

# Plenary Presentations

**PL001**

**Surface Nanobubbles**

Detlef Lohse, Joost Weijs, James Seddon, Harold Zandvliet

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Various recent studies have revealed the existence of nanoscale gas bubbles on liquid- solid interfaces. For a recent review see e.g. ref. [1]. These objects – doped surface nanobubbles – typically have heights of  $\approx 10$  nm and diameters of  $\approx 100$  nm. Their experimentally found long lifetime is in flat contradiction to the classical theory of bubble stability, as the compressive action of surface tension should press out these nanoscale bubbles (due to the tremendous Laplace pressure) within microseconds.

In this talk we will present further evidence on their existence and will report their characteristics. We will also report results from our molecular dynamics simulations of these surface nanobubbles and will present a new theory which can account for the very long lifetime of the surface nanobubbles:

The limited gas diffusion through the water in the far field, the cooperative effect of nanobubble clusters, and the pinned contact line of the nanobubbles lead to the slow dissolution rate.

This is joint work with Joost Weijs, James Seddon, Harold Zandvliet, and many others.

[1] James R. T. Seddon & Detlef Lohse, J. Phys.: Condens. Matter 23, 133001 (2011).

**PL002**

**Lessons from air bubbles**

Roger Horn

*Deakin University, Melbourne, Australia*

Lord Kelvin is quoted as saying “Blow a soap bubble and observe it. You may study it all your life and draw one lesson after another in physics from it.” Yes indeed, and of course a fair amount of physical chemistry too. Surface forces, thin film drainage, white light interferometry, capillarity, surfactant adsorption and Marangoni effects, to name some. Or look at the behaviour of air bubbles in water, and puzzle over the reasons why some electrolytes inhibit bubble coalescence and others do not; surface elasticity; what “hydrophobicity” means; the origins of surface potential; and other mysteries of the air-water interface. Air bubbles in water must be one of the most ubiquitous dispersions in the world, and yet our understanding of them remains limited.

This lecture will touch on several of the phenomena listed above, though not all of them. Part of the talk will be a review of the behaviour of air bubbles, part will focus on recent results, and part will concentrate on my current preoccupation, which is the couplings between different phenomena (for example, thin film drainage and local surface charge) that give rise to complex behaviour when bubbles (or other fluid drops) interact with each other or with solid surfaces.

# **Keynote Presentations**

**KN001**

**Non-stick water**

David Quéré

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We discuss several tricks to reduce adhesion and friction of water on solids. In these ultra-hydrophobic situations induced either by texturing the solids or by heating them, water behaves differently from what it usually does and we describe several original properties of this kind. We focus in particular on the questions of air entrainment and reduced friction, which can possibly be exploited for achieving self-propelling systems.

