porous medium saturated with water is submerged in a hot immiscible liquid (i.e. oil) having only its top surface exposed to the oil. The hot liquid triggers boiling over and right below the surface of the porous medium. The employed heating approach cancels the effect of natural convection in the surrounding liquid layers since the hot oil is above the cold porous matrix and circumvents the problem of non-uniform heating of the exposed porous surface which is a significant source of unsteadiness when heating porous substrates by electrical or radiation means from their bottom. As a result, the employed heating approach leads to smoother boiling operation.

Increased levels of gravity in the range from 1g to 9g are used as a tool (experiments conducted in the Large Diameter Centrifuge at ESA/ESTEC) to modify bubble dynamics over the porous surface. Experiments are conducted at a constant oil temperature (150^{o}C). Continuous temperature measurements inside the oil and inside the porous matrix (at 0.5, 1.0 and 1.5mm below the surface), in conjunction with high speed imaging of emerging vapour bubbles over the porous surface (i.e. bubble growth rate, bubble detachment diameter, bubble detachment mode, bubble departure velocity, bubble population density), reveal the effect of gravity level on boiling phenomena over the porous matrix. The analysis of these measurements indicates a strongly non-linear effect of increasing gravity on boiling phenomena over porous media which is not predicted by any existing model or correlation.

Effect of thermal gradients on heat and mass transfer phenomena during the immersion of a water saturated porous matrix in hot oil.

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Protecting surfaces from high heat fluxes by using porous materials saturated with liquid water is an innovative new way designed to shield a substance from absorbing excessive heat from an outside source. The use of liquid instead of gas as a coolant has the advantage that the heat of vaporization can be used as an additional cooling mechanism

The interplay between the boiling mechanisms over and just below the surface of a porous matrix and the bubbles behavior above it is experimentally studied during the immersion of a ceramic porous medium saturated with water inside a bath of a hot immiscible liquid (i.e. oil with temperature well above the water boiling point). To simplify the geometry of the problem, the porous medium has only one surface exposed to hot oil, the others being thermally insulated. Therefore, the hot oil triggers boiling solely over the exposed porous surface. The employed unconventional top-down heating approach by hot oil offers two distinct advantages compared to conventional approaches of heating porous substrates by electrical or radiation means from their bottom. These are:

- Suppression of the effect of natural convection in the surrounding liquid layers since the hot oil is above the cold porous medium.
- More uniform heating of the exposed porous surface (which is a significant source of unsteadiness with conventional heating methods) leading to smoother boiling operation.

Continuous temperature measurements inside the oil bath, on the oil-porous interface and inside the porous matrix (i.e. 0.5, 1.0 and 1.5mm below the surface) are acquired along with optical images of bubbles activity (based on fast-video recordings) over the exposed porous surface. These are cross-examined aiming at identifying a possible relation between bubbles behavior and boiling heat transfer inside the porous matrix. The influence of the oil bath's temperature, T_{oil}, on the above phenomena is studied by testing various T_{oil} values (i.e. 150, 160, 170 and 180^{o}C).

Controlling the evaporation of sessile drops by surface softness

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We demonstrate how the deformation of the substrate close to the triple-phase contact line influences the evaporation process of a sessile drop by using surfaces with similar wettability, but different mechanical properties. We show that water drops on soft surfaces (Young's modulus ~0.02 MPa) evaporate faster than on hard surfaces (Young's modulus ~1.5 MPa). The faster evaporation rates on soft surfaces can be related to a different dynamic evolution of the receding contact angle, which is a direct consequence of the substrate deformation close to the triple-phase contact line. By adjusting the substrate softness we are able to control the transition between constant contact radius and constant contact angle evaporation modes.

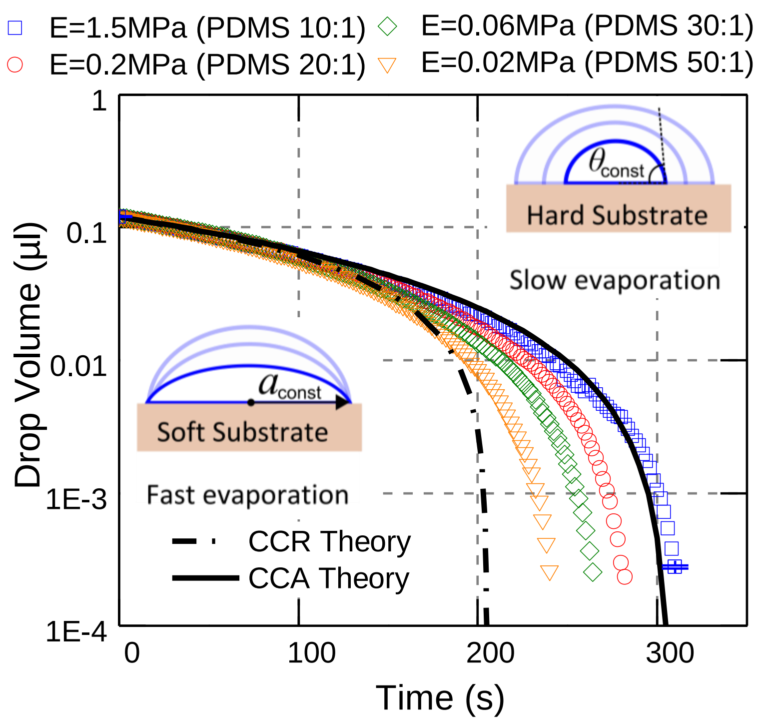

Figure 1: Volume change of a sessile water drop during evaporation. The symbols represent the experimental data on different soft polydimethylsiloxane (PDMS) surfaces. The solid and dashed lines represent the expected volume change in CCA and CCR mode respectively.

Reference

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How to choose among different kinds of superhydrophobic surfaces? Innovative test protocol on ageing of superhydrophobic surfaces

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In this paper we present the development and the set-up of a laboratory durability test protocol to compare resistance and aging of superhydropobic surfaces. Herein a new protocol is proposed to evaluate resistance of superhydrophobic surfaces (SHSs), with special attention to the feasibility. It is structured to be carried out in a common laboratory research, using easily available reagents and low-cost materials.

The protocol consists of nine different tests to simulate surface exposure to potentially harmful different environments. Tests include immersions in water and organic solvents, immersion in solutions of acid, alkali and salt, exposure to erosion, heating and UV rays. Different tests conditions and results are discussed in the paper. Superhydrophobic features of the surfaces are measured evaluating the advancing contact angle and the contact angle hysteresis with the method of the sessile drop: measures are performed before and after each test, in order to evaluate qualitatively and quantitatively the differences in superhydrophobicity.

The proposed protocol allows evaluating not only the resistance of a surface to damaging such as immersion in acid or UV irradiation, but also which is the most suitable use for a surface, considering its durability. In addition, the data analysis from the protocol can be used to provide an indication on how the procedure used for the surface realization allows achieving homogeneous surfaces.

Wedge filling: A novel way to observe critical surface phenomena

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We present results of a microscopic density functional theory study of wedge filling transitions, at a right-angle wedge, in the presence of dispersion-like wall-fluid forces. Far from the corner the walls of the wedge show a first-order wetting transition at a temperature T_w which is progressively closer to the bulk critical temperature T_c as the strength of the wall forces is reduced. In addition, the meniscus formed near the corner undergoes a filling transition at a temperature $T_f < T_w$ the value of which is found to be in excellent agreement with macroscopic predictions. We show that the filling transition is *first-order* if it occurs far from the critical point but is *continuous* if T_f is close to T_c even though the walls still show first-order wetting behaviour. For this continuous transition the distance of the meniscus from the apex grows as $\ell_w \approx \left(T_f - T\right)^{-\beta_w}$ with critical exponent $\beta_w \approx 0.46$ in good agreement with phenomenological effective Hamiltonian predictions. Our results suggest that critical filling transitions, with accompanying large scale universal interfacial fluctuation effects, are more generic than thought previously, and are experimentally accessible.

Co-adsorption in mixed protein and/or surfactant solutions studied by solution exchange experiments with pendant bubbles and thin films

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Set of complementary experimental methods is used to determine the properties of adsorption layers of solutions containing two proteins or a protein and surfactant and to qualitatively analyze the effect of the individual components: Phase exchange experiments with (i) rising bubbles to determine the surface tension by the DSA method, combined with surface dilatational rheology measurements; and (ii) thin films observations for determining the film thickness and stability.

The properties of the mixed adsorption layers and thin films have been compared in two different cases: (i) *Parallel* adsorption from mixed solutions of the two components; (ii) *Sequential* adsorption realized by exchange of the solution around the bubble or in the films.

The applied combination of experimental methods and data interpretation give the opportunity to analyze in details the role of individual components for the overall behavior and stability of the mixed system,[1] and could be further applied to other protein + surfactant blends.

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Protein/surface interactions: the role of nanoparticle chemical composition and size on the fibrinogen adsorption

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The proteins/surface interaction is considered the first event that occurs when an inorganic surface comes in contact with a biological fluids. This interaction is influenced by a series of physico-chemical factors related to the features of the inorganic surface (hydrophobicity/hydrophilicity, charge, nanotopography, curvature, reactivity, chirality), medium (pH and ionic strength) and protein characteristics (charge and resistance to structural deformation) [1-6].

The nanometric silica particles (SiO_2) and carbon are widely used in industrial applications for example as excipients in pharmaceuticals, cosmetics and as additives in plastics, rubber. These materials are also studied for applications in nanomedicine as possible carriers for diagnostic and therapeutic use [7]. Exposure to these materials, both accidental and intentional, can have harmful effects on human health. The nano particles, once penetrate into the body, may across biological barriers and enter the bloodstream. This is the cause of the increase in cardiovascular diseases upon peaks of nanosize particulate matter. Fibrinogen was selected among other plasma proteins because of its relevance to blood clotting processes and in the recruitment of macrophage and leukocyte.Conformational changes mediated by the surface of implantable medical devices are known to activate fibrinogen, leading to the exposure to receptors embedded in the native protein [8].

This study aims to elucidate the adsorption behavior of fibrinogen on substrates showing different chemical surface population (silanols and siloxane in the case of silica while carboxylic and alcoholic groups on carbon nanoparticles).The extent of the protein coverage and the irreversibility of the adsorption process were monitored by combining curves of protein adsorption and shift of ζ potential respectively. The evaluation of protein conformational change of fibrinogen tertiary structure was evidenced by Raman spectroscopy.

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Dielectrowetting Control of Droplets of Non-Conducting Liquids

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The contact angle of a droplet of a conducting liquid on a substrate can be controlled using a voltage by making the droplet part of a capacitive structure where the droplet contact area forms one electrode to create an electrowetting-on-dielectric (EWOD) configuration[1]. This principle has been used to create liquid optical devices and as a method of creating droplet microfluidic systems. However, the substrate must include an electrode coated with a thin, and typically hydrophobic, solid insulating layer and the liquid must be conducting, typically a salt solution, and have a direct electrical contact. In this work we show that reversible voltage programmed control of droplet wetting of a surface can be achieved using non-conducting dielectric liquids and without direct electrical contact.[2] Our approach uses non-uniform electric fields and liquid dielectrophoresis to alter the energy balance of a droplet on a solid surface. We show experimentally and theoretically that for thick droplets the change in the cosine of the contact angle is proportional to the square of the applied voltage and obeys a similar equation to that found for EWOD. In this limit, the important surface free energy changes occur by displacements of the contact line. We also show that as the droplet spreads and becomes thinner, changes in surface free energy can occur by a wrinkling/undulation forming in the liquid-vapor interface[3-5]. We discuss how these effects could be used to create droplet microfluidic systems without the need for direct electrical contact and without the restriction to conducting liquids.

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Capillary Rise and Imbibition in Tubes and Channels

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When a vertically mounted circular cross-section tube is brought into contact with a wetting liquid the liquid penetrates and rises under the action of capillary forces at a rate determined by viscous forces until it reaches an equilibrium height. The same physical principles apply as the tube is tilted towards the horizontal, but gravity becomes ever less influential. If the tube is replaced by a rectangular cross-section closed or open channel (i.e. with or without a top enclosing surface) then many of the same principles apply. However, the existence of 90 degree corners between the sides and the bottom/top of the channels leads to a corner filling capillary problem[1]. In this work we report experiments on capillary rise of polydimethylsiloxane oils into vertically mounted circular and square cross-section (closed) tubes and open-rectangular channels. We fit the data to both the exact differential equation describing this situation and to an analytical visco-gravitational solution valid for vertically oriented tubes. We report that for square tubes and rectangular channels liquid filaments run along the corners in advance of the main body of liquid, as predicted from corner-filling considerations[2]. We investigate the effect of tilting circular cross-section tubes towards the horizontal. We compare fitting data to the exact differential equation, to the visco-gravitational solution and to the Bousanquet solution, which is valid for horizontal tubes. We find that the edge running filaments can be observed for horizontally mounted square cross-section tubes and open-rectangular channels. We discuss the implications of these observations for microfluidics.

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Building the Pyramids: Perfect Bubble Crystals

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The use of appropriate flat-sided pyramidal containers to grow ordered foams allows single crystals to be formed[1]. In the case of face centred cubic crystals these have been prepared with up to 500 bubbles. Strained and deliberately defective crystals can also be grown. The growth of simple cubic and body centred cubic crystals is limited by instability: preliminary results are presented for these, as well as ordered bidisperse foams. In addition, a method of quantifying the structure of such crystals is described.

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≈ 14 layers
D=0.54±0.01mm

8 layers
D=2.42±0.03 mm

4 layers
D=4.72±0.04 mm

Photograph of an fcc bubble crystal produced in a 3-sided 60° pyramid. The samples consist of 8 layers of bubbles with diameter 2.42±0.03 mm. The foam crystal is imaged from the base, i.e. in a ⟨ 111 ⟩ direction.

(Pyramid fabricated with an Object 300 rapid prototype machine using Object Vero Clear polymer.)

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Tailoring carbon materials for specific applications

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Carbon Xerogels are a polymeric material that allows tailoring its physical properties (i.e. nanoporosity), chemical properties and even the final form of the material according to the requirements of the application they have been design for. This is due to the significant influence of the synthesis conditions on the polymerisation process of the precursors used. Thus, it is possible to control the meso/macroporosity independently of the microporosity and specific surface area, allowing different combinations of macro/meso/microporosity totally adapted to the necessities of the application.

