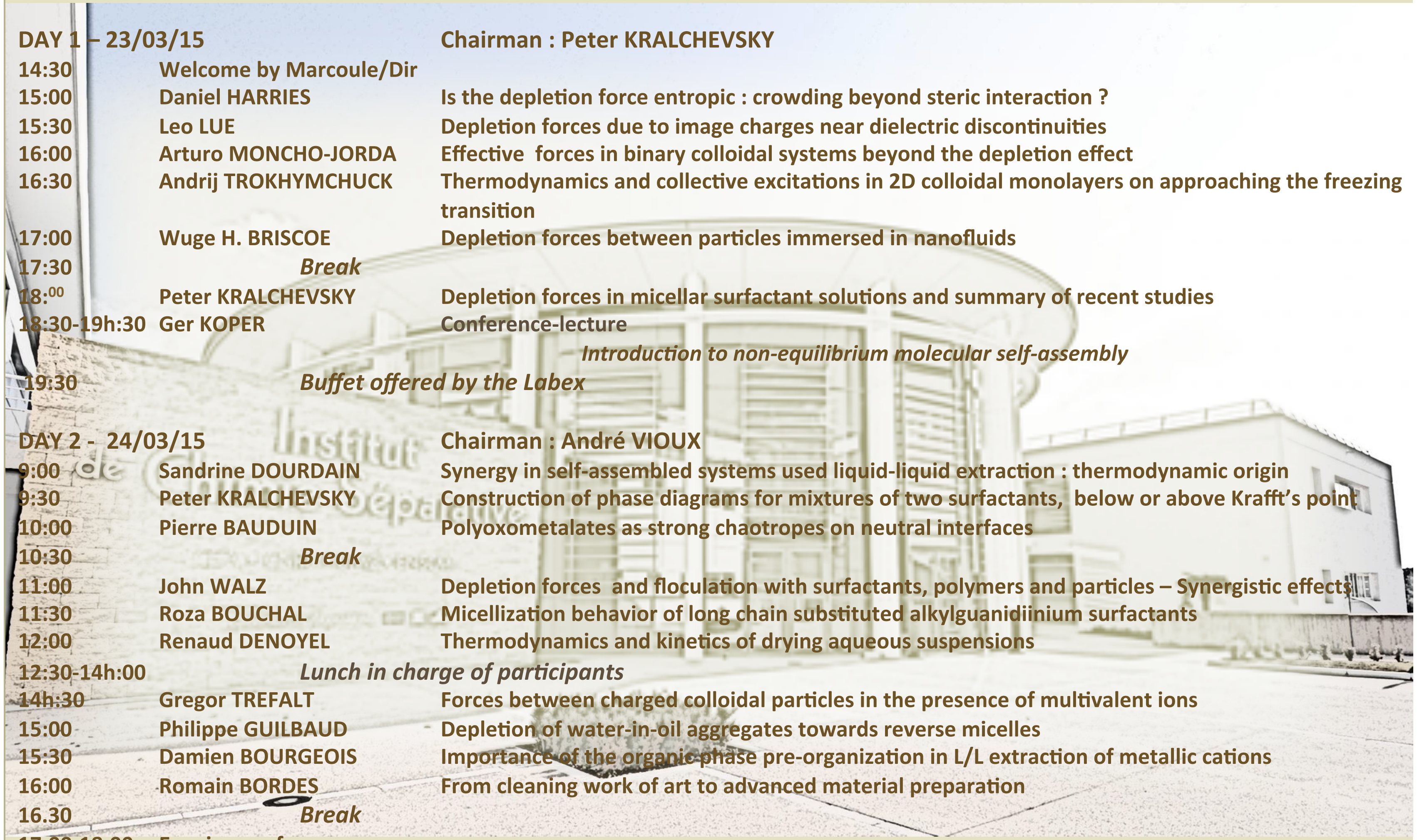
EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

COST: «Colloidal Aspects of Nanoscience for Innovative Processes and Materials» and LabEx CheMISyst 2015 Spring workshop: «Advances in System Chemistry Driving Forces»

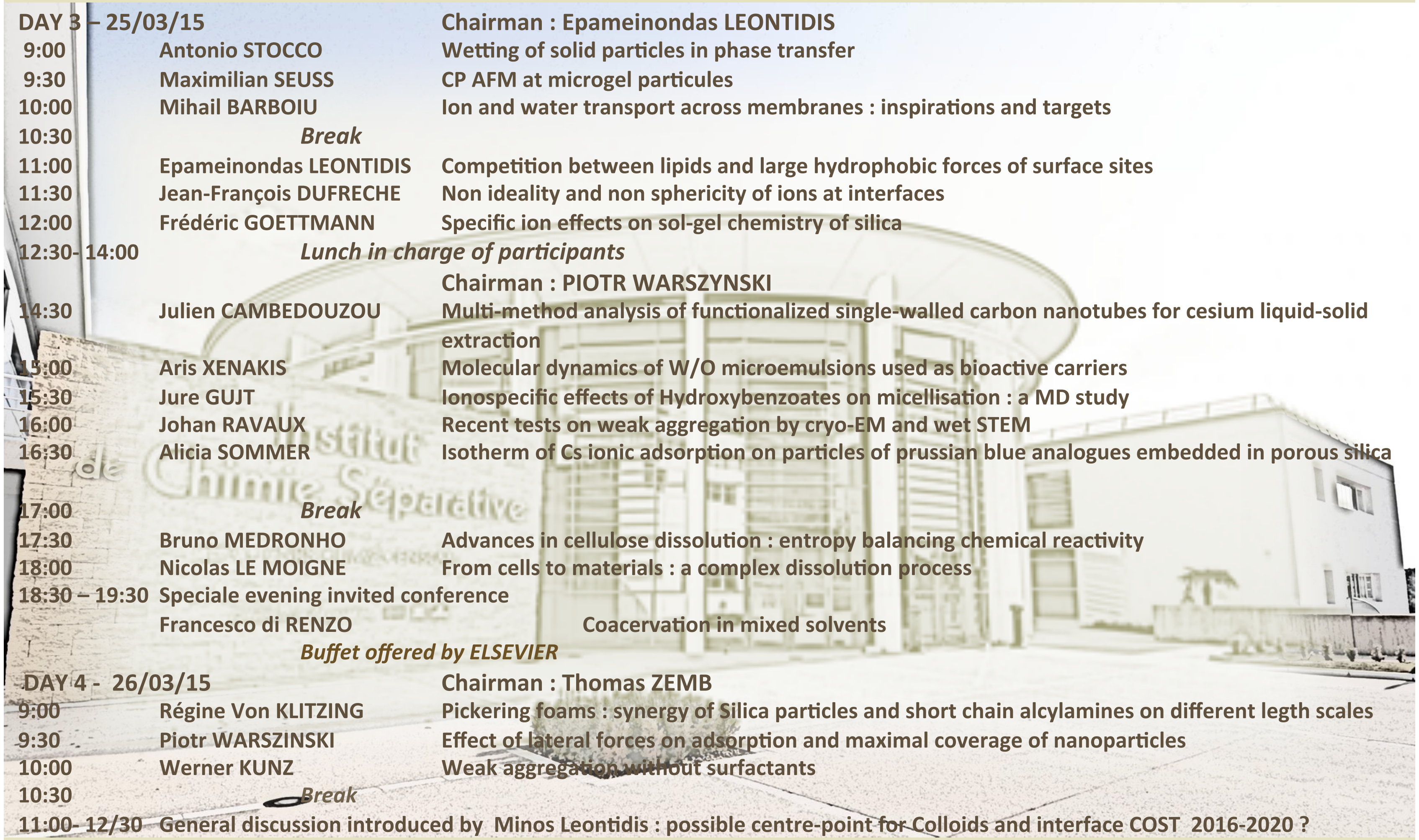
March 23rd-26th 2015

ICSM, Parc Marcel Boiteux, Codolet, France

Schedule



DAY 1 – 23/03/15		**Chairman : Peter KRALCHEVSKY**
14:30	Welcome by Marcoule/Dir	
15:00	Daniel HARRIES	Is the depletion force entropic : crowding beyond steric interaction ?
15:30	Leo LUE	Depletion forces due to image charges near dielectric discontinuities
16:00	Arturo MONCHO-JORDA	Effective forces in binary colloidal systems beyond the depletion effect
16:30	Andrij TROKHYMCHUCK	Thermodynamics and collective excitations in 2D colloidal monolayers on approaching the freezing transition
17:00	Wuge H. BRISCOE	Depletion forces between particles immersed in nanofluids
17:30	*Break*	
18:00	Peter KRALCHEVSKY	Depletion forces in micellar surfactant solutions and summary of recent studies
18:30-19h:30	Ger KOPER	Conference-lecture *Introduction to non-equilibrium molecular self-assembly*
19:30	*Buffet offered by the Labex*	
DAY 2 - 24/03/15		**Chairman : André VIOUX**
9:00	Sandrine DOURDAIN	Synergy in self-assembled systems used liquid-liquid extraction : thermodynamic origin
9:30	Peter KRALCHEVSKY	Construction of phase diagrams for mixtures of two surfactants, below or above Krafft's point
10:00	Pierre BAUDUIN	Polyoxometalates as strong chaotropes on neutral interfaces
10:30	*Break*	
11:00	John WALZ	Depletion forces and floculation with surfactants, polymers and particles – Synergistic effects
11:30	Roza BOUCHAL	Micellization behavior of long chain substituted alkylguanidiinium surfactants
12:00	Renaud DENOYEL	Thermodynamics and kinetics of drying aqueous suspensions
12:30-14h:00	*Lunch in charge of participants*	
14h:30	Gregor TREFALT	Forces between charged colloidal particles in the presence of multivalent ions
15:00	Philippe GUILBAUD	Depletion of water-in-oil aggregates towards reverse micelles
15:30	Damien BOURGEOIS	Importance of the organic phase pre-organization in L/L extraction of metallic cations
16:00	Romain BORDES	From cleaning work of art to advanced material preparation
16.30	*Break*	
17:00-18:00	Evening conference Krister HOLMBERG	Lipases at interfaces