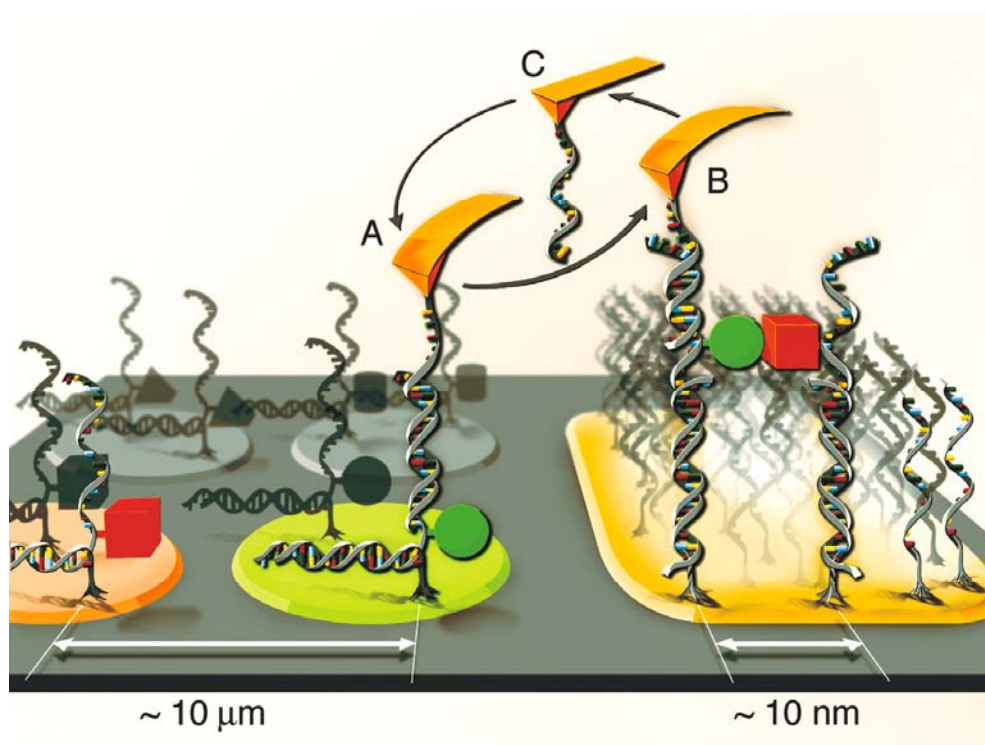
KN002

## Functional Surface Assembly by Single-Molecule Cut-and-Paste

Hermann E. Gaub

Chair for Applied Physics & Center for Nanoscience Ludwig Maximilians University, Munich, Germany

Bottom up assembly of functional molecular ensembles with novel properties emerging from composition and arrangement of its constituents is a prime goal of nanotechnology. With the development of Single-Molecule Cut-and-Paste (SMC&P) we provided a platform technology for the assembly of biomolecules at surfaces. It combines the Å-positioning precision of the AFM with the selectivity of DNA hybridization to pick individual molecules from a depot chip and allows to arrange them on a construction site one by one. An overview on different applications of this technology will be given in this talk. One recent example demonstrates the functional of receptors for small molecules. By SMC&P we assembled binding sites for malachite green in a molecule-by-molecule assembly process from the two halves of a split aptamer. We show that only a perfectly joined binding site immobilizes the fluorophore and enhances the fluorescence quantum yield by several orders of magnitude. To corroborate the robustness of this approach we produced a micron-sized structure consisting of more than 500 reconstituted binding sites. To the best of our knowledge this is the first demonstration of a one by one bottom up functional bio-molecular assembly.



S. Kufer, Puchner E. M., Gump H., Liedel T. & H. E. Gaub *Science* (2008), 319, p 594-

M. Strackharn, S.W. Stahl, E.M. Puchner & H.E. Gaub, *Nano Lett.* (2012) 12, p 2425-

M. Strackharn, D. A. Pippig, P. Meyer, S.W. Stahl & H. E. Gaub, *JACS* (2012) 134, p 15193-

**KN003**

**Hydrodynamic forces: from boundary slippage to the mechanics of soft surfaces**

Elisabeth Charlaix

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Surface forces measurements have been an invaluable tool to perform quantitative mechanical probing at a nano-scale, and have contributed to our understanding of the friction of liquids onto solid surfaces and dissipation in confined liquid layers.

But beyond the scope of friction, the measurement of nano-hydrodynamic forces has reached a precision allowing one to use them as a probe for the mechanics of soft surfaces. Direct mechanical testing of small and soft objects is indeed an unsolved problem of the nano-scale world. As surface effects become larger than volume effects, elastic forces are overcome by adhesion forces, precluding any quantitative measurements of elastic properties of soft surfaces such as ultra-thin polymer films or biologic tissues. In this talk I will show how nano-hydrodynamics can be used to measure the elasticity of nano-bubbles, or the Young modulus of thin elastomer films, opening the way toward non-contact and non-intrusive measurements of elastic properties of small and soft objects.

**KN004**

**Spatial organization and the mechanics of signal transduction at the single molecule level**

Jay T. Groves

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The T cell receptor (TCR) signaling system is able to accurately respond to input signals as small as a few individual molecules within a noisy chemical environment. At the same time, the molecular properties of individual TCR appear to lack sufficient ligand specificity or selectivity to account for the system response. In order to obtain a mechanistic understanding of such systems, methods to both manipulate and observe signaling activity down to the single molecule level in living cells are needed. I will describe a collection of such experiments in which nanopatterned supported membranes combined with various imaging strategies are enabling the first molecular-scale dissection and direct observation of antigen-triggered TCR signaling in live primary T cells. The results reveal that that signaling decisions are made locally, at the receptor cluster level. This realization has significant consequences with respect to molecular stochastic noise in cellular signaling, and these will be discussed as well.