The base materials are pure carbons (>95 wt% C) but it is possible to increase the presence of other heteroatoms (i.e. Oxygen, Nitrogen, or even metals) including them during the polymerisation step or throughout post-synthesis treatments. It is also possible to incorporate easily other nanoparticles (i.e., nanotubes, nanofibers) to enhance certain properties for the final utilisation.

An additional advantage of these materials is that they can be obtained in different forms as monoliths, specific shapes, powder, spheres, films, etc. without the need of binders or sophisticated processes.

Taking all of these into account, the possible applications of these materials are enormous, with significant results in electrochemistry and electrocatalysis, in hydrogen storage, adsorption, gas separation, catalysts support, etc.

The synthesis of these materials are optimized and developed at the laboratory scale by our research group MCAT (www.incar.csic.es/mcat) , but bigger production is also possible throughout our spin-off XEROLUTIONS (www.xerolutions.com) with a patented process.

Bubbles in humans: etiology, detection, symptoms – The role of Hyperbaric Medicine

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Industrial revolution through the invention of reliable long-lasting air pumps (compressors and vacuum pumps) has modified the working ability at ambient pressures higher and lower than normal atmospheric pressure (1 ATA): -HYPERBARIC (subsea, underground tunneling, hyperbaric facilities) - HYPOBARIC (aeronautical, space activities).

At sea level (one atmosphere or 14,7 pounds per square inch), the average human body contains about one liter of nitrogen (air: 21% oxygen, 79% nitrogen) dissolved in body tissues (chiefly in blood). Oxygen (from breathing air) has usually low content in the body as it is largely consumed in metabolic reactions. The carbon dioxide produced from these metabolic reactions (plus excess oxygen) is rapidly adjusted to pressure changes through breathing. On the contrary, if the partial pressure of inhaled nitrogen (ppN_2) changes according to ambient pressure, being higher or lower than in 1 ATA (0.79 ATA), the ppN_2 dissolved in the body will attain a matching level and some quantities of N_2 will be absorbed or desorbed from the human body until N_2 tensions in the inhaled air (lungs) and in the tissues (biological interfaces) will be again in balance.

If the ambient pressure (in hyperbaric or hypobaric exposure) decreases faster than the body can off-load the excess of nitrogen, the critical super saturation point may be exceeded, and the dissolved gas may come out of solution in the form of bubbles because decreasing pressure lowers the solubility of gas in liquid. The clinical syndrome of bubbles over all biological interfaces is known as Decompression Sickness (DCS). The type and severity of DCS is determined by the concentration (volume) and size of bubbles along with the site in the human body where they appear.

Bubbles formed in the body can create mechanical effects (impinging on nerve endings and thus causing pain, tissue tearing) or blood-bubble interfacial effects. As far as interfacial effects are concerned, bubbles appear as foreign bodies in the organism and initiate a defense mechanism. This defense mechanism triggers a cascade of reactions: vasoconstriction, leakage of liquids from the intravascular to extravascular spaces, platelets aggregation causing ischemia, blood viscosity increase and blood flow decrease. Clinical outcome of severe cases may be fatal.

Therapeutic approach of DCS is related to the compression of the bubbles through increased pressure (Boyle's law) and simultaneous inhalation of oxygen at a level higher than atmospheric pressure. This kind of treatment is known as Hyperbaric medicine (HM), and is performed in air-tight pressure chambers delivering 100% oxygen. Operation is performed by trained personnel who monitor the patient and adjust the schedule as required. HM has also shown great effectiveness in treating other illnesses due to the important increase of oxygen concentration in hypoxic human tissues. However, HM personnel is exposed to the risk of DCS under off nominal operation the chamber, e.g. accident, system failure, urgent run away.

Prevention of DCS through detection of bubbles presence is considered of high significance for the safety of involved humans in all related activities. Ultrasonic Doppler devices are customary employed to detect bubbles, emitting ultrasounds which are reflected off moving bubbles. Unfortunately, signal evaluation is largely subjective and identified scale indexes do not correspond to clinical status of DCS. Current research focuses on new methods (e.g. through electrical impedance) in order to define safer diagnostic models for prevention of DCS.

Thermodynamic and kinetic characterization of the catalysed $LiBH_4$ - MgH_2 system

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The $LiBH_4$ – MgH_2 system is of particular interest among the reactive hydride composites due to its high gravimetric capacity and the full reversibility of the sorption reactions. With the aim to realize a hydrogen storage tank based on this material, a full physico-chemical characterization of the 2:1 molar ratio composition has been undertaken, in order to obtain data fundamental for the simulation of the sorption processes and the design of the system. In particular, the reaction enthalpy, entropy and activation energy for all the sorption steps have been evaluated by PCT and coupled manometric – calorimetric measurements. Optical microscopy has been used to confirm the evolution of the different physico-chemical processes involving liquid and gas phases.

Concerning the response of the system to the exothermal absorption and endothermal desorption reaction, the thermal conductivity of the composite in the charged and discharged state has been measured by the transient source method as a function of the temperature and the density, modified by compaction, of the samples.

The effect of the density on the sorption properties and the cycling of the materials has been explored by kinetic measurements and scanning electron microscope investigations up to 20 full charging/discharging cycles on pellets compacted at pressure as high as 900 MPa. A strong effect has been noticed on the number of the so-called activation cycles and on the absorption kinetic performance, while no decrepitation and disaggregation effects have been observed, in spite of the presence of the borohydride liquid phase.

In situ generation of Ag nanoparticles on polyester and cotton fabrics by photoreduction using TiO_2 nanoparticles

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This study discusses the possibility of *in situ* generation of Ag NPs by photoreduction of Ag^+ ions from the solution, in the presence of amino acid alanine and methanol, on the surface of TiO_2 NPs deposited on polyester and cotton fabrics. Surface modification of TiO_2 NPs with amino acids such as alanine resulted in the replacement of TiO_2 surface hydroxyl groups and coordination of surface Ti atoms with a carboxyl group which simultaneously bind silver ions [1-2]. Such arrangement results in enhanced reduction properties of photogenerated electrons in TiO_2. In this system we employed methyl alcohol as an effective hole-scavenger ($E°$-($CH_3OH/{}^{\cdot}CH_2OH$) = +1.2 V) which eventually also provides an increase of the yield of the trapped electrons due to the formation of the electron-donating species ${}^{\cdot}CH_2OH$ ($E°({}^{\cdot}CH_2\text{-}OH/CH_2O)$ = -0.95 V). The net effect is that from one photon of absorbed light by TiO_2 nanoparticles two electrons for reduction of Ag ions are formed. The impregnation of polyester and cotton fibers with TiO_2 and Ag nanoparticles generated in described manner brought about certain morphological and chemical changes, which were evaluated by SEM, XRD and XPS, respectively.

Such nanocomposite textile material provides excellent antimicrobial activity against Gram-negative bacterium *E. coli*, Gram-positive bacterium *S. aureus* and fungus *C. albicans*. Maximum microbial reduction was preserved even after ten washing cycles. In spite of satisfactory laundering durability, the release of silver occurred during washing especially in the first three washing cycles when the most of the deposited silver leached from the fabric. The leaching of silver was also presented when the polyester fabrics were exposed to artificial sweat at pH 5.5 and pH 8.0 for 24 h.

In addition to excellent antimicrobial properties, TiO_2/Ag nanoparticles imparted maximum UV protection to polyester and cotton fabrics.

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Diagnostic studies to improve abuse tolerance and life of Li-air batteries

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Among different energy-storage technologies, lithium air batteries will play an increasingly important role in meeting the higher requirements of upcoming systems. However, major challenges will have to be solved if the battery is to succeed. This study was aimed to identify root-cause of these major issues toward fixing the existing, unsatisfactory state of Li based cells and also understand their performance under different conditions to improve the battery's safety in practical applications where safety and reliability of the device is crucial. The most recent example of lithium based batteries' safety problem was witnessed when the entire fleet of 50 Boeing 787s was grounded by regulators globally after a battery fire on board a Japan Airlines plane parked in Boston and after battery problems and smoke in the cockpit forced an emergency landing by an All Nippon Airways 787 in Japan.

In this work the electrochemical performance of the Li/O_2 battery under different operation conditions was studied to elucidate the effects of discharge rate, discharge depth and charge taper voltage on the performance, state of charge and abuse tolerance of the battery. Galvanostatic discharge profiles at various discharge rates showed that the effective capacity of the cell drops with increase in the discharge rate. However the cell's cycleability improved with increase in the discharge rate probably due to the ease of stripping the Li_2O_2 film formed on the electrode surface reversibly at higher rates, compared with the incomplete removal of discharge products formed within the pores at low discharge rates.

The performance of the cell discharged at different cut off voltages showed that decreasing the depth of discharge decreases the rate of capacity fade and improves the cell cycleability. Study of the cell performance at different charge taper voltages showed that the cell capacity increases with charge taper voltage for charge potentials up to 4.45 V. For charge potentials above 4.45 V, the cell performance deteriorates with increasing charge taper voltage significantly, probably due to the decomposition of the electrolyte at higher charge potentials. It is believed that a potential of 4.45 V is the edge of breakdown potential of propylene carbonate based electrolytes used in the battery and a discharge potential above this will result in the overcharge abuse of the cell.

Challenges in Translational Nanomedicine

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Nanomedicine encompasses enabling technologies to achieve and facilitate earlier and more precise disease diagnosis, effective targeted therapies (eliminating side effects), better therapy and monitoring. Furthermore, the nanomedicine umbrella is considered the enabling instrument for personalized, targeted and regenerative medicine that can deal with grand challenges of chronic diseases in an aging population. This may enhance the quality of life, support a healthier more independent aging population and instrumental for cost-effective health care. A long-term goal is 'personalization' of nanomedicine and theranostics; but can nanomedicine be personalized for prognosis, diagnosis and drug treatment? At large, and from a high risk−high gain perspective, this requires a heroic integration of multifaceted health nanotechnology platforms with genomics and epigenomics knowledge together with complex computational approaches and bioinformatics. But how and where do we start? Which diseases do we focus? Which markets should we consider? What business models should we apply? Immunological reactions to man-made nanomaterials and nanomedicines are particularly notable. Provisions in innate immunity gene profiling for nanomedicine risk assessment and safety may serve a good starting point, and forms the centre of this discussion.

INFORMATION ON MP1103

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COST Action MP1103 “Nanostructured Materials for Solid State Hydrogen Storage” deals with the future of energy storage and aims to set up a competitive and coordinated network capable to define new and unexplored ways for Solid State Hydrogen Storage (SSHS) by innovative and interdisciplinary research.

The objective is to explore in a rational way the possible feasible solutions to the problem f the SSHS by making use of the full potential of nanostructuring techniques and nanotechnology. The Action will develop innovative nanostructured materials creating the conditions for their adequate implementation in stationary and transport applications to sustain in medium-long terms the economies of European countries. One of the main aims is the establishment of a Pan-European and multidisciplinary research and communication platform that can develop the Science & Technology potential of SSHS thus contributing actively to the regional and European economy and social welfare.

This COST Action was started in October 2011 and will last for four years. Nowadays about 200 researchers coming from 24 European Countries and from 4 Institutions from non-COST Countries participate in this Action, contributing to create a critical mass of researchers in the field of the SSHS.

Four Working Groups are active for the scientific debate and the consequent synergy:

- Synthesis of novel materials with optimized properties,
- High resolution and high sensitivity characterization of atomic level structure and microstructural features,
- Characterization of hydrogen storage properties both at the laboratory level and at the scale of prototype tanks,
- Computational modelling of processes relevant to SSHS.

Formation of nanoparticle ring-like deposits at driven receding contact lines

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In order to produce well-ordered structures via evaporation, it is essential to control the evaporation flux, solute concentration, interaction between the solute and the substrate, etc. During the drying of particle suspensions, the particle deposition process can be dictated by electrostatic and van der Waals forces. However, the complex physics involved in the drying of colloidal particle suspensions and the erratic contact line dynamics of evaporating sessile drops complicate the analysis of the problem. In this work, we propose a new methodology based on shrinking sessile drops to standardize the contact line dynamics of evaporating drops, but with no observable evaporation (macroscopic scale). We used a microinjector to decrease the drop volume through a small hole drilled in the substrate. Unlike drying drops, with our methodology the particle concentration in the drop bulk remained constant during the entire process and the macroevaporation was negligible. We probed the arrangement of nanoparticles at driven receding contact lines, with low capillary numbers and at time scales shorter than during free evaporation. The electrostatic double layer interactions were modified by diluting the nanoparticles in buffer solutions at different pH values. We also examined the impact of the wettability contrast between the substrate and the particle on the deposit morphology. We found that the ring-like deposits formed at driven contact lines might be suppressed with strongly interacting particles.

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Impact of water soluble polymers on oil removal by air flotation

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Gas flotation column is one method used in petroleum field to treat oily wastewater coming from water flooding or enhanced oil recovery (EOR). It is well-known that smaller gas bubbles and bigger oil droplets favor oil removal percentage from oily wastewater. This principle has been confirmed experimentally in a Newtonian fluid: glycerol/water mixture. An increase in the viscosity raises the bubble sizes which decreases the oil removal efficiency. In the same conditions using of pseudoplastic continuous phase (high polymer weight polyacrylamide solution) shows two antagonist effects: On one hand smaller bubbles are obtained that normally favors the oil elimination, but on the other hand an uneven spatial distribution of bubbles aligned vertically as (strings of bubbles) is obtained that decreases the oil removal efficiency. Clearly the change of rheological behavior leads to a different rise of bubbles. Results show a corridor with a pronounced acceleration observed in shear thinning polymer solutions. They results in fewer contacts between bubbles and oil droplets. As a consequence water quality gets worse.

Adsorption layer properties of alkyl trimethyl ammonium bromides C_nTAB at different liquid interfaces

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The interfacial tension of aqueous surfactant solutions against air (W/A), against hexane as bulk phase (W/H) as well as against hexane vapor was measured by Drop Profile Analysis Tensiometry (PAT-1, Sinterface Technologies, Germany) for decyl, dodecyl, tetradecyl and hexadecyl trimethyl ammonium bromide ($C_{10}TAB$, $C_{12}TAB$, $C_{14}TAB$ and $C_{16}TAB$). The obtained equilibrium interfacial tension isotherms are interpreted by different thermodynamic adsorption models, out of which the Frumkin Ionic Compressibility model[1] appears to be the most suitable for the water/hexane interface. It was earlier found[2] that for the data at the aqueous solution/air interface, however, the reorientation model is superior.