DAY 3 – 25/03/15		Chairman : Epameinondas LEONTIDIS
9:00	Antonio STOCCO	Wetting of solid particles in phase transfer
9:30	Maximilian SEUSS	CP AFM at microgel particules
10:00	Mihail BARBOIU	Ion and water transport across membranes : inspirations and targets
10:30	*Break*	
11:00	Epameinondas LEONTIDIS	Competition between lipids and large hydrophobic forces of surface sites
11:30	Jean-François DUFRECHE	Non ideality and non sphericity of ions at interfaces
12:00	Frédéric GOETTMANN	Specific ion effects on sol-gel chemistry of silica
12:30- 14:00	*Lunch in charge of participants*	
		Chairman : PIOTR WARSZYNSKI
14:30	Julien CAMBEDOUZOU	Multi-method analysis of functionalized single-walled carbon nanotubes for cesium liquid-solid extraction
15:00	Aris XENAKIS	Molecular dynamics of W/O microemulsions used as bioactive carriers
15:30	Jure GUJT	Ionospecific effects of Hydroxybenzoates on micellisation : a MD study
16:00	Johan RAVAUX	Recent tests on weak aggregation by cryo-EM and wet STEM
16:30	Alicia SOMMER	Isotherm of Cs ionic adsorption on particles of prussian blue analogues embedded in porous silica
17:00	*Break*	
17:30	Bruno MEDRONHO	Advances in cellulose dissolution : entropy balancing chemical reactivity
18:00	Nicolas LE MOIGNE	From cells to materials : a complex dissolution process
18:30 – 19:30	Speciale evening invited conference	
	Francesco di RENZO	Coacervation in mixed solvents
	Buffet offered by ELSEVIER	
DAY 4 - 26/03/15		Chairman : Thomas ZEMB
9:00	Régine Von KLITZING	Pickering foams : synergy of Silica particles and short chain alcylamines on different legth scales
9:30	Piotr WARSZINSKI	Effect of lateral forces on adsorption and maximal coverage of nanoparticles
10:00	Werner KUNZ	Weak aggregation without surfactants
10:30	*Break*	
11:00- 12/30	General discussion introduced by Minos Leontidis : possible centre-point for Colloids and interface COST 2016-2020 ?	
12:30-14h:00	*End of the meeting*	

INVESTISSEMENTS D'AVENIR

COST EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

ELSEVIER

CMST COST Action CM1101
2011-2015

Colloidal Aspects of Nanoscience for Innovative Processes and Materials

Colloid chemistry is a steadily growing field of immense importance. The enormous diversity of the colloidal processes involved in novel materials and their applications in both advanced technologies and everyday life cannot be overstated. There is a compelling need for exchange, coordination and cooperation in the European colloid community.

The COST CM1101 action will combine coherently the outstanding European expertise in this field, including: theoretical modelling and experimental formation of functional and patterned interfaces; self-assembly of molecules and colloidal particles; synthesis and up-scaling of novel nano-colloidal and bio-colloidal materials; the kinetic and catalytic aspects of these novel materials; and their applications in chemical, pharmaceutical and food industries, as well as in nano-devices such as sensors, assays, photonics and bio-fuel cells.

This includes many of the Grand Challenges in energy, health and environmental protection. The COST CM1101 action will provide a platform for coordination of national programs and will stimulate academia-industry cooperation. The COST CM1101 actions main deliverables will be the increased networking in colloid chemistry through the organization of scientific events (conferences, workshops), training schools and STSMs. Through an extensive mobility program targeted to early stage researchers, it will encourage their involvement in the research at the international level.

Chair : Pr Piotr Warszynski

Editorial overview COCIS Januray 2015

Depletion forces in single phase and multi-phase complex fluids

Thomas Zemb [1] **and Peter A. Kralchevsky** [2]

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This special issue is devoted to an ambivalent paradigm: the general concept of depletion forces, first investigated as a unified general view of the indirect effect of a non-absorbing solute, on the interaction potential between two colloids, and proposed by Asakura and Oosawa (AO) [1], and discussed in a Faraday-type author meeting discussion [2].

The simplicity of the AO-result, its generality and quantitative link with solvent activity and osmotic pressure explain the success of the concept, and its usage in quantitative studies on colloidal stability of complex fluids. It was soon realised that steric stabilisation could be treated as negative depletion [3]. If the colloid becomes larger than the diameter of the non-adsorbing solutes, very simple analytic predictions, such as the sticky sphere model initially developed by Baxter [4] in the seventies and the subsequent attempts to predict phase diagram, were very successful. Due to the absence of generic way to treat complex shapes [5], the extension to nonspherical objects and solutes went on difficulties.

Strange enough, while the generality of hydration forces as discovered by Parsegian and coworkers was easily recognized, see e.g. Ref. [6], the fact that the concept of depletion forces is of the same level of generality was very recently recognized to be one of the four cardinal forces driving colloidal fluids in the “nanoscience” [2,7], as shown in Figure 1. Most textbooks still consider the electrostatic/van der Waals competition as the source of stability and phase transition of most colloidal systems.

The present issue deals with recent progresses in predictive modelling of depletion forces. 60 years after the pioneering paper by Asakura and Oosawa [1], the new developments in this field are in the following research directions:

(i) Generalizations from mere hard core interactions between the smaller and larger particles [1], to other kinds of *repulsive and attractive interparticle forces* have been presented [8]. The invited review by Harries and Sapir [9] disentangle the deep link between enthalpy/entropy compensation and depletion, along with the approach well detailed by Dill and Bromberg in their classical and extremely pedagogic textbook [10]. The effects of soft electrostatic particle/particle and particle/wall interactions on the depletion force have been investigated both experimentally and theoretically [11]. Image-charge effects and salting-out phenomena have been studied by Curtis and Lue [12] As demonstrated by Moncho-Jordá and Odriozola [13], the effective wall–wall interactions are notably influenced by the nature of the particle–particle and particle–wall interactions.

(ii) Extension of the theory to *higher concentrations* of the smaller particles (the depletant), at which the interaction force oscillates with the surface-to-surface distance, so that the depletion force is identified with the first minimum of the oscillatory structural force at small distances [11,14]. A general analytical expression for calculating the structural and depletion forces at various concentrations of hard spheres has been derived by Trokhymchuk and Henderson [14]. The thin liquid film balance invented by Scheludko in Sofia [15] is a very sensitive technique for measuring osmotic pressure of thin films of colloids. This approach allows a very detailed analysis of surface layering of nonionic and charged micelles. Quantitative check of prediction of the effect of depletion force on the disjoining pressure can be obtained, and last but not least, counting of the micelles present per unit area for different thicknesses of a thin liquid film gives a clever and independent measurement of aggregation numbers, once the cmc is known, as shown by K. Danov and coauthors [11].

(iii) New aspects of the depletion surface force related to mixed dispersions of *two and multiple depletants* are reviewed by Ji and Walz [16]. It is demonstrated that if two species of particles form dimers, the depletion attraction can be stronger than the simple superposition of the two separate depletion effects. Next, experimental examples for such synergistic depletion effects are given for binary mixtures of surfactant + polymer, and nanoparticles + polymer. Finally, a ternary mixture of large, middle-size and small particles are considered, and the effect of "condensation" of the middle-size particles on the surfaces of the large particles driven by the depletion effect of the small particles (the halo effect) is considered [16].

(iv) The effect of the *geometrical shape of depletant particles* (spheres, prolate and oblate ellipsoids, disks, needles) has been investigated by Piech and Walz [17] and reviewed by Briscoe [18]. Thus, for needles and disks the depletion energy is much higher than that for spheres, i.e. they are effective depletants. For the same aspect ratio, the depletion energy mediated by oblate spheroids is greater than that by prolate spheroids under constant number density due to their comparatively larger volume. The effect of the *internal architecture* (degrees of freedom) of the particles for the case of polymers and similar kind of soft colloids has been also investigated [13,19].