**KN005**

**Droplet Microfluidics: Fundamentals and Applications.**

Piotr Garstecki

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Microfluidics offers techniques for precise control over creation and handling of microdroplets. The research on the design of droplet microfluidic chips have inspired a range of fundamental observations on microscale multiphase hydrodynamics. The understanding built from these studies allow to construct a portfolio of systems, including passive, automated and autonomous systems that provide useful tools for execution of experimental protocols in chemistry, biochemistry, microbiology and diagnostics.

**KN006**

## **Design and Synthesis of Conjugated Polymers for Solar cells**

Mats Andersson

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The development of plastic solar cells is of great interest due to their unique advantages, such as lightweight, potential low cost and flexibility. To be a serious alternative to silicon solar cells the efficiency must be enhanced and only earth abundant materials should be used in the cells. The development of high efficiency polymer solar cells is a challenging research task and our efforts have, during several years, been concentrated on synthesizing and evaluating new materials.

Traditionally polymers are isolating materials. To make them work in a solar cell they have to be semiconducting. Conjugated polymers are ideal for this purpose. A blend of a conjugated polymer and an electron acceptor such as a fullerene makes a suitable active material for a solar cell due to extremely fast electron transfer. The specific chemical structure of the conjugated polymer determines the bandgap and thereby at which wavelength it absorbs. Recent years, considerable effort has been put into decreasing the bandgap of the conjugated polymers with the objective to extend the absorption to longer wavelengths. Thereby, a larger part of the solar spectrum can be covered. Introduction of donor-acceptor-donor (DAD) segments in the polymer backbone, creating internal push pull systems, is one way to reduce the bandgap.

We have concentrated our efforts on synthesizing and evaluating such materials. These polymers have been specifically designed to be used together with C60 or C70 derivatives in so called bulk heterojunction polymer solar cells. One such polymer, simply consisting of thiophenes alternating with substituted quinoxaline units mixed with fullerenes, shows high efficiency. Another polymer system we have focused on is based on the isoindigo segment. A number of different polymers with varying co-monomers have been designed and synthesized showing maximum power conversion efficiencies above 6%, after the use of additives to improve the morphology in the solar cells. Inverted solar cells have also been prepared and their efficiencies could be improved by using newly synthesized, uncharged, interlayer materials.

**KN007**

**Study of Film Drainage Kinetics by Thin Film Force Apparatus**

Zhenghe Xu, Louxiang Wang, Plamen Tchoukov, Jacob Masliyah

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As a surface wettability based separation technique, Flotation has been widely used to separate minerals, upgrade fine coals and recycle valuable from industry and municipal wastes. A critical step in flotation is liquid thin film drainage and rupture to achieve a stable three phase contact. Understanding and minimizing the film drainage resistance (forces) from a moving fluid are therefore of great importance both scientifically and technologically. Despite tremendous efforts, there still exists no direct measurement of thin film drainage time under dynamic conditions until a recent development of a novel device specifically designed to measure directly the drainage dynamics of thin liquid films confined between a solid surface and an air bubble in a liquid. Equipped with a bimorph force sensor, a computer-interfaced video capture and a data acquisition system, the newly designed device allows for the direct and simultaneous measurements of force barrier, true film drainage time and bubble/droplet deformation under a well-controlled external force, receding and advancing contact angles, capillary force, and adhesion (detachment) force between an air bubble and a solid. This newly designed device is capable of measuring forces over a wide range of hydrodynamic conditions, including bubble approach and retract velocities up to 50 mm/s and displacement range up to 1 mm. The device is being integrated with the optical interferometer to direct measure the separation distance between approach bubble and a stationary solid surface and bubble profile while monitoring the film drainage rate under applied external forces.

Our study demonstrates that the liquid film drainage resistance and film drainage time can be greatly diminished or accurately controlled by increasing or controlling the hydrophobicity of solid surfaces and bubble approach velocity towards a solid surface. The results show that for a given solid surface hydrophobicity, the film drainage resistance at the point where film ruptures increases linearly with increasing bubble approach velocity. The dependence of the film drainage resistance on bubble approach velocity decreases linearly with increasing hydrophobicity of the solid surface. For a strongly hydrophobic surface of advancing contact angle above 100°, the hydrodynamic resistance is negligible up to an approach velocity of 250  $\mu\text{m/s}$  (15 mm/min), indicating a slippage boundary condition of rigid hydrophobic solid surface, which was not observed between two air bubbles.