The water/hexane vapor interface appears as an intermediate situation between the W/A and the W/H interfaces. The adsorption of the members of the homologous series C_nTAB at their aqueous solution/hexane vapour interface is a competitive process of surfactant and hexane molecules. The presence of the hexane vapour results in a significant enhancement of the C_nTAB adsorption as compared with data obtained at the solution/air interface. A theoretical model for mixed adsorption layers is shown to be capable of quantitatively describe the observed equilibrium adsorption behaviour.

It is shown that the molar area of the surfactants is larger at the W/H interface as compared to the W/A interface, and that this difference is getting smaller with increasing surfactant alkyl chain length. The presence of hexane (as bulk phase as well as vapor phase) enhances the amount of adsorbed C_nTAB molecules[3]. There are no quantitative models that allow interpretation of the interfacial dynamics yet, neither the adsorption kinetics in terms of dynamic interfacial tension nor the dilational visco-elasticity.

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Nickel doped manganese oxide electrodes for redox supercapacitors

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Shear-thickening properties of hydroxypropylmethyl cellulose/sodium dodecylsulfate mixtures

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Interaction between hydroxypropylmethylcellulose (HPMC), a nonionic associative polymer, and sodium dodecylsulfate (SDS), an anionic surfactant, takes place when SDS concentration is higher than the critical aggregation concentration (cac) and ends when SDS concentration is higher than the polymer saturation point (psp)[1]. The interaction results in HPMC-SDS complex formation which has a significant influence on rheological properties of HPMC/SDS mixture, and leads to a characteristic dependence of the zero shear viscosity on SDS concentration[2]. In this work, influence of shear rate on HPMC-SDS interaction was investigated. HPMC/SDS mixtures were prepared with SDS concentrations varied from 0.00 to 2.50% wt, covering range before, within, and after the HPMC-SDS interaction. HPMCs of different molecular weights were used, where concentration of HPMCs in the mixtures was adjusted so that the overlap parameter $c[\eta]$ (where $[\eta]$ is the intrinsic viscosity, c – HPMC concentration) was set to 3, 6, and 12. HPMC/SDS mixtures show a typical Newtonian plateau at low shear rates, which is then, on further increase in shear rate, followed by an expected power low decrease in viscosity. However, above a critical shear rate in HPMC/SDS mixtures of sufficiently high overlap parameter and within a characteristic SDS concentration range, shear-thickening flow is observed. The increase in viscosity is accompanied with an increase in the first normal stress difference. The shear-thickening flow takes place in HPMC/SDS mixtures prepared with HPMCs of all three molecular weights tested, and is primarily governed by the overlap parameter. On increase in HPMC molecular weight magnitude of shear-thickening increases while the onset of the shear-thickening flow takes place at lower critical shear rates. The shear-thickening flow is attributed to shear-induced structure formation in HPMC/SDS mixtures.

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Dynamic properties of mixed nanoparticle/surfactant adsorption layers

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The behaviour of nanoparticles at liquid – fluid interfaces depends on the extent of their hydrophobicity and can be similar in some respects to that of conventional surfactants. At the same time, the adsorption layers of nanoparticles were investigated to a less extent because of the later interest to these systems. In particular, the information on the surface rheological properties of the dispersions of nanoparticles is scarce. In this work the adsorption films of silica nanoparticles modified by a cationic surfactant (cetyltrimethylammonium bromide, CTAB) at the air-water interface were investigated by the dilational surface rheology and optical methods. Special attention was paid to the slow changes of surface properties with the surface age. The surface tension and dynamic dilational surface elasticity were measured as a function of CTAB concentration. The whole surfactant concentration range can be divided into four regions characterized by different surface rheological behavior. Depending on the CTAB concentration, the surface elasticity close to the equilibrium may reach extremely high values (~ 1000 mN/m) and strongly depends on the applied surface strain. This occurs at surfactant concentrations below the region where the dispersion becomes turbid, indicating particle aggregation in the bulk. The Brewster angle microscopy and ellipsometry show that the adsorption layer becomes fragile and inhomogeneous in this region.

The impact of hop products on beer foam

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Hop products have been lately used in brewing industry as replacement of leaf hops. The increasing use of these products in beer production is supported by their chemical stability, better storage and easier dosing as compared to leaf hops. Most of these products affect beer foam. The aim of this work was to assess the impact of selected hop products, their concentration, pH and surface tension on the foam structure and stability in matrices of model solution, model beer and real commercial beer. Each sample was used to create foam in a defined way and the foam was analyzed by image analysis and by the NIBEM-T method (Haffmans). The analyses led to structural and stability characteristics of foams.

A Mechanistic Wall Heat Flux Partitioning Model of Nucleate Boiling Under Impinging Jets

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This lecture presents details of an experimental investigation of boiling heat transfer under impinging water jets. An experimental approach has been adopted to develop a mechanistic wall heat flux partitioning (WFP) model of nucleate boiling under impinging jets. Bubble dynamics has been investigated using high-speed imaging and an intrusive optical probe. This approach allowed the development of the required closure sub-models of the mechanistic wall flux partitioning model. The developed sub-models incorporated the effects of bubble generation frequency, bubble diameter and bubble density considering the following conditions: jet velocity 0.4-1.7 m/s, water sub-cooling 10-28 °C and surface superheat 0-30 °C. The developed WFP model, incorporating the proposed sub-models, has been used to predict the local rate of heat transfer at stagnation and at up to ten jet widths. Overall agreement between the proposed WFP model and the experimental heat flux is within ±30%.

A Computer-Aided Molecular Design Approach for the Synthesis of Novel Chemicals and Mixtures

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This work presents an optimization-based Computer-Aided Molecular Design (CAMD) approach to the development of novel chemicals and mixtures. The method employs group contribution (GC) models which are based on the experimentally measured contributions of chemical functional groups to the properties of particular molecules. This supports the development of transferable structure-property links which are used in reverse formulations to identify molecules or mixtures with desired characteristics. Molecules are described as a set of functional groups allowed to link together based on connectivity constraints imposing chemical principles to establish feasible structures. GC models facilitate the calculation of pure component (e.g. boiling point, surface tension etc.) and complex mixture properties (e.g thermodynamic equilibria etc.). Utilizing molecular characteristics as performance measures within an optimization-based formulation the method enables the synthesis of novel molecular structures or conventional but previously overlooked molecules. The resulting molecules exhibit optimum features in a wide range of chemical, physical, environmental, safety or other properties. They are subsequently introduced in models representing the application systems in which they will be utilized, using information extraction methods to avoid tedious computations. This enables the evaluation of their impact in the economic performance of their host systems as well as the identification of optimum system features that best fit each molecule/mixture.

The presented technology enables the fast and reliable evaluation of a vast number (millions) of characteristics leading to efficient chemicals. It is illustrated in the development of new pure and mixed fluids for efficient power generation from renewable energy sources using Organic Rankine Cycle (ORC) systems[1,2]. Such systems are receiving increased attention as they are reasonably compact and flexible, enabling power generation from low-enthalpy sources. Their operation is based on the vaporization of a single or mixed working fluid to drive a turbine, hence the characteristics of the employed fluid have a direct and major impact in the system performance. Numerous molecular properties are considered as important performance measures during CAMD including viscosity, thermal conductivity, molar heat capacity, heat of vaporization, flammability, toxicity and so forth. The resulting fluids indicate higher economic and operating performance than conventional choices.

This work further explores the potential of implementing CAMD methods in the development of polymer materials. Numerous applications require polymers that exhibit high performance in several important properties such as endurance to increased temperatures, increased safety and high selectivity or permeability toward specific compounds, to name a few. CAMD can be used to investigate and identify materials that can replace conventional options and improve the performance of products or applications in which polymers are utilized.

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Effect of different tissue surfaces on decompression induced bubble growth from gas saturated solutions

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Decompression illness (DCI) is a pathophysiology caused by bubbles[1] which grow in the body during or after a reduction in ambient pressure (decompression) that can affect divers, astronauts, pilots and compressed air workers.

Gas bubbles are not uncommon, and have been observed to form in the body after most scuba dives, even those which follow the recommended protocols conservatively[2]. These can sometimes trigger DCI whose symptoms vary in severity from the simple skin rash to coma or death. With around 7 million active recreational scuba divers worldwide and more extreme forms of diving becoming popular[3], understanding the process of physiological bubble formation is particularly important.

The study of bubble formation and growth in vivo, of which little is known to date[4,5], can improve preventive measures against DCI and is also relevant in physiology as an example of adaptive response to extreme environmental stress, and more broadly for hyperbaric oxygen treatment and to study the degree of tolerated embolism to the body, with broad medical applications (ultrasound microbubble contrast agents or surgical and mechanical ventilation embolism risks, as well as skin transplants applications).

After introducing the topic and aim of this research, a new experimental set-up that allows the recording of bubble growth on tissues *during* hyperbaric decompression is presented. It allows the observation of the growth rate of selected bubble, but also bubble density per unit surface area, comparing how these vary for different tissue surfaces, decompression profiles and gas saturated liquid composition.

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Laser beams interaction with droplets in pendant position

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The interaction of distilled water droplets (having volumes of 3-4 µl) in pendant/hanging positions in air, with pulsed laser beams emitted at 532 nm is described. At 532 nm the distilled water absorption is very low and the interaction of a water droplet with the laser radiation is dominated by unresonant phenomena, i.e. laser beam is not absorbed by the droplet's content.

In this case, following the collision of the laser beam, on the droplet are produced deformations as well as mechanical vibrations. The conditions in which the droplets lose material as a consequence of the impact with laser beams are explored and introduced. The effects produced on the droplet were studied pulse by pulse and depend on: the droplet's content, the beam wavelength, power and focusing, the irradiation geometry and the adhesion of the droplet to the capillary on which it is suspended. The laser pulses energies were varied in four steps: 0.25 mJ, 0.4 mJ, 0.7 mJ and 1 mJ. The laser pulse full time width at half maximum was 5ns and the typical beam waist diameter on the droplet was 90µm which was kept for about 300µm. because the beam had a relatively low divergence around the focus point.

The droplet's shapes evolution was visualized by recordings performed at 10 kframes/second. Following a droplet interaction with the laser beam one may also produce at a controlled moment in time, nanodroplets propagating at high (probably supersonic) speeds and microdroplets propagating at slower speeds. One may also produce suspended droplets of smaller dimensions than the initial one as well as micro/nano gas bubbles in the suspended droplet's material/volume.

In a second set of experiments the behaviour of the microdroplets of Rhodamine 6G in distilled water was recorded at high speed, at resonant interaction with similar laser pulses, and at the same power levels. The phenomena considering that the droplets contents are Newtonian liquids produced at interaction with the laser beams, are discussed[1].

A discussion is made about the relation between the unresonant and resonant interaction of the laser beams with microdroplets, from the point of view of mechanical effects and optical effects induced in the droplet.

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Photocatalytic hydrogen evolution under visible light over CdSeS

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Hydrogen is considered to be a potential candidate for a non-polluting energy source due to its environmental friendly and renewable characteristics. Photocatalytic H_2 production from water splitting using semiconductor photocatalysts has drawn considerable attention as a promising way of resolving global energy and environmental problems. The development of visible-light driven photocatalysts is indispensable for the utilization of the main part of the solar spectrum, which is of great importance for the practical application of the semiconductor photocatalytic system [1].

Until now, cadmium sulphide (CdS) and cadmium selenide (CdSe) nanoparticles have been reported to generate hydrogen in the semiconductor photocatalyts system. But there is no any report to showing the catalytic activity of CdSeS alloys.

In this study, we present the catalytic properties of CdSeS towards hydrogen evolution from water phase. This catalytic process is studied by gas chromatography. The results demonstrate that CdSeS alloys show better activity than CdSe and CdS core nanoparticles.

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Interfacial characteristics of colloidal dispersions: The apparent wall slip and its detection

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Studying the flow of colloidal dispersions in confined configurations, one should be careful about possible anomalous behavior at solid-liquid interface. Concentration of disperse phase in proximity to the wall can decrease due to steric reason or other reasons and, as a result, a concentration gradient and corresponding changes of local viscosity are set. Then the flow close to the wall takes place at essentially lower viscosity than viscosity in the bulk flow. This effect is called the apparent wall slip[1] (AWS) and can be characterized by slip velocity as a function of applied shear stress. The macroscopically observable effect of AWS depends on the gap thickness: the smaller gap thickness the larger change of flow rate. In the viscometry with extremely thin gaps, the neglect of AWS slip can result in misinterpreting of primary viscometric data.

In this contribution we describe methodology, called AWS viscometry[2], which enables us to detect both viscosity of colloidal dispersion and slip coefficient which characterizes the flow behavior at solid-liquid interface. Due to dependence of AWS contribution to flow on gap thickness we can detect both viscosity and slip coefficient via viscometry measurements done at various gap thicknesses for the same shear stress. Treating data using nonlinear regression enables us to detect both viscosity and slip coefficient. Therefore we are able to describe full behavior of colloidal dispersion flowing around solid wall. Principles of AWS viscometry are shown on example of aqueous kaolin dispersions.

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Kinetics of hydration of carbonated shell on surface of NaAlSi glass fibers

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Glass fiber fabrics are used in dry and wet atmosphere and in water at elevated and changeable temperatures. The changes of environment conditions may initiate processes in the glass fibers that lead to a new its equilibrium state and changed physical properties of fabric. Some of them may be irreversible. It is accepted [1,2] that interaction of alkali silicate glasses with water or mineral acids proceeds by ionic exchange by diffusion of Na^+ ions to glass surface and H^+ or H_3O^+ from water into the bulk of material to fill the vacancies of Na^+ ions. It looks that Na^+ ions and H_2O and CO_2 from atmosphere form the shell of $Na_2CO_3{\cdot}H_2O$ and $Na_3H(CO_3)_2{\cdot}2H_2O$ mixture on the surface of elementary glass fibers. Such shell can be dissolved in water and acids (leached) and decomposed partly and/or dehydrated by heating [3]. There are studied the weight loss of leached and not leached fabric of K-glass [composition: $(18\text{-}22)Na_2O{\cdot}(3\text{-}5)Al_2O_3{\cdot}(73\text{-}79)SiO_2$] after heating at different temperatures and followed long term weight recovery process at room conditions. The experimental weight recovery- time curves were fitted to exponential regression function of

$$M(t) = M_0 - M_1 \exp(-t/T_1) - M_2 \exp(-t/T_2),$$

that characterizes the sample weight M(t) increase by two additive mechanisms. Here ($T_2 \geq T_1$). The parameters M_1, T_1 characterize the first mechanism and M_2, T_2 the second one. The experimental weight recovery-time curves of leached and non leached (having a shell) samples show increased an irreversible weight loss in samples heated before at elevated temperatures. The irreversible weight loss has to be associated with the loss of Na^+ ions and partly destruction of the shell. As a result the absorption of CO_2 is not prospective. Regression analysis shows that weight increasing after heating are well described ($R^2 > 0{,}99$) in time intervals during weight stabilization time by exponential function written above. For the samples with a shell, the values of T_1 increase from 0,017 h- 0,04 h and T_2 increase from some hours to 125 h (for sample heated at higher temperatures) and to 255 h (for less heated samples) for later t = 100 h. The both processes are going simultaneously. Leached and more heated sample has only one T_1 (about 0,096 h) process of the early weight increasing. Such results lead to an opinion that T_1 process at the beginning of weight stabilization characterizes the velocity of water absorption on the surface determined by surface roughness and process T_2 characterizes the leaving of water molecules from surface into volume (probably by diffusion), that allows to absorb next water molecules and to continue restore the weight. Then the late T_2 characterizes the saturation with water the all volume of shell. For its part an increase of early T_1 along heating temperature characterizes an increase of surface roughness of carbonated shell and glass fibers (in a case of leached samples) and late T_2 the volume loss.