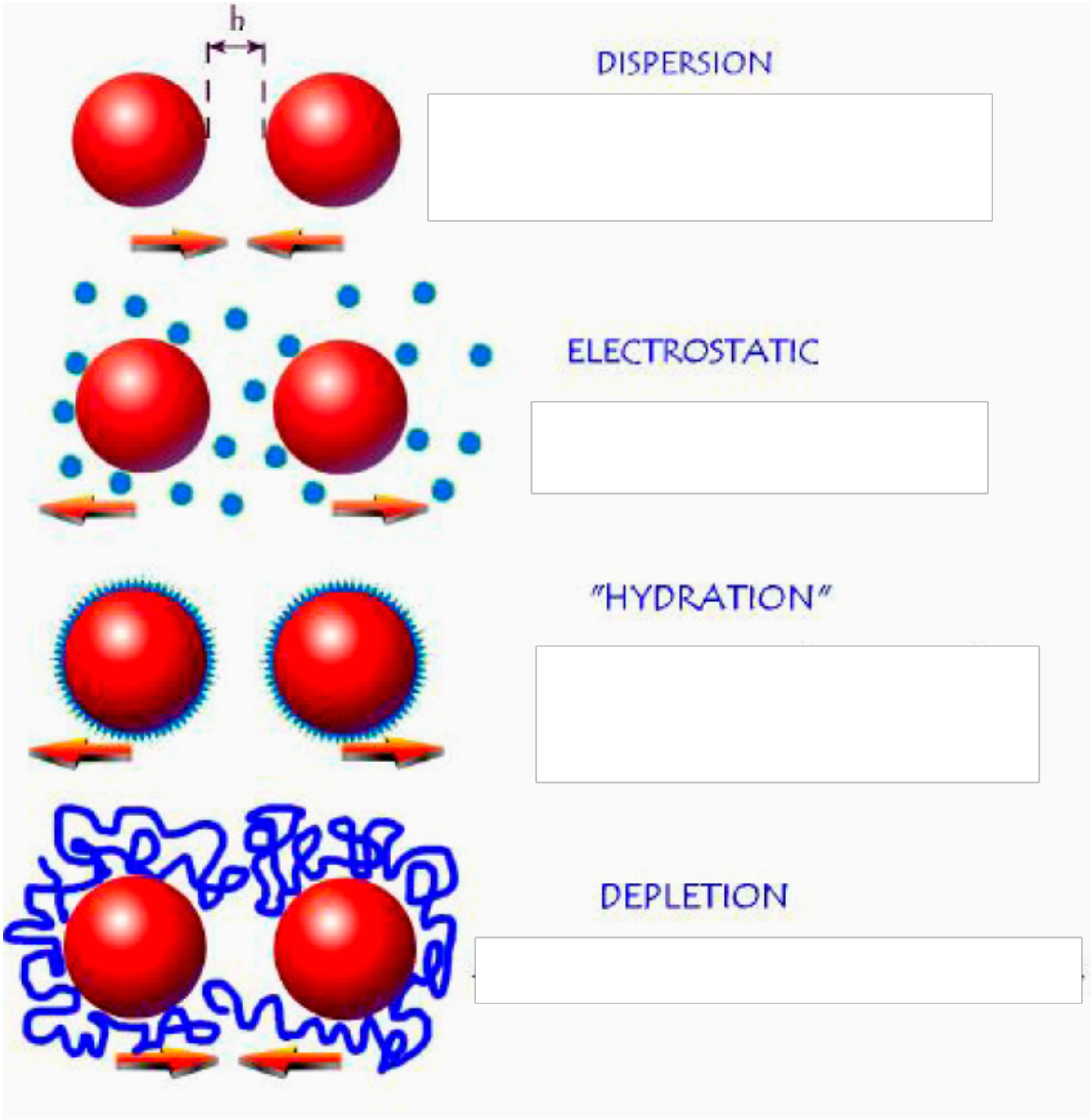
(v) Another research direction is the role of *depletion forces in biological systems*. Indeed, 20–30% of the cellular volume is occupied by soluble proteins and macromolecules. Depletion forces due to the proteins in such a crowded environment are conjectured to contribute to vesicular traffic/clustering, membrane fusion, actin bundling and amyloid fibril formation. Given the noncovalent nature of depletion forces, they are highly adaptable to dynamic cellular processes [18]. The DNA molecules are compacted in the central part of the cell owing to the depletion effect of proteins and ribosomes. The DNAs are so tightly confined that they have been observed to explode out of the cell and could expand up to 100 times in volume in its liberated nucleoid state [20]. The compaction of double-stranded DNA by negatively charged proteins and colloids, and the single-molecule DNA conformational dynamics has been investigated by Yoshikawa and coworkers [21].

(vi) The role of *depletion forces in dynamic processes* represents an additional research area. The effect of polymer-induced depletion attraction on the diffusion and sedimentation of colloidal particles, and on the suspension rheology is reviewed by Remco Tuinier et al. [22].

(vii) Finally, the depletion force drives *the formation water-in-oil agglomerates* in non-aqueous media – from weak aggregates to reverse micelles, as supposed by H.-F. Eicke [23] in the seventies. However, the importance of the third component as a structuring nucleating species could not be demonstrated at that time. Progress in small angle scattering of weakly scattering systems, as well as the molecular dynamics could demonstrate this in the case of weak aggregates that are the intermediary form between organometallic complexes and more classical "reverse micelles" containing hundred molecules or more per micelle. These weak reverse aggregates of 10-20 molecules seem to occur frequently [24]. In the case of ionic aggregates containing 10-30 ions, such as the DOLLOP discovered by Gebauer and Cölfen in 2008 [25], or even the surfactant-free microemulsions [26], and for which the structural unambiguous proof of existence has been available only recently [27]. The recognition of weak aggregation, with a diffuse interfacial film that can be understood as an interphase[28]

Thus hydration force combined to depletion effects and steric stabilisation, opposed to the entropy favouring always dispersion as molecular fluids, seem to be a consequence of the interplay between van der Waals and electrostatic forces as in DLVO, which is limited to the two top interaction mechanisms in Figure 1. The same weak non-covalent interactions have to be considered together with curvature and packing in molecular tectonics [29-30]. The influence of “weaker” forces triggers the formation of weaker thermodynamically stable structured aggregates, which will be the topic of next special issue of current opinion, to appear in 2016

Figure. 1. The four cardinal forces governing complex fluids. At molecular scale, dispersion is favoured by entropy. Entropic effects can also be considered as a molecular driving force [2].



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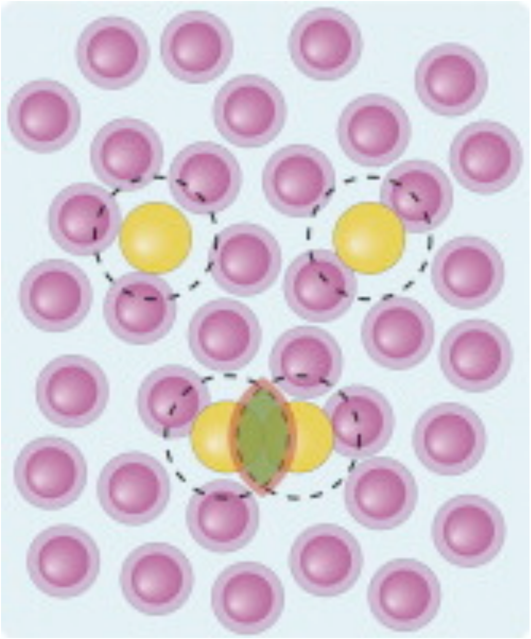
First session : Depletion Forces: from practice to theory in systems chemistry

Opening lecture

Is the depletion force entropic: crowding beyond steric interaction ?

HARRIES Daniel



Cosolutes excluded from macromolecules create effective attractions between the excluding macromolecules, and promote their self-association. This “depletion force” serves an important stabilizing role in many biological and technological processes. Specifically, many osmolytes and polymeric crowders that are excluded from protein surfaces stabilize the more compact folded state. Yet, these excluded cosolutes operate through several, thermodynamically distinct, mechanisms. Here we review the experimentally found mechanisms and link these to possible underlying molecular interactions. One class of excluded cosolutes comprises protective osmolytes. These tend to induce attractive depletion forces that are enthalpically dominated but entropically destabilizing. Whereas polymeric crowders may act by similar mechanisms to osmolytes, in many other cases they induce depletion forces dominated by favorable entropy. These different thermodynamic mechanisms are intimately related to the effective interaction of cosolute with each macromolecule. The venerable Asakura-Oosawa model for depletion forces assumes that the cosolute-macromolecule interaction is entirely steric, thereby predicting fully entropic depletion forces. Augmenting this steric repulsion core with a “soft” repulsion shell adds an enthalpic contribution to the depletion force, which may even dominate all other contributions. Further, considering that cosolute-macromolecule effective interactions are temperature-dependent results in a depletion force that can be concertedly dominated by enthalpy and entropically disfavored, as observed experimentally for protective osmolytes. In this core-shell description, to account for depletion forces that are enthalpically dominated and entropically disfavored, it is sufficient to consider an effective microscopic cosolute-macromolecule soft shell that comprises an entropic attraction and an enthalpic repulsion. We show how the full gamut of cosolute effects can be rationalized using these simple considerations regarding the nature of the cosolute-macromolecule effective interaction.