KN008

**Self-assembly of onions induced by charge and rheological properties in anionic/nonionic surfactant solutions**

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Surface and bulk properties of mixed nonionic tetraethylene glycol monododecyl ether (C<sub>12</sub>EO<sub>4</sub>) and dialkyl anionic sodium bis(2-ethyl hexyl)sulfosuccinate (AOT) mixtures in aqueous solution were studied and self-assembly of onions (multilamellar vesicles) with uncountable bilayers induced by charge were obtained. An attractive net interaction exists between the two surfactant molecules and a negative interaction parameter values ( $\beta^m$  and  $\beta^s$ ) indicate a synergism in the non-ideal mixing behavior. Onions, i.e., the densely packed multilamellar vesicles with uncountable bilayers are directly observed in a bluish sample solution by charging the swollen nonionic lamellar phases with addition of anionic surfactant, AOT. The addition of ionic surfactants into nonionic lamellar phase, through electrostatic repulsion of the ionic headgroups, will suppress the Helfrich undulation and induce the transition from planar lamellas to vesicles. Similarly, in AOT-rich region, upon addition of the nonionic ones, the planar lamellar gel phases of AOT/H<sub>2</sub>O mixture can also be transformed into closed vesicle gel-phases due to the reduction of the Coulombic force. Rheological measurements show that both of the storage modulus (G') and the loss modulus (G'') increase with the increase of membrane charge density. Interestingly, the addition of NaCl into the mixed systems causes the phase transition from micelles to vesicles. As increasing the amount of salts, the bilayers of the lamellar phase exhibit more flexible due to the electrostatic shielding of electrolyte, along with a decrease of the solution viscosity, the G', and the G''. It is believed that the ionic charges act crucial roles in the flexibility of bilayer membranes. The obtained multilamellar architectures are facile for long-term storage of multiple components and can effectively slow their release.

References:

[1] R. Dong, J. Hao, "Complex fluids of poly(oxyethylene) monoalkyl ether nonionic surfactants", *Chem. Rev.* **2010**, *110*, 4978-5022.

[2] R. Dong, Z. Zhong, J. Hao, "Self-assembly of onion-like vesicles induced by charge and rheological properties in anionic–nonionic surfactant solutions", *Soft Matter* **2012**, DOI: 10.1039/c2sm25505g

KN009

## Self-Assembly of Amyloid Fibrils: from Single Molecule to Building Blocks for Functional Nanomaterials

Raffaele Mezzenga

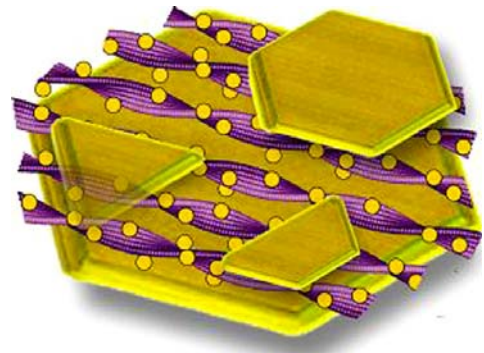
ETH, Zurich, Switzerland

Aggregation of proteins is central to many aspects of daily life, ranging from food technology and pharmaceutical science, to blood coagulation and health disorders, such as sickle-cell disease, arterial thrombosis, or eye cataract formation. In particular, association of proteins into amyloid fibrils is a highly specific process occurring both in-vivo, such as in the Alzheimer, Parkinson or prion-related neurodegenerative diseases, and in-vitro, as in the case of processed food proteins.

Recently, however, protein fibrils are emerging as unique building blocks to assist the design of functional materials in a wide range of contexts and applications. The possibility to efficiently mix them with other components, more traditionally used in the design of high-performance materials, enables new opportunities in materials science and nanotechnology.