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Ecotoxicity assessment of surface modified alumina nanoparticles on *V. fischeri*

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Environmental risks posed by engineered nanomaterials (ENMs) are of major concern and are currently estimated by numerous ecotoxicity tests. The complex nature and behavior of ENMs has led to the adoption of customized experimental ecotoxicity practices, thus even enabling the possible introduction of artefacts to the inherent toxic properties of ENMs. In addition, the lack of standardized ENMs handling procedures for ecotoxicity testing prevents the development of experimental protocols for regulatory purposes. To investigate whether the ENMs handling affects their ecotoxic properties, a suite of ENMs dispersion techniques was adopted and tested. For this purpose, two surface modified alumina nanoparticles (OS1 and OS2, Sasol) were dispersed to water and subjected to ecotoxicity testing towards bacteria *Vibrio fischeri*. Several factors including the mixing duration, the salinity of the dispersion water, the initial tested concentration of ENMs and the centrifugation of the obtained dispersions were examined, in order to assess the handling implications to the resulted ecotoxic effects on *V. fischeri*. The results of this study highlight a number of issues concerning the ecotoxicological risk assessment. Briefly, it is discussed how and to what extend the aforementioned factors affected the toxicity of the tested ENMs.

Experimental and Numerical Investigations into the Coating Process of a Single Particle

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One of the fundamental steps in the fluidized bed (FB) process is characterized by collision between a liquid drop and a particle. This is facilitated by atomizing and injecting a liquid into fluidized bed made of particles. Important parameters are size ratio, shape of the particle, its wettability; drop properties and collision conditions. However, very little concrete experimental and verified numerical information is available as to what are the relevant factors to facilitate uniform coverage of particles by drops.

An apparatus was built to allow deterministic impact of a particle and drop to occur in midair. Using high speed imaging the impact of three different particles with water drops is studied at different relative velocities (see Fig. 1a). Possible collision outcomes are elucidated in terms of particle-drop diameter ratio, Weber number, and particle wettability. Three distinct regimes of bonding, ripping and coating, and shattering are identified and discussed in this novel study.

In conjunction with experiments the impact of a drop onto a particle is studied numerically using the interface compression and interface reconstruction in a multiphase flow approach using open-source code OpenFoam. Such simulations support the understanding of underlying physics and allows for examining various factors mentioned above efficiently. In a first step a two-dimensional system with a contact angle of 80° was used. A qualitative comparison between experimental and numerical results shown in Fig. 1 demonstrates a satisfactory agreement. Thus, the future research will focus on extending the numerical studies to a fully three-dimensional approach where both interfaces liquid-solid and liquid-air can be examined in detail to better understand the coating process.

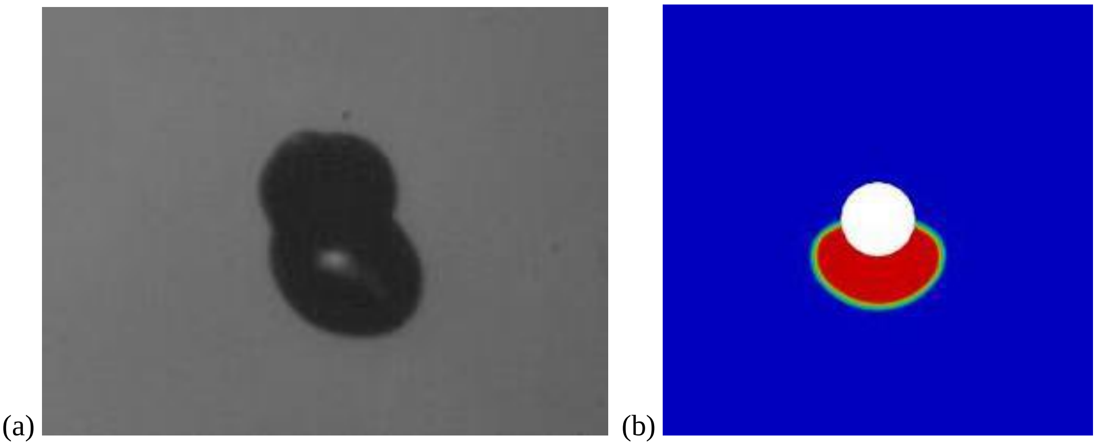

Figure 1 – (a) Image showing the drop-particle configuration (“bonding”) after an impact event obtained by measurements and numerical simulations. The drop was water and particle was Nylon with contact angle of ~90 degrees. The head-on collision relative velocity was 1.5 m/s. (b) head-on collision of drop and particle (contact angle 80 deg.) with relative velocity of 0.5 m/s

Particulates for stabilizing foams and emulsions: the challenges remain

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Since Pickering[1] has published his successful attempt to stabilize oil by using $CaSO_4$ and $CuSO_4$ particulates many scientists have tried to follow up in his steps and apply the same (or similar) approach to more challenging systems. Particle stabilized foams or emulsions are still a very attractive option despite the failures of many to achieve long term stability in the presence of even tiny amounts of surfactants. The desire to get a formulation stabilized only by particulates that could have extra function, beside their stabilizing power, is still the main driver for people entering the field and exploring opportunities for their wider applications.

With the plethora of newly synthesized particles bearing new functionalities and reduced surfactant sensitivity, the hopes that this might become possible have gone up. In my presentation I will try to summarise the available practical solutions and consider them in the light of potential industrial use, away from the bench in a real working environment.

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Flow behavior of complex interfaces: the case of surfactant vesicles

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In several applications, from detergents to foodstuff and pharmaceuticals, the dispersed phase of liquid-liquid systems is made of “complex” droplets which are endowed with their own internal microstructure (e.g., liquid crystalline, gel-like, compound droplets)[1,2]. Here, we review the literature in this field and then focus on the case of surfactant multilamellar vesicles (SMLVs)[3], which are characterized at rest by an almost spherical structure consisting of onion-like stacked bilayers separated by solvent molecules. While many studies have been so far addressed to the phase behavior of surfactants in water, only limited information is available in literature on flow-induced morphology of such systems.

In this work, single SMLVs are investigated under simple shear flow by using a video-microscopy rheo-optical apparatus. Two different setups allow the observation of the sample both along the vorticity and velocity gradient directions. As with liquid droplets, SMLVs are deformed and oriented by the action of shear flow while keeping constant volume, but exhibit complex dynamic modes (i.e., tumbling, breathing and tank-treading) which are typical of unilamellar vesicles. The analogies and differences with the behavior of isolated droplets and capsules is discussed on the basis of non-dimensional scaling parameters. Furthermore, the results are interpreted in terms of the internal microstructure of SMLVs as visualized by 3D reconstruction of confocal microscopy images.

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HORIZON 2020 Programme: Opportunities for research funding protection and exploitation of research results

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The talk gives an overview of two topics related to project proposals to the new EU framework programme Horizon 2020 scheduled for the years 2014-2020. The first part focuses on a certain restructuring of the programme priorities from the 7th Framework programme (FP7) towards the Horizon 2020 programme whose goals are identified in the EUROPE 2020 strategy as smart, sustainable and inclusive growth. The priorities address in a larger extent enabling technologies and societal issues in which excellent science will be playing a dominant role. Brief information on Horizon 2020 and FP7 project calls within fields relevant to the conference audience will be provided as well.

As soon as project calls are announced, partners usually start to prepare their project proposals. At this stage partners should focus not only on research work plan but also on Intellectual Property (IP) issues as these also should be obligatorily addressed in project proposals. Therefore the second part of the talk will be devoted to explanation of basic principles of Horizon 2020 IP rules (definition of background and results including access rights; results protection, exploitation and dissemination) and comparison to the FP7 ones with special focus on research results exploitation and currently widely discussed issue of open access to data.

Experimental Investigation of Phase Inversion for Stable Emulsion Formation

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Emulsions are metastable systems, composed at least of two immiscible phases, and are relevant for many industrial applications and for several products like pharmaceuticals (e.g., microemulsions and vesicles for drug delivery), foodstuff (e.g. ice cream, mayonnaise), detergents etc. Some of the physical mechanism leading to emulsion phase separation are: i) coalescence, ii) collision, iii) Ostwald ripening, iv) creaming & sedimentation. To stabilize emulsions, surface active agents, molecules with an amphiphilic character, are added in order to decrease interfacial tension between the two phases. The classical emulsion preparation process consists in dissolving the surfactant in the continuous phase, in which it has to be soluble, and to add the dispersed phase under appropriate agitation. An alternative preparation method, known since fifties, but where a deep understanding still lack, is based on the phase inversion[1,2,3,4,5], a process whereby water-in-oil (W/O) emulsion inverts into an oil-in-water (O/W) and vice versa to produce fine emulsions by low energy stirring. In this work we describe the formation of stable emulsions by phase inversion. Static optical and confocal image and have been acquired in order to characterize phase transition.

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RF-plasma and UVC Pretreatment of Surfaces: Self-cleaning and Antimicrobial Effects

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Two new innovative findings presented in this study are: a) TiO_2-cotton fabrics obtained by pretreatment with UVC light (185 nm) at atmospheric pressure introduced functionalities into the cotton surface enabling the chelation/binding of TiO_2. This was possible since the molar absorption coefficient of O_2 and N_2 is very low at 185 nm and b) the radiofrequency (RF-plasma) pretreatment of cotton surface lead to the formation active binding sites on the cotton at atmospheric pressure. This unexpected RF effect was due to the drastic localized heating of the cotton leading to intermolecular H-bond breaking between the cellulose surface-OH groups of adjacent molecules with the formation of functionalized groups in the cellulose fibers. The discoloration kinetics of the wine stain on the TiO_2-cotton pretreated by RF at atmospheric pressure for 10 min was the most favorable. The red wine stains discoloration under Suntest simulated light was monitored by Diffuse Reflectance Spectroscopy (DRS) and by the CO_2 evolution during the stain mineralization. By X-ray photoelectron spectroscopy (XPS) it was possible to monitor the decrease of the C, N, and S-species on the textile topmost layers during the discoloration process. The XPS $Ti2p_{3/2}$ peak shifts indicating Ti^{4+}/Ti^{3+} oxido-reduction taking place during the photocatalysis. X-ray diffraction showed the formation of the anatase phase on the cotton. By X-ray fluorescence the loading of TiO_2 before and after the discoloration process was found to be ~0.8%. High-resolution electron microscopy (HRTEM) shows transparent TiO_2 anatase 8-18 nm coating the cotton with layers ~31 nm (± 10%). These 3-4 TiO_2 layers on the cotton did not affect the touch or handling properties of the cotton enabling the potential commercial use of the TiO_2-cotton fabrics.

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Smart & Green interfaces meet EU policy

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Horizon 2020 will be soon reality. More than ever excellent research and development is not enough. R&D results have to be implemented on the market and the society. The best way to achieve this objective is to be well visible, understood, and supported. How to do that?

There are plenty of experience from FP7 (and earlier FPs) as well as from other European funding programmes and even not European programmes on bringing the Innovation community and the Policy makers together.

We will consider three aspects of the “meeting process”: contents, tools and target audience. The first step needs an analysis in depth on how the topic considered contributes to the main policy papers of the moment. That would mean today for example: how to we help meeting the global challenges, implementing Europe 2020 and EcoAP? Where are the benefits for the society, for the policy makers…?

The second step is more practical: which tools are the most effective? “Policy briefs” on the OECD model?, “Recommendation papers, Roadmaps?”, “Electronic news?, “List of best practices, observatory and scoreboard?, “Using social networks?”… We should develop a tailor made mix of all these tools!

The last point is maybe the more crucial one. The final target audience is clear: the EU policy makers. But what about all the multipliers, working groups, lobbyists…?

Bringing R&D results on Smart & Green interfaces to EU policy is a long way but it works and it is worth! All Aboard!

Microstructural evolution of ball-milled Mg-Ni powder during hydrogen sorption

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Magnesium is considered as one of the most attractive hydrogen storage materials, mainly because of high storage capacity (7.6 wt.%), lightweight and low cost. Nevertheless, high thermodynamic stability, high hydrogen desorption temperature and relatively poor hydrogen absorption-desorption kinetics at temperatures below 350^{o}C impedes the use of Mg in industrial applications. To improve the hydrogen storage properties of magnesium, nano-sized Mg powders have been produced by mechanical alloying. Among Mg-based alloys, binary Mg-Ni is the most remarkable due to its favorable thermodynamics.

In the present work, ball-milling blends of commercial polycrystalline Mg and Ni powders was carried out using a SPEX 8000 Mixer Mill for different durations ranging from 1 to10 hours. X-ray powder diffraction experiments indicated that milling up to 10 h results the formation of stochiometric hexagonal Mg_2Ni line compound.[1] Morphology studies were performed on a FEI QUANTA 3D dual beam scanning electron microscope. The compositional changes were quantified by energy dispersive X-ray analysis. Repeated dehydriding-hydriding cycles were carried out in a Sievert's-type apparatus. In order to characterize the microstructural changes during a complete dehydriding transformation, the 3rd desorption was interrupted at different hydrogenation stages (25, 50 and 75% of de-hydrogenation). Convolutional Multiple Whole Profile fitting analysis of the corresponding X-ray diffractograms was applied to reveal the evolution of competiting phases and the microstructural parameters, such as average coherent domain size, lattice strain and lattice parameter.[2]

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Highly dense carbon monoliths with anomalously high volumetric capacitances.