Depletion forces due to image charges near dielectric discontinuities

LUE Leo

The depletion force is an effective inter-particle attractive interaction that is entropically driven by the exclusion of co-solvent molecules. For large co-solvents, such as polymers, the exclusion is primarily driven by excluded volume interactions. However, the exclusion of co-solvents, such as electrolytes, can be caused by other mecha- nisms. In this review, we summarize the literature on inter-particle depletion forces that arise from repulsive image-charge forces between low-dielectric particles and electrolytes. In particular, we emphasize the results from a variational perturbation theory for describing the salting-out behavior observed in moderately concen- trated salt solutions. The theory predicts an unscreened force with a range given by the Bjerrum length and a magnitude proportional to the osmotic pressure of the salt solution. The force becomes significant at the same salt concentration where salting-out behavior is typically observed

Effective forces arising in binary colloidal systems with attractive/repulsive interactions: beyond the depletion effect

MONCHO-JORDA Arturo

The interplay between attraction/repulsion between particles in binary colloidal mixtures leads to a very rich behaviour. In addition to the well known depletion attraction, other phenomena such as haloing, bridging, or repulsion through attraction may appear, which strongly affect the stability and phase behaviour of the colloidal suspension.

Thermodynamics and collective excitations in 2D colloidal monolayers on approaching the freezing transition

TROKHYMCHUK Andrij

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While in basic science monolayers usually are considering as a separate class of two-dimensional (2D) problems, in applied science monolayers very often appear to be the part of more complex phenomena related, for instance, to colloidal film stability, structural and depletion forces, colloidal fluid spreading, etc. Like bulk colloidal dispersions, the colloidal monolayers exhibit a full spectrum of physical properties that are determined by the forces acting between particles and depend, primarily, on the particle concentration. In this report we present a set of computer experiment data on structural ordering, phase equilibria and phase transformations, some dynamic properties of the two-dimensional assembly of colloidal particles interacting via effective depletion interaction of a varying radius. The main attention is paid to discuss the properties of colloidal monolayers and their sensitivity to the radius of effective attraction, experienced by colloidal particles, in the range of particle concentrations close to freezing transition. We have shown, that when the radius of attraction is comparatively large, i.e., larger than roughly 30% of the particle core diameter, the colloidal monolayer exhibits gaseous, liquid, and solid phases, analogous to an atomic substance. At the same time, the monolayer of purely repulsive hard-core colloids does not show the liquid phase, although undergoes the freezing transition to solid state. From other side, by analyzing the ordering particles in the monolayer, we found that if the radius of attraction is approximately 15% of the particle diameter, the dense colloidal monolayer shows the same ordering behavior as one composed of purely repulsive particles. Colloidal monolayers with a radius of attraction larger than 15% show an enhanced tendency to crystallization, while disorder occurs for monolayers with the radius of attraction being shorter than 15% of the particle hard-core diameter.

Depletion forces between particles immersed in nanofluids

BRISCOE Wuge H.

Understanding depletion forces between colloidal particles mediated by nanofluids, i.e. liquids containing hard or soft nanostructures, is immensely important in a number of industrial processes. We anticipate added complex- ities due to enhanced and multifactorial inter-depletant interactions associated with their size, shape, surface chemistry, and concentration. Here we briefly review recent efforts in direct measurement of depletion forces mediated by nanofluids, as well as a number of related studies on the phase transition in binary colloid mixtures with large size and shape asymmetry, a process in which depletion forces play an important role. We will also discuss the often under-appreciated importance of depletion forces mediated by proteo-nanofluids (liquids con- taining proteins) in facilitating cellular organisation. Some challenges and outstanding questions will emerge

Depletion forces in micellar surfactant solutions and summary of recent studies

KRALCHEVSKY Peter A.

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The depletion force can be considered as a special (limiting) case of the oscillatory structural force at short distances between two surfaces. Here, we consider analytical expressions for the structural force in the depletion zone and compare their predictions with experimental data. In the case of particles that interact as hard spheres, an expression for the depth of the depletion minimum as a function of the particle volume fraction ϕ is available. This expression has been used to predict the rise of the contact angle α of plane-parallel foam films from nonionic surfactant solutions with the increase of surfactant concentration – a depletion effect due to the nonionic micelles, which can be treated as hard spheres. Further, knowing the theoretical α-vs.-ϕ dependence, from the experimental values of contact angle the micelle aggregation number has been calculated, and the results agree well with data obtained by other methods. In the case of electrically charged particles, the depletion effect is strongly affected by the soft and long-range electrostatic repulsion. This interplay of electrostatic and depletion effects can be quantified by upgrading the Poisson-Boltzmann theory of electric double layer to take into account the presence of charged particles (macroions). The resulting theoretical model predicts the equilibrium thickness, h_0, of plane-parallel films formed from micellar solutions of ionic surfactants in excellent agreement with the experiment. Recent results on depletion-force effects are summarized.

General lecture

Introduction to non-equilibrium Molecular Self-Assembly

KOPER Ger J.M

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Self-assembled structures such as micelles and vesicles have frequently been discussed as model systems for biological cells because they can mimic their ability to compartmentalize matter for biological and material processing such as DNA-replication and nanoparticle synthesis respectively. However, in contrast to most synthetic self-assembling systems the natural systems are not equilibrium processes. Attention is therefore now focusing on non-equilibrium self-assembling systems where energy input is required to sustain the self- assembled state. These systems have the potential to adapt themselves and enter into different self-assembled states depending on environmental conditions whereas their equilibrium counterparts can only assemble or disassemble.

Recently, such a self-assembling system using a chemical fuel[1] and presently more examples are being worked on. The thermodynamic description of such non-equilibrium processes[2] invokes some interesting questions regarding the nature of the entropy production, the relation between the driving forces and the dissipation rate, and the energy transduction pathways. In particular, an interesting question is whether multiple stationary states can be found in such systems and this will be discussed during this presentation.

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[1] DOI: 10.1002/anie.201001511. [2] DOI: 10.1007/s10765-013-1464-5.

Synergy in self-assembled systems used in liquid-liquid extraction: thermodynamic origin

DOURDAIN Sandrine

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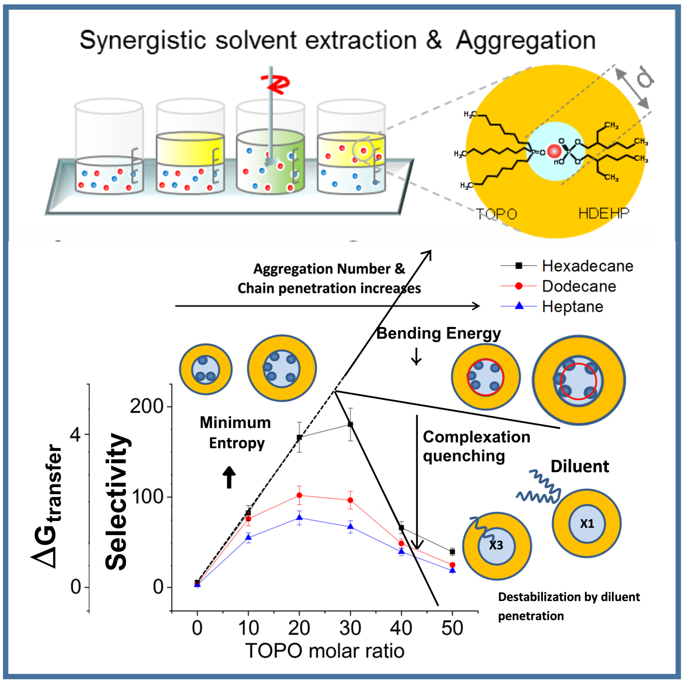

In solvent extraction, a concentrated solution of mixed salts is contacted with a reverse microemulsion. Some salts are selectively extracted. When mixed surfactants are used in the formulation of the microemulsion, “synergism” of yet unknown origin emerges: when, for a defined formulation of the solvent phase, there is an increase of distribution coefficients for some salts from a mixture. The origin of synergism is still not fully understood in chemical engineering because modelling implies complexation and not micellisation. In order to achieve predictive modelling, aggregation number, coordination numbers and complexation numbers must be distinguished.

To determine the origin of this synergism, we determine free energy of co-assembly in mixed aggregates. Aggregation in any point of a phase diagram is followed not only structurally by SANS, SAXS and SLS, and also thermodynamically by determining the concentration of monomers coexisting with reverse aggregates. Using the industrially used couple HDEHP/TOPO forming mixed reverse aggregates, and the representative couple U/Fe1, we show that there is no peculiarity in the aggregates microstructure when the maximum of “synergism” is obtained. We compare for the first time the free energy of aggregation necessary to form mixed aggregates containing extracted ions in their polar core, and the free energy of extraction difference between target and non-target ions, as deduced from the synergistic selectivity peak.2 In addition, modifying the diluent allowed us to attribute the synergy to a combination of entropic effects favoring extraction, opposed to perturbation of the first coordination sphere by penetration and surfactant film bending energy, leading to a general mechanism at the basis of ion selectivity for metal recovery.

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Construction of phase diagrams for mixtures of two surfactants, one of them below, and the other one - above the Krafft's point

KRALCHEVSKY Peter A.

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By analysis of experimental data, a quantitative theoretical interpretation of the solubility limit of medium- and long-chain fatty acids and alcohols in micellar solutions of water-soluble surfactants is presented. A general picture of the phase behavior is given in the form of phase diagrams. The effects of electrostatic interactions and counterion binding are taken into account. The results can be useful for a quantitative interpretation and prediction of the phase behavior of mixed solutions of two (or more) surfactants, one of them below, and the other one - above the Krafft's point.