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Carbon monoliths showing high density (up to 1.2 g cm^{-3}), high electrical conductivity (9-10 S cm^{-1}), high content of surface oxygen groups (up to 2411 µmol CO g^{-1}) and large specific surface area (1000-1600 m^{2} g^{-1}), are studied as supercapacitor electrodes. Two-electrode cells having 2 M H_2SO_4 solution as electrolyte were used for the electrochemical study. The starting monoliths, which were produced by ATMI Co, were additionally treated either under N_2 flow at 800 ºC to modify the carbon surface chemistry or under CO_2 flow at that temperature to increase the specific surface area and modify the micropore size distribution. The monoliths show specific (gravimetric) capacitances in the range 240-300 F g^{-1} and volumetric capacitances in the range 230-350 F cm^{-3}. The volumetric capacitances, which are the highest ever reported for porous carbon monoliths, are explained by the high specific capacitance and high density of the monoliths.

Electrochemical performance of hierarchical carbon structures materials obtained from lignin infiltration of zeolite templates

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Carbon materials with hierarchical pore structure have been prepared using the liquid phase impregnation (LPI) technique with lignin solution as carbon precursor and Y and Beta zeolites as templates. Lignin is the second most abundant biopolymer in nature and constitutes an underutilized by-product traditionally of the papermaking industry and now also from the expanding cellulosic ethanol one.

The obtained carbons have a bi-modal porous structure. They contain microporosity coming both from the removal of the zeolite walls and lignin devolatilization, and a mesoporosity network resulting from the removal of the non-infiltrated zeolite. The use of lignin as precursor results in carbon materials with interesting surface chemistry features, such as nitrogen pyridone/pyrrolic and pyridinic groups, and a variety of oxygen surface groups.

The electrochemical characterization in aqueous acid media revealed a high contribution of pseudocapacitance in these materials and good capacitance retention when using high sweep rates and specific currents. They can be easily in-situ electrooxidized, producing an increment of surface oxygen groups that enhances the pseudocapacitance. This seems to be a consequence of the presence of edge sites in the carbon fraction formed from the infiltration in the zeolite. The electrooxidized carbon materials showed a capacitance as high as 280 $F \cdot g^{-1}$ at a current density of 50 $mA \cdot g^{-1}$, while being able to keep a capacitance of 155 $F \cdot g^{-1}$ operating at more than 20 $A \cdot g^{-1}$ thanks to their adequate porous texture. These results point out the potentials of the use of biomass wastes, like lignin, as carbon precursors in the production of hierarchical carbon materials for electrodes in electrochemical capacitors.

Smart bionanostructures and interfaces via direct reaction of functionalized catechols

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Mussel-adhesive proteins have been the subject of intensive scientific research associated to their remarkable ability to strongly adhere to virtually all surfaces. This behavior has been attributed to their varying amounts of the non-essential catecholic aminoacid DOPA[1].

Herein we report a new synthetic approach for the fabrication of such catechol-based materials with adherent properties. The mechanism is based on a simple polymerization process in the presence of ammonia[2], in a way reminiscent of melanization reactions. The initial molecule of choice was a catechol bearing a long alkyl chain. The resulting material after polymerization, spontaneously self-assembles in the form of nanoparticles that easily stick to different surfaces and materials. As an application, the NPs have been successfully implemented for water remediation of heavy metal ions and are being explored nowadays for drug delivery.

On the other side, when this material is placed in non-polar solvents such as hexane, the NPs are dissolved and the polymer is used to obtain coatings thanks to their adhesive properties. Coatings are effective on a representative variety of substrates, both at the nano-/macroscale, without any pretreatment or interphase modification. Whereas a long alkyl chain affords coatings with a persistent hydrophobic character, this methodology can be extended to several other catechols with different ring pendant groups, providing additional surface functionalities such as oleophobic, anti-fouling or anti-bacterial activities[3].

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Stabilization of colloids by addition of salt

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We calculate the interaction potential between two colloids immersed in aqueous mixtures. We calculate the effective interaction due to the combination of preferential solvent adsorption at the colloids' surface and preferential ion solvation. The ion-specific interaction strongly depends on the amount of salt added as well as on the mixture composition. We show that contrary to the classical DLVO behavior, neutral or even charged colloids can be stabilized by *addition* of salt. The theory is supported by experiments.

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Photocatalytic activity of nanocomposite based on polyaniline and TiO2 nanoparticles

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During recent decades, photocatalysis has attracted much attention as an emerging successful technology for purifying wastewater from industries and households. TiO_2 is one of the most investigated semiconductors in the field of photocatalytic degradation of pollutants due to chemical stability, adsorption capability and photocatalytic efficacy for decomposition of organic compounds in air and water. The wide band gap of TiO_2 (3.2 eV) allows it to absorb the photons of ultraviolet light that occupies only small fraction of solar spectrum, which limits its wider use. One of the possible ways to utilize the broader part of the solar spectrum is sensitization of TiO_2 with suitable sensitizer [1]. High absorption coefficients in the visible part of the spectrum, high mobility of charge carriers (consequence of presence of extend p-conjugated electron systems) and good environmental stability of conductive polymers make them a good choice for TiO_2 sensitization. Moreover, many conductive polymers in their doped or undoped states are efficient electron donors and good hole transporters upon visible light excitation [2]. The subject of this work was in situ synthesis and characterization of Polyaniline (PANI)/TiO_2. Its potential applicability as photocatalyst was checked using a typical photodegradation reaction of Rhodamine B (RB) in a suspension. RB is a stable organic dye occasionally used as a model compound for estimation of activity of TiO_2 based photocatalysts, in reactions of photodegradation. PANI/TiO_2 nanocomposite was synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate in water, in the presence of colloidal TiO_2 nanoparticles of an average diameter of 5 nm. The resulting nanocomposite powder was used for photocatalytic degradation of RB. Its photocatalytic activity has been compared with activity of neat colloidal TiO_2 nanoparticles. Obtained nanocomposite has enhanced absorption in visible part of spectrum and showed higher efficacy toward discoloration of RB compared to bare TiO_2.

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Growth, sliding and detachment of a bubble near a wall: effect of the wetting conditions

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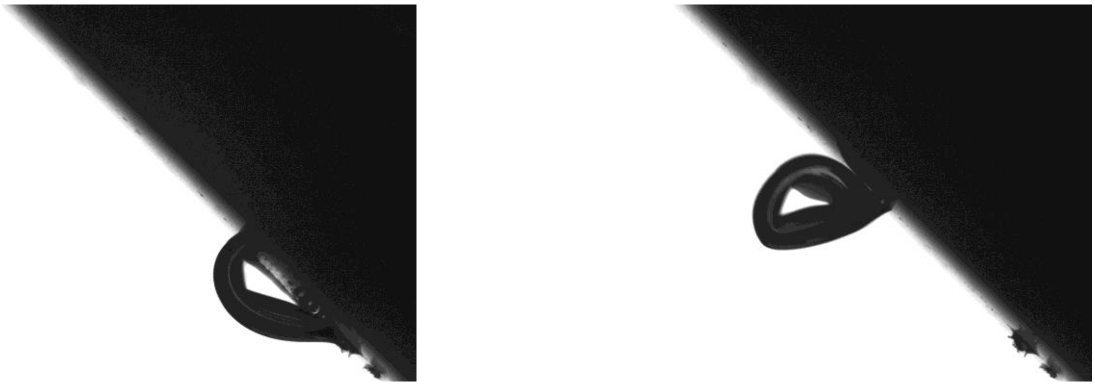
The growth and departure of bubbles nucleated on a wall are of particular interest in industrial situations such as the gas/liquid contactors in chemical processing, vapor nucleation in evaporators or inkjet printing devices. In most of these industrial configurations, the bubble grows in a shear flow and most of the studies[1,2] aims to predict the radius of bubble when it detaches from a force balance analysis. Such an approach appears to be limited by the modeling of the capillary term and more precisely by the modeling of the contact angle hysteresis.

In this presentation, we will first show the necessity to take into account the effect of the contact angle hysteresis to improve the prediction of the bubble radius at departure. Then we will present some experimental results on the sliding and detachment of a gas bubble nucleated under an incline. The substrate is a Teflon plate ensuring a high contact angle (θ_r=63° and θ_a=107°) and a large hysteresis (~44°) for the liquid used (water). Results of the measurement of the maximal stable volume of the bubble with respect to the inclination angle and comparison with theory will be first given. Then some aspect of the sliding of the bubble and its detachment will be presented



Sliding and detachment of a bubble on a Teflon wall.

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Dynamics of three phase contact lines of evaporating nanofluid droplets

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We describe an experimental investigation of the concomitant evaporation and (de)wetting behavior of sessile drops of ethanol, either pure, or containing small amounts of titanium oxide nanoparticles. Pure ethanol behaved in a more or less "ideal" manner, with constantly decreasing contact radius, at essentially constant contact angle. However, distinct "stick−slip" pinning behavior of the triple line occurred when nanoparticles were added to the base liquid. Increased nanoparticle concentration enhanced the "stick−slip" behavior. The observed behavior is attributed to the effects of particle accumulation near the contact line, caused by the now-established advective flow during evaporation. "Slip" behavior can be explained by hysteretic energy barriers, somewhat akin to line tension. The "stick" behavior was not complete: some triple line drift occurred ("pseudo-pinning"). It is postulated that this may be due to small-scale pinning of the triple line by deposited particles, or to increased effective viscosity due to high, local nanoparticle concentrations.

Furthermore, the dynamics of the three phase contact line for water and ethanol is experimentally investigated using substrates of various hydrophobicities. Different evolution of the droplet profile is found to be dependent on the hydrophobicity of the substrate. A simple theoretical approach based on the unbalanced Young force is used to explain depinning of the contact line on hydrophilic surfaces or the monotonic slip on hydrophobic substrates. A second part to the work involves the addition of different quantities of titanium oxide nanoparticles to water and a comparison of the evaporative behaviour of these novel fluids with the base liquid (water) on substrates varying in hydrophobicity i.e. silicon, Cytop® and PTFE is presented. Stick-slip behaviour observed is found to be dependent on nanoparticle concentration. Evaporation rate is closely related to the dynamics of the contact line. These findings may have an important impact when considering evaporation of droplets on different substrates and/or containing nanoparticles.

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Structure of “coffee-ring” nano-deposits following drop evaporation

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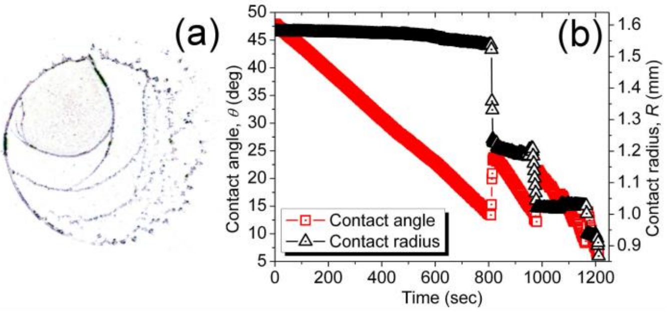
Sessile drops of a monodisperse nano-suspension (SiO_2 in water) were found to evaporate following a stick-slip regime[1] of the three-phase contact line, *i.e.* immobility of the triple line followed by rapid recession, the cycle being repeated. “Coffee-ring” deposits remained after full evaporation, corresponding to the “stick” phases. Examination revealed an unexpected, disordered region formed at the exterior edge of the closely-packed nanocolloidal crystalline structure. To assess the role of advective particle velocity, during evaporation, on particle structuring, experiments in reduced pressure environments were undertaken. Lower pressures invoke higher evaporation rate and consequently advective speed. Such experiments revealed the promotion of hexagonal packing at the very edge of the crystallite with increasing velocity[2]. Quantification of particle velocity and comparison with measured deposit shape for each case allowed us to provide a tentative description of underlying mechanisms governing nanoparticle deposition. Behaviour is governed by the interplay between fluid, and hence particle, flow velocities (the main ordering parameter) and wedge constraints and disjoining pressure (the main disordering parameter). Furthermore, the formation of a second, disordered region of particles at the interior edge of the deposit (towards the bulk fluid) was found and attributed to the rapid motion of the triple line during the “slip” regime. Additionally, the magnitude of the pinning forces acting on the triple line of the same drops was calculated. These findings provide further insight into the mechanisms of the phenomenon and could facilitate its exploitation in various nanotechnological applications.



(a) Micrograph of coffee-stain left after evaporation of aqueous suspension drop containing 0.125% wt. SiO_2 nanoparticles. (b) Evolution of contact angle (squares) and contact radius (triangles) for same drop.

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Added mass coefficients of bubbles near gas-liquid interface and of ellipsoidal bubble pairs by CFD simulations

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The added mass coefficient C was calculated for bubbles in different flow situations using the volume of fluid (VOF) model. The full non-stationary 3D model equations were solved numerically using CFD over small initial time interval in order to obtain the information about the bubble initial acceleration from which the added mass coefficient of the bubble(s) can be calculated. The methodology was described in detail in our paper [1]. Several geometrical configurations were considered, which are physically relevant and difficult to treat analytically. We studied a single or multiple spherical and ellipsoidal bubble(s) near boundaries or in different spatial configurations. The effect of the key control parameters (bubble aspect ratio, dimensionless distances) on the added mass coefficient is presented. Easy-to-use closed formulas (correlations) are provided for the values of C, where possible.

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Evaporation and adsorption of drops on solid and porous substrates

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This presentation compares the results of a new numerical model for drops on permeable and porous substrates with experiments. The model describes the dynamics of the solvent, the evaporation process at the drop-air interface, the convective-diffusive transport of the solute molecules and the adsorption of the solute particles onto or within the substrate. For the absorption of the droplet, the flow within the porous medium is described by Darcy's law and driven by the capillary pressure. The concentration of the solute particles is controlled by convective and diffusive transport and depends on the local rates of evaporation, the rates of absorption on and in the substrate and possibly on mechanisms occurring in the precursor film, if present. Due to their non-linearity, the governing equations have to be solved numerically. The spatial derivatives are discretized using a finite volume method. Time integration is performed with a combination of a fifth-order accurate Gear method and a first-order accurate implicit Euler method. A sensitivity analysis is performed by variation of physical properties and an accuracy analysis on the numerical approach is carried out.