Polyoxometalates as strong chaotropes on neutral interfaces

BAUDUIN Pierre

We show here for the first time that widely used polyoxometalates (POMs), that are large polyanions (»1nm) of the early transition metals, present an extremely strong chaotropic effect in the millimolar range on electrically neutral systems. On one hand the specific ion effect of POMs have been compared to “classical” Hofmeister’s salts by their effects on the cloud point of a polyethoxylated surfactant. On the other hand POMs were found to strongly adsorb on different polar and electrically neutral interfaces, i.e. water-micelle interface and water-air interface covered by polyethoxylated- or sugar-based non-ionic surfactants, respectively by using two completely independent techniques small angle X-ray scattering and ion flotation. The present finding suggests that the many biological effects of POMs, such as their antiviral and antitumor activities, are likely to be related to their general propensity to adsorb at hydrophilic interfaces as highlighted here.

Depletion forces and flocculation with surfactants, polymers and particles — Synergistic effects

WALZ John

We provide an overview of recent work focused on investigating the depletion interaction in colloidal systems containing multiple depletant species (i.e., more than one system component that contributes to the depletion interaction between dispersed colloidal particles). Experimental studies in systems containing polymer/surfactant and polymer/nanoparticle mixtures clearly show that complexation of the two solutes into a larger depletant can produce a synergistic effect, such that the depletion force is significantly larger than the sum of the forces arising in systems containing only one of the components. For the polymer/nanoparticle system, this synergy leads to much lower polymer critical flocculation concentrations. In addition, computational studies in a system containing charged nanoparticle depletants of two vastly different sizes (e.g., nanoparticles and submicroparticles) predict the formation of a halo of the submicroparticles around the larger dispersed colloids (i.e., microparticles). These studies clearly show that attempting to predict the depletion interaction in mixed depletant systems using measurements or predictions obtained from systems containing only a single depletant can lead to quantitative, and even qualitative, error.

Micellization behavior of long chain substituted alkylguanidinium surfactants

BOUCHAL Roza

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Keywords: Guanidinium surfactants, critical micelle concentration, krafft temperature, enthalpy of micellization.

We studied the self-assembly behavior of long-chain substituted guanidinium surfactants. For this purpose, we synthesized long-chain substituted mono-alkyl guanidinium chlorides with variable chain length (C10-C16). These compounds were characterized by means of conductivity, surface tension and isothermal titration calorimetry (ITC) measurements in order to determine the Krafft temperature T_k, critical micelle concentration *cmc*, and enthalpy of micellization ΔH°_{mic}.

Clear relationship between alkyl chain length and self-aggregation behaviour and was observed

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Thermodynamics and kinetics of drying of aqueous suspensions

DENOYEL Renaud

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The situation where a solid is obtained after drying from a suspension is encountered in many situations of every day life or industrial processes: preparation of ceramics, paints, detergency, coffee ring effect etc.. The final structure of the solid obtained after drying a suspension of particles is often difficult to predict: it depends not only on the chemical composition of the suspension, particles and fluid, but also on the kinetics of drying. The faster the drying process, the stronger will be the temperature and pressure gradients through the system making the control of local parameters and the modeling of the process difficult to handle. In the present work, the drying is studied at a very low rate, with a full control of pressure and temperature within the system thanks to an experiment placed within a differential microcalorimeter that provides a full control of temperature gradients and ensure a differential pressure measurement towards pure water. The drying of suspensions can be followed as a function of relative pressure (i.e. solvent activity), starting from P/P°= 1 down to P/P°=0 with a resolution better than 10^{-4} in the whole range. The activity of water above the suspension can then be measured and followed above the suspension in a quasi-equilibrium way as a function of the suspension concentration, going continuously from a state of suspension, where DLVO forces are involved, to that of a porous solid, where capillary forces are involved during the emptying of the pores. The desorption curves of silica suspensions are here measured and analysed through various models issued from colloidal or capillarity theories.

Forces between charged colloidal particles in the presence of multivalent ions : Experiments and Poisson-Boltzmann Theory

TREFALT Gregor

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We have measured forces between charged surfaces across aqueous solutions with colloidal probe technique based of atomic force microscopy (AFM). The measurements were done in presence of different multivalent ions. Two types of particles were used, positively charged amidine (AL) and negatively charged sulfate latex (SL). First, symmetric SL-SL and AL-AL forces were measured and fitted with Poisson-Boltzmann (PB) theory, whereby surface potentials and regulation parameters of the two surfaces were extracted. Next asymmetric AL-SL force-curve was measured and compared with predictions from PB theory, where previously fitted parameters for AL and SL surface were used. One example of such experiment in the presence of $K_4Fe(CN)_6$ salt is shown in Figure 1.The PB theory was able to accurately predict forces down to distances of about 5 nm even in the presence of multivalent ions. These results seem to be in contradiction with theories that go beyond mean-field and take into account ion-ion correlations [1-3]. In contrast to our results these theories predict the failure of the mean-field PB in solutions of multivalent ions. We suspect that ion-ion correlations are important at distances below 5 nm, and that they substantially modify the surface potentials. However, at larger distances mean-field approach is accurate provided that effective surface potentials are used.

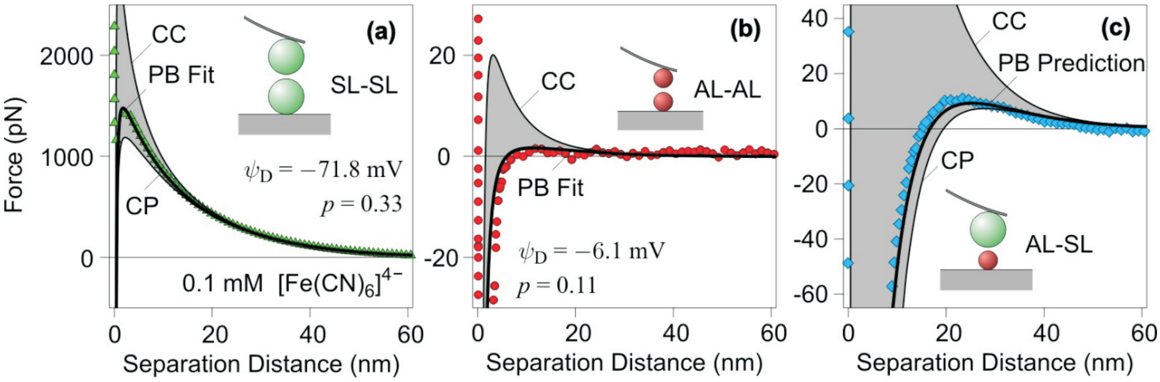

Figure 1. Force profiles involving amidine latex (AL) and the sulfate latex (SL) measured in 0.1 mM $K_4Fe(CN)_6$ solutions of are compared with PB theory. In symmetric systems, involving (b) SL-SL and (c) AL-AL particle pairs, the theory is used to determine the surface potentials and regulation parameters *p* indicated in the figures. (c) PB theory is validated by comparing its prediction with force measurements in the asymmetric AL-SL system. Charge regulation effects are essential, since constant charge (CC) and constant potential (CP) conditions differ widely.

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Depletion of water-in-oil aggregates: from weak aggregates towards reverse micelles

GUILBAUD Philippe

We assemble here all available descriptions of oil-soluble surfactant aggregates with or without solutes, assumed to be located in the polar cores of reverse micelles. The presence of solutes is crucial for the formation of a well-defined interface, thus inducing a transition from a loose reverse aggregate into a more structured micelle. This transition can be followed by the concomitant decrease of the “critical aggregation concentration” (c.a.c.). The less organized state as reverse aggregates is predominant when no “nucleating” species such as water, salts, or acids are present. One way to understand this weak aggregation is a depletion driving to aggregates as pseudo-phases introduced by Tanford. Analogues coexisting pseudo-phases seem to exist: weak oil-in-water (o/w) aggregation with the so-called surfactant-free microemulsions, containing loose aggregates, and re-entrant phase diagrams presenting a lowest aggregation concentration (l.a.c.), as described in the seventies.

Importance of the organic phase pre-organization in L/L extraction of metallic cations

BOURGEOIS Damien

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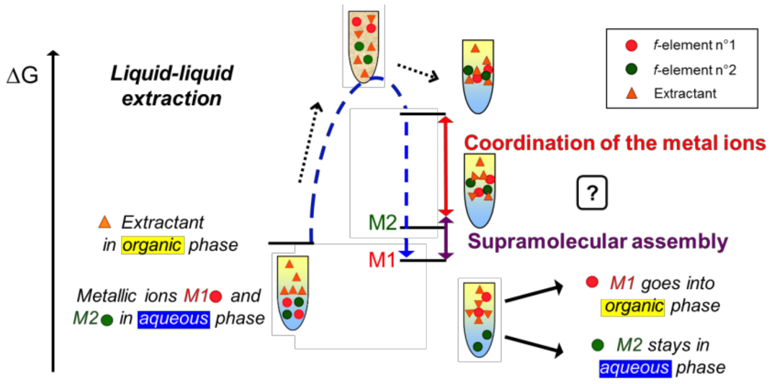
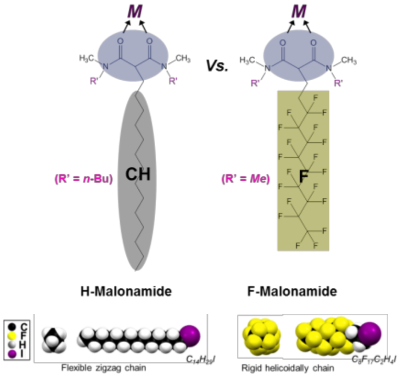
Recycling of valuable metals appears nowadays as solution of growing interest for a sustainable supply strategy. Palladium (Pd), along with other platinum group metals (PGM) and rare earth elements (REEs), represents one of the crucial issues for recovery processes. Valuation of nitric effluents containing REEs and PGM is more and more envisioned, especially in the frame of e-wastes recycling. We recently compared the behaviour of Pd and Nd during liquid-liquid (L/L) extraction from nitrate media with malonamides.[1] During these fundamental studies, we evidenced that Pd extraction is driven by metal complexation, whereas Nd extraction deserves supramolecular ordering (aggregation) of the extracting system.