Two useful experimental results without adsorption were reported in the literature and the model has been validated by comparison to experimental results concerning drop mass loss rate and contact angle histories. Well-known coffee-stain rings are found to occur due to convection in the drop while inhomogeneous evaporation at the drop interface enhances the effect. In the case where a precursor film was proven to exist, differences in mass loss rates are explained with the Kelvin effect. In spite of the uncertainty of adsorption parameters also the penetration depth and absorbed volume in a porous medium compares well with experimental results from literature.

Thermoresponsive PNIPAM-g-PEO nanoparticles for delivery of NSAIDs

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Core-shell nanoparticles from thermally-responsive biocompatible graft PNIPAM-g-PEO copolymers can incorporate NSAID indomethacin at room temperature and release the drug under controlled conditions at 37 ^{o}C. The aim of the present investigation is to clarify the mechanisms of inclusion and discharge processes.

Extensive studies are performed on dynamic, equilibrium and rheological properties of the adsorption layers of aqueous polymer solutions at the air/solution interface. The investigated systems contain various ethanol quantities. Copolymers with different degrees of grafting are probed. Additional information is acquired from measurements of surface forces by the microinterferometric foam-film techniques, equipped with Scheludko-Exerowa cell.

The obtained results provide valuable input about indomethacin entrapment and release mechanisms by the PNIPAM-g-PEO nanoparticles. These data supply important knowledge about fine-tuning of drug uptake and release by core-shell nanoparticles. The investigations give grounds for certain generalizations about the optimization of the nanoparticles' design and their more efficient functionalization in view of both the targeted and similar NSAID systems.

Acknowledgements:

The financial support of NSF of the Ministry of Education, Youth and Science (Bulgaria) by Projects MU03/137 and BG 051PO001–3.3.06–0038 are gratefully acknowledged.

Atomization of biocolloids: a perspective for regenerative inhalation therapy?

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Proper lung function is dependent on its huge surface area which must be open and available for the gas-exchange. In case of damage of the cellular ultrastructure (e.g., by burning, inhaling caustics or irritants) it may be hypothesized that lost functions of some regions of the lungs can be restored by regenerative medicine approach, i.e. by seeding of cells with progenitor (precursor) potential[1]. The idea of presented research is related to a possible application of biocolloidal aerosol as a carrier of living cells.

The classical inhalation therapy consists in delivery of medicines as aerosol targeted directly to the respiratory system. By this method, local action of inhaled material is achieved (important issue in asthma, COPD and lung infections) but also the systemic absorption may be expected (it is useful e.g., for vaccination[2]). Here we tested various techniques of aerosol generation from biocolloids, i.e. liquid systems containing living cells. Three types of model cells were selected to assess the stress-dependent effects on biological activity during spraying in different types of medical atomizers (nebulizers): pneumatic, ultrasonic, vibrating-mesh and mechanical devices (nasal spray pumps and PennCentury Microsprayer). Cell integrity and survival have been tested by several bioassays, selected suitably to the biological entities used. Aerosol size distribution was measured with a diffraction spectrometer (Malvern Spraytec).

The results of the study indicate that atomization techniques used in classical aerosol therapy are unsuitable for spraying of living cells due to very high hydrodynamic stresses (Fig.1). On the other hand, mechanical spraying (e.g., by Microsprayer device) allow to obtain aerosol with almost intact cells (survival rate above 90%), however the average droplet size obtained is an order of magnitude higher than produced in nebulizers. This factor sets limitations for using these aerosols for cell delivery into deep lungs because of poor penetration of large droplets via tracheobronchial tree.

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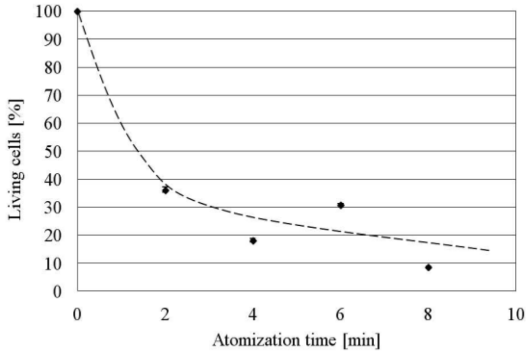

Fig. 1. Model-bacteria cell inactivation during atomization in a vibrating-mesh nebulizer

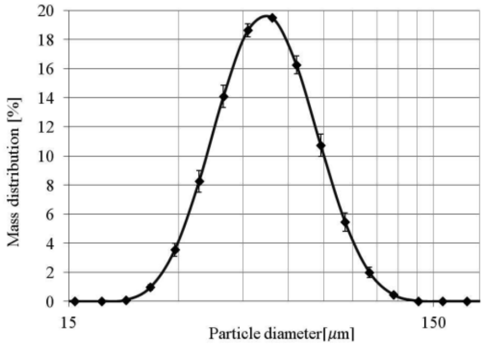

Fig.2. Size distribution of droplets emitted from Microsprayer device.

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Mg-C nanocomposites for hydrogen storage

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Mg-C and MgH_2-C nanocomposites are prepared by ball milling using different kinds of carbon additives and magnesium with different particle size. The samples consist of 5-10 μm Mg/MgH_2 particles, surrounded and/or coated by carbon flakes. Mg and MgH_2 in the as-milled materials show nanocrystalline microstructure (50-100 nm), as the grain and particle size reduction, caused by the milling, depends on the type of the carbon used for the composite production. High-pressure DSC analysis shows that the hydriding process starts at about 200^{o}C for all materials studied, but the hydriding mechanism looks different for the composites with different kind of carbon additive, supposed to play a catalytic role and protecting magnesium from oxidation. It was also found that the incorporation of carbon into the surface of the MgH_2/Mg particles creates high density of defects, leading to the formation of easy accessible for hydrogen sites and enhances its diffusion into the magnesium grains. The composites containing finer magnesium experience absorption capacity deterioration with hydriding/dehydriding cycling, but for some of the carbon additives this worsening is not so strong. More pronounced positive effect on the hydrogen sorption characteristics of magnesium was found for these carbon additives, which provide better protection of the Mg surface from oxidation and particles agglomeration during hydriding/dehydriding cycling. Possible explanation of the improved dehydriding behavior of these composites, related to the fine particle and grain size and better contact between the carbon and MgH_2/Mg particles was proposed.

Hydrodynamic interactions of a bubble pair and bubbles in clusters

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An arrangement of gas bubbles rising in line in a liquid (bubble chain) is natural geometric configuration of them considering the common bubble formation at a capillary or an orifice. A pair of bubbles rising in tandem then represents a structural unit of such system. The bubbles are often sufficiently clean so free-slip condition apply at their surfaces and bubble rises with Reynolds number of order 10^1 - 10^2 in low viscosity liquids.

We conducted the experiments with ultrapure water and silicon oils to explore dynamics of these bubble configurations and to compare it with a theory[1,2]. The three dimensional path of bubbles during the rise was reconstructed from double side view using high-speed cameras. The influence of particle separation and Reynolds number will be presented. Interestingly the small variance of bubble sizes has shown to be responsible for a scatter of the data obtained in ultrapure water[3]. It should be noted that an influence of surfactants on the structure of bubble aggregates and their stability remains almost unexplored experimentally at the mesoscale so far.

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Measurement of temperature field in a droplet by Laser Induced Fluorescence and by Fluorescence Lifetime Imaging Microscopy

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Droplet evaporation plays an important role in many technological applications including spray cooling and inkjet printing. The temperature distribution inside the droplet and at the liquid-gas interface significantly affects the evaporation rate and the thermocapillary flow in a droplet, hereby influencing the deposit formation in the inkjet printing technology or cooling efficiency in the spray cooling application.

Temperature measurement at the liquid-gas interface of a droplet is a challenging task, especially when intrusive measurement techniques have to be avoided. In this work two non-intrusive temperature measurement methods are applied and compared.

The first is the well-established Laser Induced Fluorescence (LIF) method, in which a fluorescing dye is excited by a laser beam. The spectral intensity of the emission depends on temperature. In the two-color/single-dye LIF, emitted light intensities at two different wavelengths with different temperature sensitivities are compared with each other in order to extract the temperature. Until now LIF has been used for measurement of average temperature over a spot of a minimum size of 200 mm. We combine LIF with Confocal Laser Scanning Microscopy (LSM). This combination allows scanning the temperature over the whole droplet volume with high spatial resolution.

The second method is Fluorescence Lifetime Imaging Microscopy (FLIM). This technique benefits form the dependence of the fluorescence lifetime of some dyes upon temperature. The dye is excited by a pulsed laser. After excitation the duration of the luminescence of the dye is measured. The duration is defined as the point, when the intensity reaches a certain threshold relative to the intensity at excitation. Typically the decay follows an exponential function while the order of magnitude for the lifetime is a few nanoseconds.

In our setup the lifetime is measured by the confocal laser scanning microscope pixel by pixel. We use in our experiments the Kiton Red dye (Sulforhodamine B) for characterization of water droplets. The Laser excitation wavelength is 404 nm.

Both non-intrusive methods are used in our work for measurement of the temperature inside evaporating water droplets and at the liquid-gas interface. The advantages and disadvantages of both methods are discussed.

Bubble bouncing with a free surface in hypergravity conditions

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We report novel experimental observations of the effects of the gravity level on the bubble rise and bouncing with a free surface. Experiments have been carried out at the Large Diameter Centrifuge (LDC) at ESTEC, where gravity level was changed from $1g_0$ to $19g_0$, with $g_0 = 9.81$ m/s². Millimetric air bubbles are released from a nozzle and rise rectilinearly in ethanol until they collide with the free surface. At this moment, the bubbles bounce a few times before coalescing. The bubble size is determined in the detachment process at the nozzle by a competition between the surface tension and the buoyancy force. We find that the bubble size decreases with the gravity level in very good agreement with the simplified model. Ellipsoidal bubbles rising rectilinearly in ethanol with $We > 3.75$ have been observed, as opposed to Moore's theory. The terminal velocity has been found to increase with the gravity level, although at higher gravity bubbles are smaller. The dynamics of the bubble center during the bouncing process can be approximated by a damped oscillator. The frequency of bouncing process increases with the gravity level, in reasonable agreement with a simplified model based on the assumption that the free surface acts as an elastic membrane, driven by capillary and gravity forces.

Molecular mechanisms of nanoparticle-cell interaction: physico/chemical properties determining membrane-dependent cell signalling events

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Investigating the molecular mechanisms of the interaction of nanoparticles with living cells is of particular interest with respect to nanomedical and biotechnological aspects. But also, with the growing importance of nanotechnology the probability of an unintended human exposure against nanomaterials is exponentially increasing. In addition to directly cytotoxic effects, subacute reactions like apoptosis, proliferation and inflammation may contribute to the toxicity of these materials (1).

Using carbonaceous particles of different size classes, in our previous studies we identified the initial molecular steps of sub-acute toxic effects of nanoparticles in different types of epithelial cells (2). Molecular analyses of membrane compartments of alveolar lung cells demonstrate that carbon nanoparticles in lung epithelial cell induce changes in the lipid composition of lipid raft signalling platforms. These molecular events are triggering the ligand-independent activation of the surface receptor EGF-R (epidermal growth factor receptor). Intervention experiments using antioxidants but also biophysically active 'compatible solutes' demonstrate that the nanoparticle-specific generation of oxidative stress is the initial event of the observed adverse effect and these events can be prevented by stabilization of lipid rafts and macromolecules located within the signalling platforms (3). Using a set of poorly soluble nanoparticles and their non-nano counterparts, we were able to establish an in vitro cell-based test battery which we suggest as early screening method for the safety of nanomaterials.

Currently the system is evaluated for modern metal-based nanoparticles which are designed for diagnostic and therapeutic applications in humans. Interestingly, in addition to the capability to trigger oxidative stress properties including particle shape appear to modify the molecular events occurring during nanoparticle cell interaction.

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Microbubble contrast agents in ultrasound imaging and therapy

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Ultrasound imaging is one of the most routinely used clinical imaging tool for medical diagnosis. Comparing with other modalities it is non-ionizing, real-time, far more accessible and low cost. The advent of microbubble contrast agents has opened up exciting possibilities of obtaining quantitative information relating to tissue vascularity, tissue perfusion and even endothelial wall function. Furthermore it has been shown that microbubbles can be used, together with ultrasound, to facilitate drug and gene delivery. In this presentation we will introduce the microbubbles, how they interact with ultrasound, why they are useful and future opportunities and challenges.

A microbubble is a gas bubble typically consists of an inert gas core stabilized by lipid, albumin or polymer coating. Microbubbles are microns in size and are small enough to pass pulmonary circulation. Due to the coincidence of the resonance frequency of these micron-sized bubbles being within the diagnosictic ultrasound frequency range, they have become established as the most effective form of contrast agent available for ultrasound imaging [1].

Significant technical advance has been made in the past decade in the fabrication of the bubbles, measurement and modeling of their acoustic behavior, and their imaging with ultrasound. Currently ultrasound imaging system operating in the so-called contrast-specific mode is sensitive enough to detect a single microbubble, making use of their unique nonlinear oscillation behavior under ultrasound excitation.

Microbubbles have been increasingly used in a wide range of clinical and pre-clinical applications. As the microbubbles flow with blood cells they provide an excellent means of determining physiologically relevant microcirculation parameters from the contrast enhanced image sequences. This has been investigated for a number of clinical conditions, notably the assessment of myocardial function [2], diagnosis and treatment monitoring of tumours [3] and characterizing atherosclerotic plaques[4]. Recent development of ultrasound molecular imaging promises highly sensitive functional information and is revolutionizing the role that microbubbles and ultrasound can play in clinical and pre-clinical applications [5] . Furthermore, microbubbles and ultrasound have been used to help open up cell membranes and facilitate the delivery of therapeutic agents [6]. These progresses will be described and future opportunities and challenges discussed.

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Langmuir-Blodgett films of 2D metal oxide nanosheets as textured crystalline interfaces

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Oxide nanosheets are the oxide equivalents of graphene. They have a thickness of ~1 nm and can have lateral dimensions of over 50 μm. Oxide nanosheets are made by exfoliation of layered metal oxides in aqueous solution through a series of ion exchange processes. Both insulating and semiconducting nanosheets can be made. We studied the mechanism of exfoliation and restacking of lepidocrocite-type titanates into $Ti_{0.87}O_2$ nanosheets in solution by small angle x-ray scattering, and developed a new method to monitor the kinetics of exfoliation by differential scanning calorimetry. The resulting colloidal nanosheets are truly 2D single-crystal objects.