We also developed a complementary approach in which Nd extraction is studied both with H- and F-malonamides. Both extracting molecules bear the same hydrophilic complexing head, and differ from their hydrophobic tail (hydrocarbon vs fluorous).[2] Thus, only long-distance interactions vary. Coordination chemistry and supramolecular ordering studies will be discussed in detail, with focus on the general relevancy of our conclusions for the development of efficient systems.

Keywords: Palladium, Rare Earth Elements, L/L extraction, complexation, agregation.

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From cleaning work of art to advanced material preparation

BORDES Romain

Romain Bordes, S. Wassén, T. Gebäck, D. Bernin, E. Schuster, N. Lorén, A.M. Hermansson, M. Baglioni, M. Raudino, D. Berti, U. Keiderling, Bordes, K. Holmberg and P. Baglioni

During the development of new systems for practical applications, many aspects have to be considered. In this presentation, two examples will highlight this, namely the formulation of nanofluids for cleaning of delicate materials and the use of kinetics to control the morphology of phase separated materials in order to control mass transport properties.

Special evening invited conference

Lipases at interfaces

HOLMBERG Krister

Brajesh K. Jha, Lay-Theng Lee, Pedro Reis, Hanna Gustafsson and Krister Holmberg
Chalmers University of Technology, 412 96 Göteborg, Sweden

Formulations containing both surfactants and enzymes are established in the detergent area and are common also in several other applications. Knowledge about possible interactions between enzyme and surfactant is essential in the optimisation of such systems.

We have been particularly interested in the combination of lipases and various types of surfactants. Being an enzyme with considerable surface activity, lipases can be expected to interact strongly with surfactants and such interactions are likely to affect the enzymatic activity.

Surfactant-lipase interactions have been studied both in aqueous bulk solution and at the air-water, oil-water and solid-water interfaces. Events at an interface are believed to be of particular relevance to lipases since this class of enzymes are known to operate at a hydrophobic surface. Aggregation in bulk was studied by NMR and by calorimetric titration and lipase-surfactant interaction at the air-water interface was investigated by surface tension measurements and by neutron reflectivity. Measurement of the electrophoretic mobility of surfactant-stabilized emulsion droplets was used to study lipase-surfactant interaction at the oil-water interface. Interaction at the interface between a hydrophobic solid surface and water was investigated by ellipsometry and by surface plasmon resonance.

We have undertaken a detailed study of how lipase competes with the normal fat metabolites for a place at the triglyceride-water interface. Our results demonstrate that 2-monoglycerides, the end product of fat degradation by the body's 1,3-specific lipases, is more interfacially active than the lipase and thus expels the lipase from the interface. This self-limiting effect may open a new way to control fat digestion. To prove our point, we appreciably reduced triglyceride oil hydrolysis in a model gastro-intestinal system by interfacial engineering of the oil. We anticipate that our findings can contribute to the development of new approaches for controlling fat metabolism.

We have also used mesoporous silica with pores specifically designed to accommodate a lipase as host for the enzyme. The lipase-loaded silica particles were dispersed in a solution containing the substrate. Very high enzymatic stability was obtained is such systems.

Second session: Thermodynamics and kinetics of self-assembly and phase transfer

Wetting of solid particles in phase transfer

STOCCO Antonio

In this talk I will present a critical review on wetting of spherical particles at the fluid interface relevant to phase transfer.

Theoretical and experimental results for planar solid interfaces will be compared with the ones obtained for spherical particles attached to liquid-gas or liquid-liquid interfaces. The latter can be seen as a solid spherical interface which undergoes wetting and dewetting dynamics. For particles whose sizes are larger than a micron, wetting may undergo as for planar surfaces. However for particle sizes lower than a micron, a far-field view describing interactions in terms of surface energies no longer holds. At small length scales, colloidal and short range interactions affect the profile of the contact line and the equilibrium contact angle may differ from the angle defined by the Young-Laplace equation. Line tension effects, interfacial friction, and the interfacial tension of particle decorated interfaces will be also discussed in the talk.

CP-AFM at microgel particles

SEUSS Maximilian

Abstract missing

Ion and water transport across membranes: inspirations and targets

BARBOIU Mihail

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Adaptive Supramolecular Nanosystems Group, Institut Européen des Membranes, ENSCM-UMII- UMR-CNRS5635, Pl. E. Bataillon CC047, 34095 Montpellier Cedex 5, France.
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The remarkable properties of natural water channel proteins in terms of permeability and high rejection of ions inspired many groups to use artificial membranes for desalination, mainly aquaporin-embedded. The next step may be related to increase this enormous potential imagining that natural conduction activity obtained with natural compounds can be biomimicked using simpler compounds displaying natural functions. We attempt to describe systems with constitutional selective artificial structures for water/ion transport.

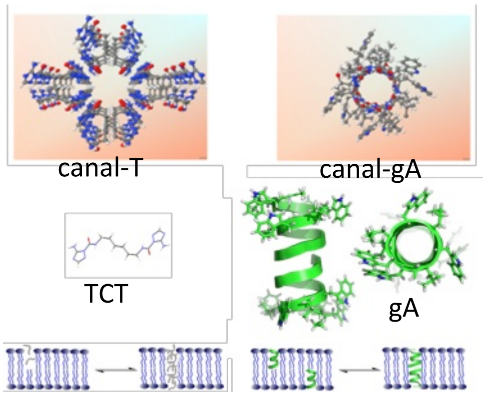

Fig.1 Comparison of canal-T made of self-assembled TCT and canal-gA made of a dimer

Carefully designed small bolaform compounds are synthesized and their self-association properties are studied. The bolaamphiphile triazole, TCT self-assembles to form stable T-channels in lipid bilayers and transports cations. Like in gramicidin A channels, the carbonyl moieties, pointing toward the T-channel core are solvated by water. The constitutional self-assembly process results in pore-forming structures (barrel-shaped) generating cationic transport. A crystal structure of TCT could be obtained showing four double-helix entities tightly interacting and resulting in the formation of T-channels. Possible self-assembly of T-channels for increasing TCT concentrations in contact with bilayer membrane were postulated. Rather than mentioning possible applications, I will describe the results achieved so far and try to convince the audience that the targets are exciting.

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Competition between lipids and large dydrophobic ions for suface sites. Surface solvation phenomena.

LEONTIDIS Epameinondas

Large hydrophobic ions are surface active. In the presence of a lipid monolayer they compete for interfacial sites.

In this work we are studying the interactions between DPPC monolayers and tetraphenylborate anions. The large anions expand the monolayers at 25 C, since they are attracted to the surface with a mean force potential larger that 10Kt. At 12C the effects are quite dramatic, leading to the gradual disappearance of the liquid condensed phase. This strong meso/macroscopic event is accompanied by interesting changes at microscale. The individual crystals of the condensed phase become gradually smaller, as lipid molecules solvate the ionic impurities. In addition the lipid chains in the crystals acquire an upright conformation, quite unusual for DPPC. These observations highlight the potential effects of hydrophobic ions on lipid membranes, especially since they are used to study the membrane dipole potential through the TATB assumption.

Non ideality and non sphericity of ions at interfaces.

DUFRECHE Jean-François

DUFRECHE Jean-François, B. Siboulet, S. Hocine (ICSM), P. Turq (UPMC-Paris 6), J. Molina (Kyoto University), G. Allaire (E. Polytechnique), A. Mikelic (Univ Lyon 1)

Description of ions at interfaces are commonly based on simple approaches (such as the Poisson-Boltzmann equation) for which the ions are described as simple spherical charges. Yet complex specific effects are actually important in numerous applications. For exemple, ionic correlations can completely modify the interface and ions with the same charge can exhibit completely different behaviours in simple systems. Another significant issue is given by the ionic transport properties that are sometimes dramatically modified by the interface and the ion interactions. As a matter of fact, a modern theory of electrolyte requires an accurate and general treatment of these complex and subtle specific effects.

With separation chemistry as an example, we show how it is possible to model the latter by a coarse graining procedure based on a molecular approach. A rigorous average of the solvent configurations gives a general model, which can be solved both for equilibrium and transport properties by taking proper account of specific effects. For molecular ions, such uranyl, rotation is especially important. For porous media, an homogenisation procedure can predict the dynamical properties of the system (Darcy's law, electrokinetic phenomena, etc.) and the role of non-ideality is at moderate and high concentration especially important.