We optimized the conditions for Langmuir-Blodgett (LB) deposition of nanosheets to >99% monolayer coverage on glass, silicon and PET. The resulting LB films present well-defined microtextured crystalline surfaces that may be used for a variety of purposes: as crystalline interfaces on amorphous substrates; for selective adsorption of ions or other species; in photocatalytic and other electrochemical interface processes; or as crystalline templates onto which other materials can be grown epitaxially. As an example of the latter, we show the growth of $SrRuO_3$ on $Ca_2Nb_3O_{10}$ and $Ti_{0.87}O_2$ nanosheet LB films. Depending on nature of the nanosheet interface, [001] oriented films grew on $Ca_2Nb_3O_{10}$, and [110] oriented films on $Ti_{0.87}O_2$. The magnetic properties of $SrRuO_3$ were shown to be influenced by the underlying seed layer.

Hydrogen Storage and Supercapacitors

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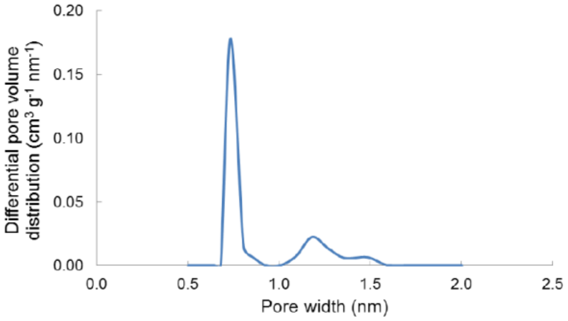
The use of nanoporous carbon has been widely investigated in essentially all energy storage applications encompassing hydrogen storage, methane storage, supercapacitors, fuel cells and Li-ion batteries. Common constraints in much of this work relate to the purity of the carbons used, their reproducibility, the control of the pore structure and the physical form of the materials. Phenolic resin derived nanoporous carbons have now been developed where all of these parameters can be readily controlled. These have been investigated in cryogenic hydrogen storage where they have been used as a stable baseline material for round robin and other test development studies[1],[2]. They have also shown good storage capacity (2.5% wt) despite relatively low surface areas (810m2/g) which might be attributable to the pore structure which is centered at ~7nm which many papers suggest is the optimum for cryogenic storage.



The materials have also been evaluated in both aqueous[3] and non aqueous supercapacitors. Operating in propylene carbonate[4] it has been shown that the presence of controlled size and volume micro and transport pores leads to a major improvement in both energy and power density. A common feature of the carbon materials required for all of these applications is that the production of materials with very high surface areas and pore volumes does not provide the best solution. The applications are invariably constrained by the system volume and the more critical parameter is the available area, or pore volume, per unit volume. In the case of gas storage, whether hydrogen or methane, the minimization of the free volume is also critical. The production of controlled structure materials that can meet both electrical thermal conductivity requirements will be discussed.

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Patterned surface treatment by microplasmas to obtain area selective wettability of surfaces

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For biomedical and electronic applications like biosensors, flexible printed circuits, RFID antennas and MEMS, patterned surfaces manufactured by subtractive processes based on lithography, etching, or laser ablation are well established. Due to better cost and resource efficiency a new additive process has been developed based on a novel patterning technology using plasma functionalization or coating at atmospheric pressure, called plasma printing. In this process microcavities with structure widths down to 10 µm are formed temporarily by contacting a substrate with a suitably designed plasma stamp. Inside these microcavities partial discharges, special cases of dielectric barrier discharges (DBDs), can be ignited for surface coating and modification processes in a similar way as already demonstrated for common DBD arrangements.

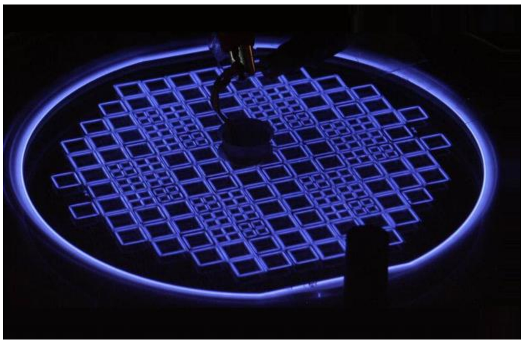

Figure 1: Local plasma treatment at atmospheric pressure of a 100 mm diameter silicon wafer carrying a wet-chemically etched topography with a height difference of 50 µm between recessed and elevated areas.

Depending on the application field, various adapted set-ups of the plasma printing technology are possible. For surface functionalization of even non-flexible materials, like glass, wafers or thicker polymer sheets, flat metallic or dielectric stamps with closed cavities were used. Area-selective hydrophilic properties can so be achieved by plasma activation. Using nitrogen-containing atmospheres more than 10 primary amino groups per nm^2 can be introduced into polyolefine surfaces.

With these technologies moreover patterned chemical functional coatings with different monomers, e.g. aminopropyl-trimethoxysilane, glycidylmethacrylate or acetylene, has successfully been demonstrated for structure widths down to 50 µm. Moreover (super-) hydrophobic patterns can be achieved using multilayer coatings using silanes or fluorocarbon based monomers.

Selective treatment of porous materials like foams, non-wovens or textiles is possible. First experiments with superhydrophobic polyester-based textile material show that it is possible to obtain area-selective hydrophilizations with high resolutions down to 50 µm. The plasma treatment may be controlled such that back side of the textile remains superhydrophobic, thus e.g. preventing penetration of adhesives or dyes[1].

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Wall Shear Stress Induced by Taylor Bubbles in Inclined Flow Channels

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The motion of single air bubbles in flat channels is experimentally investigated. The electrodiffusion technique of near-wall flow diagnostics is applied to measure the wall shear stress distribution under large rising bubbles. The measurements are synchronized with the visual observation of bubble movement by a high-speed camera. The analysis of video records provides information on the bubble shape and terminal velocity. The experiments are carried out for three different channel configuration (with heights of 1.5, 4, and 8 mm), cover a wide range of channel inclination angles (from horizontal to vertical position), and dealing with both the bubbles in stagnant and in co-flowing water. The directionally sensitive, two-strip electrodiffusion probe is proved to be an effective tool to investigate the near-wall flow response to translating bubbles. It provides information not only on the wall shear rate distribution, but also detects the location of near-wall flow reversal, gives an estimate of the thickness of liquid film separating the large bubble from the wall, and provides also the characteristics of capillary waves appearing in the bubble tail region. The effect of channel inclination angle on the modification of wall shear stress distribution along the upper and bottom wall is also discussed.

A model system for foam fractionation

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Foam fractionation is an industrial process in which compounds with different surface activities are separated using foam. We present a model system relevant to this process, consisting of foam moving through an inverted U-tube connecting two reservoirs of surfactant solution. The Foam Drainage Equation [1] is used as the basis for a theoretical analysis of this process. Exact analytical formulas for key properties of the system may be found in the limit of infinite leg length and zero bend length. Numerical calculations and experiments were conducted and support the main theoretical results [2].

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Modeling of Three Phase Flow by Incompressible Smoothed Particle Hydrodynamics

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In this study, a two dimensional Incompressible Smoothed Particle Hydrodynamics (ISPH) method for modeling incompressible, immiscible three phase fluid flows has been developed. Surface tension coefficients are decomposed into phase specific coefficients and surface tension force is exerted by implementing continuum surface force (CSF) model. To complement this, a unique color function is associated with each phase and then smoothed out to improve the robustness of the method while a threshold has been implemented for choosing reliable normals to increase the accuracy of computed surface tension force. Furthermore, artificial particle displacement has been employed to ensure uniform spread of particles throughout the computational domain. Several test cases have been simulated to ensure the capability of the method in handling various three phase flow combinations.

Having an analytical solution, the formation of a lens shape from a circular droplet under surface tension forces has been studied to facilitate testing the accuracy of the proposed method. Results show that this test case is highly sensitive to initial particle positioning, favoring an arrangement obtained from two phase diamond droplet relaxation over a droplet simply carved out of an equally spaced particle arrangement. Simulations have been carried out in three different resolutions, revealing that an abrupt cut at the tip of the lens is responsible for the inaccuracies incurred at low resolutions. The results obtained from high resolution simulations at different surface tension ratios using improved initial condition are found to be compatible with analytical solution of the equilibrium lens length. To further test the capabilities of the proposed method in handling dynamic problems, a droplet levitation test case has been simulated for different surface tension ratios. It is observed that, higher surface tension ratios result in faster break up from surface due to larger force exerted at triple junction. Furthermore, higher surface tension ratio resulted in larger maximum droplet velocity and higher stopping height. As the last test case, droplet spreading with a contact angle of 90◦ has been considered. With minor modifications, the method has been able to simulate contact line dynamics for a variety of Eotvos (Eo) numbers, demonstrating the flexibility of the method and its capability in handling density and viscosity differences between phases. Results obtained for Eo << 1 and Eo >> 1 are compatible with analytical results available for these two extremes while a transition form spherical cap to puddle shape occurs for Eo values in between. The simulations conducted and the comparison of the results show that the proposed ISPH method is capable of handling different three phase flow problems common to many natural phenomena and engineering problems.

Hybrid metal-organic framework structures studied by advanced transmission electron microscopy

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Metal-organic frameworks (MOFs) consist of metal ion centers linked to by organic linkers to create crystalline porous networks. In recent years, MOFs have received much attention because of their high specific surface areas and pore volumes, applicable in gas (H_2) storage, catalysis, and photovoltaics.[1] Also, many types of MOF crystals can be loaded with catalytically active materials like Pd, Au, Cu and Ru in the form of nanoparticles, leading to a heightened activity in e.g. olefin hydrogenolysis and methanol synthesis or with semiconductor nanomaterials like GaN or ZnO for improved optical properties.[2]

Characterizing these delicate materials is far from trivial. Most of the common characterization techniques like X-ray diffraction of nitrogen adsorption for this type of materials offer global information only. However, in the case of nanostructured and/or -sized systems or upon loading with nanoparticles, local structure information is of pivotal importance. Transmission electron microscopy (TEM) is ideally suited for this, as it can provide structural information down to atomic resolution. However, MOFs can be considered as soft matter and are very sensitive to electron beam illumination, making TEM investigation of MOFs challenging. In the first TEM on MOF study, the relatively stable pores of MIL-101 (Cr) were imaged intact.[3] Improved TEM technology allows pore imaging of far less stable MOFs like MOF-5 and ZIF-8 nowadays.[4] Advanced TEM techniques like tomography make it possible to determine the distribution of the nanoparticles within the MOF framework. Combining imaging with spectroscopy in the electron microscope allows distinguishing between chemical species within the frameworks and measuring bonding at the local scale.[1]

This presentation is intended to illustrate the potential of modern TEM as a characterization technique for MOFs and nanoparticle-loaded MOFs, as well as for other types of (porous) soft matter.

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Design rules of swirl nozzles for steam attemperation

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The precise control of the steam temperature is a critical element for safe and efficient plant operation. The desuperheater takes care of this process, also called attemperation, by atomization of directly injected water. The present research aims at design rules for the pressure swirl nozzles of Pentair V&C.

Various spray characteristics are measured with LDA, High-speed video camera and a Malvern Spraytec. Inlet water temperature has been varied up to 85°C. Four different nozzle types have been examined.

The breakup length of the spray turns out to be well predicted by a correlation of Han et al.[1]. Also the spray angle is well predicted with a correlation given by Lefebvre [2]. To avoid the breakup region of the spray, with a length of typically 5 mm, velocity measurements have been carried out at 15 mm from the nozzle. Variation of this position the range 10 to 20 mm yielded 5 % changes at maximum. This is as expected since kinetic energy is practically conserved in the process, typically only 1 to 2 % of the incoming energy is converted into surface energy, and drop inertia dominates added mass. Drop size distributions have been measured at various distances from the nozzle. The correlations produced in this study give spray conditions at about 25 mm downstream of the nozzle for atomization in air. Vaporization in high-temperature steam is subject of future study.

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Stability of coffee-based foamed system: the Frappe Coffee

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Frappe coffee is an instant cold refreshment very popular in Greece and other Mediterranean countries and with a growing interest in USA. An important feature of Frappe coffee is its foam lying on top of the coffee liquid mixture. It is both esthetic and sensory reasons that require this foam to be stable over approximately an hour which is a typical time for drinking this type of coffee. Experiments are performed with two different types of instant coffee (100% Arabica freeze dried/Commercial product) employing three sucrose proportions to adjust sweetness to usual drinking standards (sweet, medium, bitter). Sucrose is a common carbohydrate sweetener which acts also as foam stabilizer. Frappe coffee foam stability is registered by monitoring the liquid drainage out of the foam volume with two simultaneous techniques: (i) electrical measurements (non-intrusive/continuous) for the evolution of the local liquid fraction at a specific height in the foam and (ii) volumetric measurements (non-intrusive/intermittent) for the evolution of the global liquid fraction over the entire foam volume. Results of each technique are compared and discussed. To our knowledge this is the first time that such measurements are performed to investigate this appreciated coffee-based food system.

Inviscid oscillations of constrained bubbles and drops

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In the instruments for measurements of the interfacial elasticity and viscosity, shape oscillations of the bubble or drop may occur when the drop is forced at higher frequencies. For better understanding of these shape oscillations, a linear inviscid theory is developed using variational principles (via Lagrange's equations and Lagrange's lambda-multipliers). The theory allows determining eigenmodes (i.e. eigenfrequencies, eigenmode shapes and damping of eigenmode oscillations), but also response of the bubble shape to a motion of its support or to volume variations. Present theory covers also the cases previously analyzed by Strani and Sabetta[1] and Bostwick and Steen[2]. It can be applied to both bubbles and drops. Overall, the theory is flexible, as it can easily adapt to any type of constraints, and compared to previous treatments, it is also easy and intuitive.

The theory prediction has been compared to experiments. Good agreement is found for the case of small bubbles, which have spherical static shape. Experimental results for larger bubbles and drops deviate from the theory, as a neck is formed. It is shown that this deviation correlates well with a ratio of bubble volume to the volume at its detachment.