Specific ion effects on the sol-gel chemistry of silica

GOETTMANN Frédéric

Romain Castellani, Frédéric Goettmann, Arnaud Poulesquen

Abstract missing

Multi-method analysis of functionalized single-walled carbon nanotubes for cesium liquid-solid extraction

CAMBEDOUZOU Julien

Single-walled carbon nanotubes (SWNTs) represent promising candidates as solid matrix for the liquid-solid extraction of pollutant ions [1]. They indeed combine an important specific surface with excellent mechanical properties, high chemical resistance, and interesting electrical properties. Moreover, they can be shaped in the form of buckypapers, which constitutes solid membranes easy to handle.

In this communication, we describe a simple procedure to functionalize SWNTs by Diels Alder reaction with organic moieties possessing at least a double or triple carbon-carbon bond [2]. We exemplify the case of dimethyl-acetylene dicarboxylate (DMAD) grafting [3]. Thanks to a careful characterization of grafted SWCNTs, we were able to quantify the functionalization rate, and to estimate the grafting homogeneity. The functionalization rate turned out to be moderate, with an average of more than 1 DMAD moiety every nm of nanotube length. It is shown that such a grafting rate preserves the SWNT electronic properties.

We finally show the results of Cs+ sorption experiments. After a preliminary exchange between the methyl groups of DMAD and Na+ ions, we measured the sorption isotherm of Cs+. A maximum sorption capacity of 250 mg of Cs+ per gram of buckypaper is measured, opening interesting perspectives in the field of cesium capture.

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Molecular dynamics of W/O microemulsions used as bioactive carriers

XENAKIS Aristotelis

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W/O microemulsions are attractive colloidal self-assembled dispersions that may be used as vehicles of various bioactive molecules. Elucidation of their structure and dynamics is a key factor for any further applications. In particular when bioactive molecules are encapsulated, it is important to determine their localization within the various microdomains of the system and the eventual structural alteration they may induce.

The aim of this work was to formulate medium chain triglycerides (MCT) based W/O microemulsions and to effectively solubilize hydroxytyrosol (HT), a dominant hydrophilic antioxidant of Extra Virgin Olive Oil with the addition of a small amount of biocompatible emulsifiers. Moreover these nanodispersions in the presence and absence of HT were structurally characterized using Dynamic Light Scattering (DLS) and Electron Paramagnetic Resonance (EPR) spin probe techniques [1].

Finally, W/O microemulsion nanostructure's studies were carried out by means of Coarse-Grained Molecular Dynamics (CGMD) simulations. In general, CGMD simulations allow significant computational cost reduction, a critical prerequisite when studying phenomena such as reverse micelle formation, which span the time scale of microseconds.

The Martini force field [2] has been successfully employed in the past for analogous systems [3, 4] and here it has been utilized in the description of three representative model systems, namely a) MCT/lecithin/monoglycerides, b) MCT/lecithin/monoglycerides/water and c) MCT/lecithin/monoglycerides/water/HT, in accordance to their experimental counterparts. Generally, CGMD simulations provided further insight in the shape, size and self-assembly characteristics of the system under study.

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Ionospecific Effect of Hydroxybenzoates on the Micellisation of Dodecyltrimethylammonium Chloride: A Molecular Dynamics Simulation Study

GUJT Jure

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The hydrophobic effect - an entropic effect which results in an increase in the entropy due to the disruption of the hydrogen bonding network in liquid water – is the driving force for the self-assembly of amphiphilic molecules, such as surfactants, and the folding of proteins [1]. The micellisation of ionic surfactants is, however, also influenced by electrostatic interactions between charged headgroups and ions present in the solution [2-6].

When ions with an aromatic ring are present in the solution of ionic surfactants, the type of functional groups and their relative position can also have a large impact on the micellisation and the structure and stability of resulting aggregates. Recently it has been shown, that the relative position of carboxylic and hydroxylic group in hydroxybenzoate (HB) anions can dramatically affect their transport properties in aqueous solutions [7,8] and also the micellisation of cationic surfactants such as dodecyltrimethylammonium chloride (DTAC) [3,4]. In the presence of a relatively low concentration of 2-HB anions (and to a lesser extent in the presence of 3-HB anions) the transition from spherical to rod-like micelles can occur. The goal of our research is to understand this phenomenon on the molecular level. We have therefore performed atomistic molecular dynamics simulations in order to study the formation and structure of DTAC micelles in the presence of all three isomers of HB anions. While an attempt to simulate such systems has already been made for the 2-HB isomer and cetyltrimethylamonium chloride (CTAC) [9], there is no simulation study published so far that would systematically investigate the influence of 3-HB and 4-HB anions on the micellisation of DTAC.

In this contribution we will present the results of MD simulations of systems with DTAC and all three isomers at different HB/DTAC molar ratios. The simulations were started either from a random configuration of unimers and HB ions (bottom-up approach) or from an infinitely long DTAC cylindrical micelle (top-down approach) and the structure of the resulting micelles was subsequently analysed. Results obtained from either approach are consistent and qualitatively agree with the experiment. We have found that 2-HB induces a different internal structure of the DTAC micelles than the other two isomers and incorporates itself differently and more deeply into the micellar core. We will also discuss the observed fusion of micelles facilitated by the hydrogen bond formation between HB anions incorporated into the micelles participating in the fusion.

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Recent tests on weak aggregation by cryo-EM and wet STEM

RAVAUX Johan

Observation of liquids, soft materials or biological tissue are impossible with classical electronic microscopy, due to the extremely high vacuum in the microscope the sample be damaged or evaporated. Cryo-EM is the best tool to investigate this type of materials, this technique consist to freeze samples of liquid or soft material so quickly that its internal structure gets locked into solid form. Some soft materials or liquid are frequently studied for different field of research in the ICSM. The investigations of this type of samples are mostly carried out by scattering method, that is to say by indirect observations. For a better understanding, and characterization of soft materials or liquid, direct observations are needed. For this purpose, some "wet" techniques of observation by ESEM have been developed in the L2ME (microscopy laboratory of ICSM) using controlled humidity devices. Techniques of wet-stem or ESEM allows the visualization of materials usually not observed by SEM such as highly hydrated material or liquid which can be directly in the liquid, and without any sample preparation. But, this techniques also shows some limitations, especially for liquid observations and very sensitive to the electron beam samples. In this case, the cryo-EM is very well adapted and allow high resolution studies of hydrated materials and liquid, this type of experiments were performed at the Technion in Haifa in collaboration with Pr DANINO Group .Through some examples from different fields of research (micellar phases, Metal organic framework, emulsions) we will show the capability of Wet and cryo techniques and their complementarity.

Assessment of isotherm of ionic adsorption of Cs on particles of Prussian blue analogues (PBA) embedded in porous silica

SOMMER-MARQUEZ Alicia

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Efficiency of sorbing materials is often the goal of many separation processes. The efficiency of single-sorbate sorption performance is best based on a complete single-sorbate sorption isotherm curve. A new synthesis of inorganic monoliths with hierarchical porosity functionalized with different PBA: $K_xCoFePBA$, $K_xCuFePBA$ or $K_xZnFePBA$ for the removal of cesium ions from aqueous outflows was done. The sorbents were tested on a complete single-sorbate sorption isotherm curve, until equilibrium was reached. The data were adjusted first to assess interpretations given by Langmuir plots. Sorption is frequently described in terms of adsorption isotherms (Langmuir, Freundlich), but Cs ions sorption in PBA has been recognized as an ion-exchange mechanism, mainly[1]. Prussian blue analogues are highly selective for these ions[2-4]. This statement is observed and confirmed for the obtained materials. The functionalized monoliths were tested in Cs^+ ions removal from aqueous solutions containing largest Na^+ concentration. The $K_xZnFePBA$-monolith sample presents the biggest quantity adsorbed Q_{Cs} (mmol/gZnFC) = 2.3.

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Advances in cellulose dissolution: entropy balancing chemical reactivity

MEDROHNO Bruno

Work in developing new solvents for cellulose has been following a “trial and error” empirical character. It is clear that a better understanding of the dissolution of cellulose has deep implications, not least for industrial developments. The underlying hypothesis of most current work is that cellulose insolubility is due to the fact that there are strong intermolecular hydrogen bonds between cellulose molecules and that bringing cellulose into solution is dependent on breaking these hydrogen bonds. In this brief analysis we will see that hydrogen bonding mechanism alone cannot explain the low aqueous solubility. Our recent work rather emphasizes the role of cellulose charge and the concomitant ion entropy effects, as well as hydrophobic interactions.

From cells to materials: a complex dissolution process

LE MOIGNE Nicolas

Nicolas Le Moigne, Guilhem Arrachart, Klervi Dalle, Caroline Devile, Patrick Navard

Plant cells and micro-organisms such as micro-algae present complex and heterogeneous structures made of biopolymers such as polysaccharides, proteins, lignins… generally organized in several concentric layers. These specific structures are of great interest to build up bio-based materials. However, they exhibit complex behaviour during processing such as differential dissolution capacity in solvents. Swelling and dissolution mechanisms of plant cells and microalgae will be described. The role of their microstructural features as well as those of selective treatments intended to improve dissolution will be discussed.

Special evening invited conference

Coacervation as driving force for colloidal self-assembly

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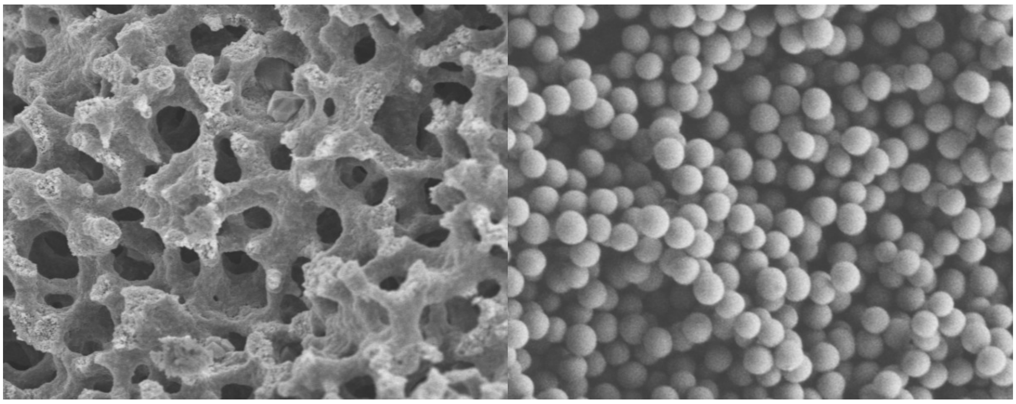
Phase separation phenomena plays an important role in the self-assembly of mesostructured materials. Several examples are presented, in which a specific configuration of a surfactant or polyelectrolyte system is induced and stabilized by the condensation of silica species in one of the phases.

In the case of the already classical synthesis of micelle-templated mesoporous silicas, the modification of the hydrophilic properties of non-ionic surfactants induces important changes in the topology of the mesophases. In the presence of an apolar component, the continuous transition between swollen micelles and microemulsions is at the basis of the formation of meso-macroporous foams.

Better defined coacervation phenomena can be observed in the case of the formation of macroporous foams by spinodal separation of polyelectrolyte solutions. The chemical control of the phenomenon is achieved by the hydrolysis of silica precursors and allows a fine tuning of the scale of phase separation, at the basis of the industrial production of silica monoliths for analytical devices.

A still debated example of coacervation has been proposed as the driving force of the synthesis of silica spheres by the Stöber method. Some observation suggests that the formation of these materials does not follow the originally proposed mechanism of nucleation and growth but corresponds to the aggregation of ethoxylated silica precursors through coacervation in the hydroalcoholic solution.



Different regimes of coacervation induces different topologies of materials

Pickering foams : synergy of os Silica particles and short chain alcyamines on different length scales

Von KLITZING Régine

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Particle stabilized foams are an interesting type of dispersion with applications in various fields of technology from mineral processing to the food industry. Nevertheless, the detailed mechanisms of how (nano)particles stabilize foams are not fully resolved, yet.

It has been shown that combining nanoparticles and suitable surfactants can lead to increased foamability and foam stability compared to the surfactant-only system without nanoparticles.

As a model system, we use hydrophilic silica nanoparticles that do not attach to the water/air interface until they are modified with alkylamines which render them hydrophobic, so they become surface active. The particle hydrophobicity was adjusted by varying the amount of adsorbed amine and/or the carbon chain length.

The systems were characterized at various length scales from the nanometer to the centimeter scale. Results from surface pressure isotherms suggest the formation of a colloidal network around the air bubbles, whereby the network density correlates strongly with the foamability. We determine the contact angle of the nanoparticles at the air water interface via x-ray reflectivity. Diffusing wave spectroscopy was used to probe the particles inside the foam as well as the system's temporal evolution.

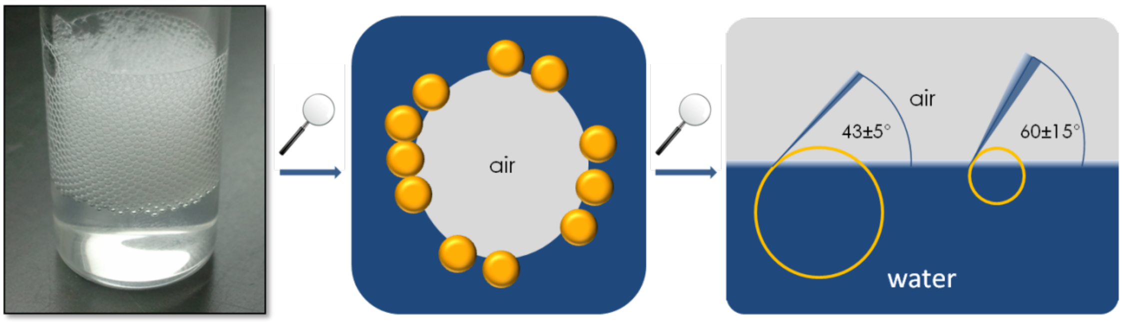

Fig. Foam stabilization by nanoparticles – a multi-scale problem

A. Carl, A. Bannuscher, R. von Klitzing (2015): "Particle stabilized aqueous foams at different length scales - synergy between silica particles and alkylamines" *Langmuir* 2015, **31**, 1615–1622.

Effect of lateral forces on adsorption and maximal coverage of nanoparticles

WARSZINSKI PIOTR

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The effect of confinement on the interactions of charged colloids is still under debate. However, there is experimental evidence that charged surfaces modifies lateral repulsion between adsorbing latex particles [1] or dendrimers. Using simple electric double layer concept based on the charge density distribution resulting from the solution of the Poisson-Boltzmann equation we evaluated electrostatic interactions between spherical particles at charged interface. We used the resulting force - distance relationships to determine the effective interaction range. Then, using the concept of the effective hard sphere diameter we evaluated the limiting coverage in the random sequential adsorption process depending on the particle size (relative to the Debye screening length), particle and interface charge and type of boundary conditions (constant charge vs. constant potential). We found that charge of the interface affects packing density of particles if κa < 5. Packing of dielectric particles depends non-monotonously on surface charge – repulsion at weakly charged surface is higher than in the bulk. High surface charge favours packing of nanoparticles.

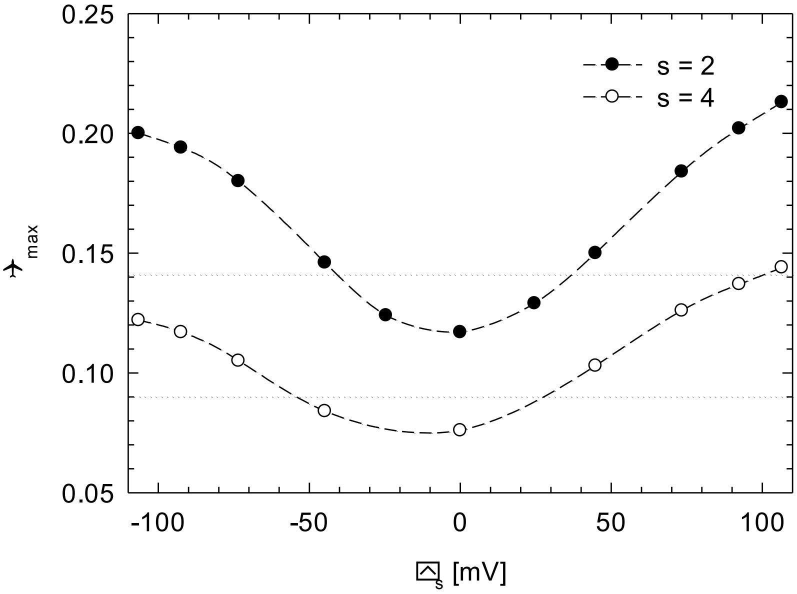

Fig. 1. The dependence of limiting coverage by charged particles on the surface potential of the interface (κa = 1 - 10 nm particles in 10^{-3} M salt solution, c.c. boundary condition, s - denotes the dimensionless value of particle surface charge).

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Weak aggregation without surfactants

KUNZ Werner

Two immiscible liquids (e.g. one polar, one apolar) can be mixed through the addition of a sufficiently high amount of a third liquid, which is miscible with both of the other liquids. This is well-known. What is much less known is the fact that such ternary, homogeneous, transparent, yet surfactant-free mixtures can exhibit structures similar to those found in classical direct, reversed, and bicontinuous microemulsions. We unambiguously characterized these structures with the help of various scattering techniques and confirmed their existence also with MD simulations. The understanding of the origin of such a structuring allows us to extend the classical, often DLVO-based picture of interfaces. Further, it has also consequences on the macroscopical behavior of these mixtures, e.g. the partial vapour pressures of the components. Even a sort of c.m.c. can be inferred from electrical conductivity and surface tension measurements in these surfactant-free mixtures.

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Final Session
General discussion
Thursday 10h30-12h30

OPEN SCIENTIFIC AND TECHNOLOGICAL QUESTIONS DRIVING :

TOWARDS A NEW COLLOID AND INTERFACES EUROPEAN NETWORK ?

Propositions :

Colloids and Interfaces for sustainable carbon-neutral energy production ?

Colloids and interacial chemistry for recycling ?

Colloids and interfaces for green chemistry processes ?

Others… ?

Round-table discussion chaired by Epaminodas Leontidis (Cyprus),

With participation of :
Regine Von Klitzing (Berlin),
Peter Kralchevsky (Sofia) ,
Piotr Warszynski (Krakow) ,
Thomas Zemb (Montpellier)

And all volontary participants bringing issues for a proposal 2016-2020

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