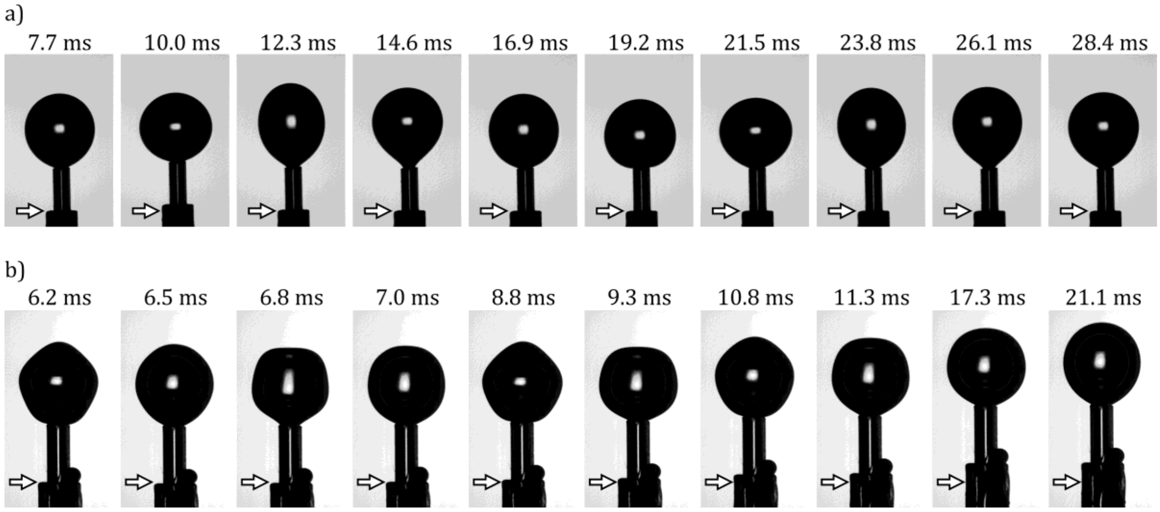

Figure: High-speed record of a ubble oscillating at a tip of capillary, a) D = 1.48 mm, bubble oscillates mostly at first eigenmode, b) D = 1.19 mm, oscillates mostly at third eigenmode

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Experimental analysis of high Weber number drop impacts onto superhydrophobic surfaces

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This work allowed to study the drop impact on hydrophobic and superhydrophobic surfaces with an innovative apparatus used to create drop, with different diameter, and accelerate them to a target.

It is evaluated not also the outcome of the impact (deposition or rebound) but also the rebound time, when rebound occur, and the maximum spreading, for different velocity impact (from 4 to 8 m/s) and drop diameters (from 0.98 to 1.78 mm).

A rebound map for impacts has been proposed. For superhydrophobic surfaces the effects of drop diameter and impact weber number on rebound time are compared with correlation found in the literature.

For hydrophobic surfaces, at highest velocity impact, an upper 'probabilistic' limit of no rebound is evaluated.

Shape oscillations of bubbles in solutions of surface-active agents

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The effect of surfactants on the shape oscillations of a bubble, which is attached at a tip of a capillary, is studied. In the experiments, shape oscillations of a bubble are invoked by a motion of a capillary, to which the bubble is injected. Decaying oscillations are recorded and their frequency and damping are evaluated. By changing the excitation frequency, three lowest oscillation modes are studied. Experiments were repeated in aqueous solution of several surfactants (terpineol, SDS, CTAB, Triton X-100, Triton X-45) at various concentrations.

Generally, these features are observed: Initially a surfactant addition leads to an increase of the oscillation frequency (though surface tension is decreasing); this effect can be attributed to the increasing interfacial elasticity. The decay time of oscillation is strongly decreasing, as a consequence of energy dissipation linked with Marangoni stresses. At a certain critical concentration, frequency decreases abruptly and the decay time passes by a minimum. With further addition of surfactant, frequency decreases, and the decay time slightly lengthens. Above critical micelle concentration, all these parameters stabilize.

Interestingly, the critical concentration, at which frequency drop occurs, depends on mode order. This clearly shows that the frequency drop and minimum decay time are not a consequence of some abrupt change of interfacial properties, but are a consequence of some simpler phenomena, which still need to be explained.

Drop on demand inkjet printing

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Inkjet technology has evolved into a technology which plays an important role in the graphical printing industry and in many emerging new industrial and medical applications[1]. Also for Océ, inkjet has become one of the main printing technologies for the near future. Our piezo inkjet technology has unique capabilities due to its ability to deposit a wide variety of materials on all kind of substrates in well-defined patterns. The requirements for the inkjet printing technology will increase. The near future demands for the generation of adjustable small drop volumes, higher drop velocities, higher drop repetition rates, low cost price, etc. The physics behind the chain of processes comprise (i) the two-way coupling from the electrical to the mechanical domain through the piezo electric actuator, (ii) the coupling to the acoustic domain inside the ink channels, and finally the coupling to the fluid dynamic domain with free surface flow, i.e. (iii) the drop formation and (iv) the drop impact, spreading and solidification. Especially with the many new materials, the control of the interaction of the jetted fluid with the different types of substrates is crucial. Furthermore, (v) wetting of the nozzle plate and (vi) air bubbles, which require the modeling of two-phase flow, can have a negative influence on the printhead performance.

The drops coming out of the nozzle can be measured with all kind of optical techniques[2]. Single drops can even be captured for further analysis. What is happening inside the printhead is much more difficult to measure. The most important measurement uses the piezo actuator also as a sensor, which is especially in the research on jetting stability an important capability. However, this measurement gives only the average pressure inside the ink channels. Therefore, the modeling of the physical phenomena is an essential part of the research[3]. Added to the measurements, the modeling reveals the chain of processes, which lead to the final goal: firing droplets of ink at a very high rate with any desired shape, size and velocity, and a reliability as high as possible. With controlling techniques the performance of printhead can be optimized effectively[4].

To comply with the increasing and diverging requirements for today's inkjet technology, a fundamental understanding of the underlying processes is very important. For that, we are already collaboration with many academic groups in the Netherlands and we are looking for ways to expand this network further.

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Multiscale analysis of gas absorption in liquids

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One of the main research activities of the TIPs Laboratory is the development of theoretical, numerical and experimental methods for the characterization of gas-liquid absorption in industrial systems. This is a multi-scale problem: the analysis of phenomena at different scales and their coupling is required to improve the design and the operation of these systems.

At the interface scale, an original experimental tool and a dedicated procedure for the characterization of the chemical absorption of CO_2 (see Fig. A) in various liquids has been developed[1]. This tool is currently used in collaboration with industry for studying new generation aqueous amine solutions[2] for efficient CO_2 capture and regeneration technologies.

At the inclusion scale, the coupling between mass transport phenomena and chemical reactions during the absorption of a gas in a liquid has been characterized by direct numerical simulations, considering bubbles[3] and liquid droplets[4] (see Fig. B). A new experimental set up and a data post-processing method for the characterization of the dynamics and the morphology of ellipsoidal bubbles[5] have also been developed (see Fig. C).

At the scale of the industrial system, the results obtained at the scale of the interface or at the scale of the bubble have been used for the development of models aiming at the analysis or the optimization of various processes such as ozonation[6] and sodium bicarbonate production[7].

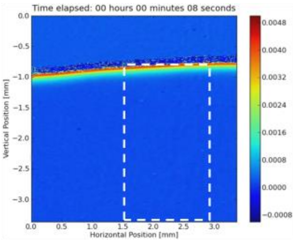

Fig. A

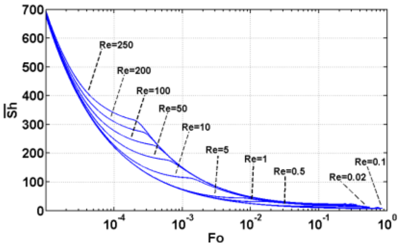

Fig. B

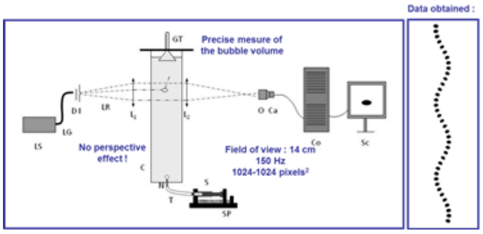

Fig. C

(a) Boundary layer development during the absorption of CO_2 in a liquid, visualized by interferometry; (b) time evolution of the Sherwood number of a liquid droplet falling in a gas; (c) sketch of the experimental set up and superposition of post-processed images acquired during the rise of a bubble.

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Foaming Emulsions

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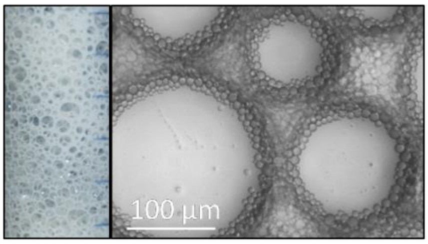

Figure 2. Emulsion droplets in foams.

Foams made from emulsions are found in many industrial products, where either they are purposefully created for reasons of function and texture or they are an unwanted side product due to the foaming of an emulsion during preparation or use. Interestingly, depending on the volume fractions of the components and on the type of surfactant and oil used, emulsions can strongly increase the stability of foams or decrease it. Although research has been conducted on emulsions as anti-foams, their use as stabilising agents for foaming has so far been less explored.

We have studied model foam-emulsion systems using a single surfactant to stabilise both the oil drops and the air bubbles. We observed changes from very unstable to long-lived foams. We found that in the case of rather stable foams, the confinement of emulsion droplets in the network formed by the bubbles plays an important role. In order to understand the role of confinement, we have studied the behaviour of emulsions in capillary tubes (1D confinement). Interesting new effects have been evidenced, related to creaming of emulsions under circular confinement. The relation between these findings and the peculiar behaviour of foamed emulsions will be discussed.

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Microporous Materials from Particle-Stabilised Liquid Foams

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Vincenzo Buscaglia, Maria Teresa Buscaglia, Giorgio Battilana, Francesca Ravera, Libero Liggieri

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Solid foams have remarkable potentialities as structural or functional materials in a variety of applications, such as shock dumping/absorbers, thermal and sound insulation, advanced filtration and separation membranes, hot gas cleanup, CO_2 and other pollutant adsorption, catalyst supports, components of rechargeable lithium batteries and electrolytic capacitors.

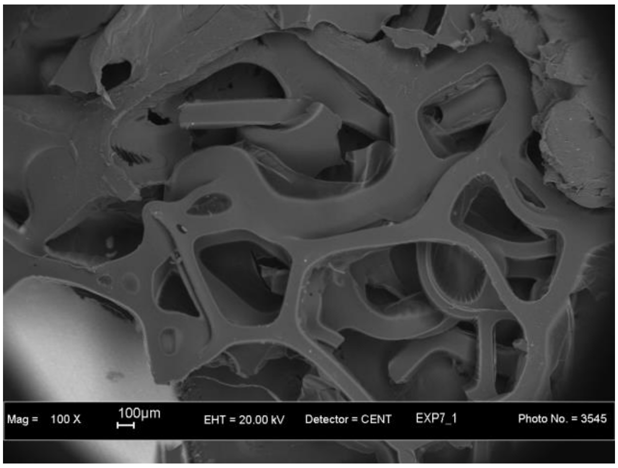
The production of these microporous materials from particle-stabilized liquid foams (or emulsions) represents an attractive route for cost reductions and energy saving. To this aim it is however necessary to achieve an accurate control of the structure and stability of the foam during the various phases of the processing.

We present here a study aimed at the production of solid foams with tailored structural and chemical features, after drying and/or sintering of liquid foams stabilized by associations of ceramic or carbonaceous nanoparticles with surfactants.

Beside optimizing the protocols adopted for the solid foam production, the interfacial properties of the single particle-laden liquid interfacial layers have been characterized in order better understanding their relation with the properties of the obtained foams as well as the definition of "key" features of the NP-surfactant systems responsible for specific structural, morphological and functional characteristics of the material.

Aknowledgements: National Research Council and Ministry of Industrial Development, National Joint Research Programme "Clean Carbon"

Reference: Zabiegaj D., Santini E., Guzmán E.., Ferrari M., Liggieri L., Buscaglia V., Buscaglia M.T., Battilana G., Ravera F. (2012): Nanoparticle laden interfacial layers and application to foams and solid foams. *Submitted to Colloids and Surfaces A.*



Solid foam after processing of a liquid foam stabilised by Carbon Soot plus CTAB. image size= 2.2 x 3.1 mm.

Closing the cycle with hydrogen

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The growing population and growing demand for resources, e.g. energy and materials, requires a change of the economic system. The current economy was developed with the industrialization and is based on the following steps: mining of the resources, fabrication of the products; the consumption converts the products into garbage and finally deposition of the waste. This leads to a depletion of the resources and a negative impact on the environment.

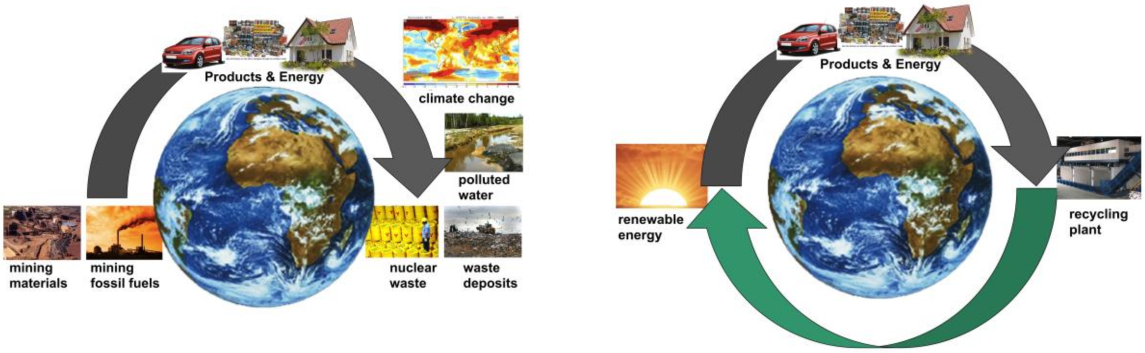

Fig. 1 The economic system established during the industrialization (the past 200 years) on the left hand side and the future economic system based on a closed cycle.

The fossil fuels are the main source of energy in the current economic system. The reserves of fossil fuels are limited and there combustion leads to an increase of the CO_2 concentration in the atmosphere. Furthermore, the world wide demand for fossil fuels is increasing with time and the economy of the industrialized society entirely depends on the availability of the fossil fuels.

There are just two ways to close the cycle[1]: remove the carbon from the energy cycle and introduce hydrogen as an energy carrier for the solar energy or to extract CO_2 from the atmosphere and to reduce it with hydrogen to synthetic fuels. An energy system based on hydrogen suffers from the limited energy density in a hydrogen storage material. On the other hand, the extraction of CO_2 from the atmosphere with the today known processes are energy demanding and requires a large surface area. However, the production of hydrogen from renewable energy and the storage of hydrogen, i.e. the reaction of hydrogen with a metals or CO_2, leading to a high energy density material are the crucial steps in the future energy system.

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