In this talk I will discuss our recent contribution to the understanding of the association processes converting globular proteins into amyloid fibrils, and I will emphasize how these processes can be exploited to design new classes of hybrid nanocomposites in which the protein fibrils serve not only as unique building blocks, but also provide outstanding functionalities to the final hybrid materials. In particular, the talk will address how amyloid fibrils allow the reduction of inorganic salts into metal nanoparticles, which can then be used in combination with amyloid fibrils to generate hybrids nanocomposites with targeted functionalities.

I will discuss how the resulting nanocomposites can serve fields as diverse as food science, biomaterials, biosensors and optoelectronics, simply by changing the constituent building blocks, and I will illustrate this via relevant examples given for each specific category of the above-mentioned fields. Emphasis will be placed on nanocomposites made of  $\beta$ -lactoglobulin and lysozyme fibrils, since these two proteins are non-toxic (e.g. food-grade) and have both fundamental and practical relevance. Furthermore, by varying the processing conditions, these proteins can be converted into fibrils of varying structures and properties, such as semiflexible protofilaments, multistranded twisted ribbons and helical ribbons, which, once mixed with other inorganic or organic components, allow a very accurate control on the final mechanical and functional properties of the resulting nanocomposites.



### References

1. "Understanding amyloid aggregation by statistical analysis of atomic force microscopy images" Adamcik, J. et al., *Nature nanotechnology*, **2010**, 5, 423.
2. "New biocompatible thermo-reversible hydrogels from PNIPAM-decorated amyloid fibrils". Li, C. et al. *Chem. Comm.* **2011**, 47, 2913.
3. "Amyloid Fibrils assisted synthesis of TiO<sub>2</sub> nanowires and their role in photovoltaic applications". Bolisetty, S. et al. *Adv. Funct. Mater.* **2012**, 16, 3424.
4. "Biodegradable Nanocomposites of Amyloid Fibrils and Graphene with Shape Memory and Enzyme Sensing Properties" Li, C. et al. *Nature nanotechnology*, **2012**, 7, 421.
5. "Protein Fibrils from a Polymer Physics Perspective" Adamcik, J.; Mezzenga, R.; *Macromolecules*, **2012**, 45, 1137.

**KN010**

**Stimulus-Responsive Endoskeleton Droplets**

Patrick T. Spicer

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The delivery of suspended active ingredients from a carrier fluid to a surface is the central function of commercial drug formulations, shampoos, detergents, cosmetics, and pesticides. Successful delivery of a particle to a surface requires transport of the particle sufficiently near to allow contact and adhesion. Once deposited, the particle should remain there even if flow continues. Solid particle shape has been found to enhance adhesion and uptake during drug delivery, while subsequent shape-change improves targeting and selectivity, but many actives are delivered by liquid droplets. We have designed a droplet to optimize adhesion, retention, and delivery by blending the shape-preserving and shape-changing properties of a solid particle with a liquid's ability to wet a surface and deliver active ingredients via diffusion: a stimulus-responsive endoskeleton droplet. Endoskeleton droplets with a rod shape enhance delivery from a flow by increasing collision probability for a given volume, possess a true liquid surface that favors adhesion, and can change shape after contact to better grip the targeted surface and avoid wash-off. Endoskeleton droplets have been produced using microscopic methods that make partially molten emulsion droplets, mold them via deformation, and then cool them to crystallize and preserve the deformed shape. The stability of the endoskeleton droplets' shape is the result of a balance between the elasticity of an internal crystalline network and the Laplace pressure exerted by the liquid-liquid interface. Upsetting the balance of forces by environmental stimuli, such as melting, can trigger shape change and improve contact with a targeted surface. Anisotropic droplets that selectively change shape can improve adhesion to targeted surfaces and access more complex droplet shapes via controlled collapse and arrest during heating.

KN011

## Synthesis of Nanoparticles for Catalytic Applications

Richard Tilley

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Liquid phase synthesis is a powerful method for the formation of uniform sized nanoparticles and nanoparticles with a faceted morphology. General strategies for the formation of nanoparticles and through chemical synthesis will be outlined. The results presented will include the formation of catalytic metals such as gold core palladium shell nanoparticles, below and magnetic nanoparticles and silicon and germanium quantum dots. The growth mechanism of how the particles form will also be presented along with HRTEM observations. Biomedical and catalytic applications will be discussed.

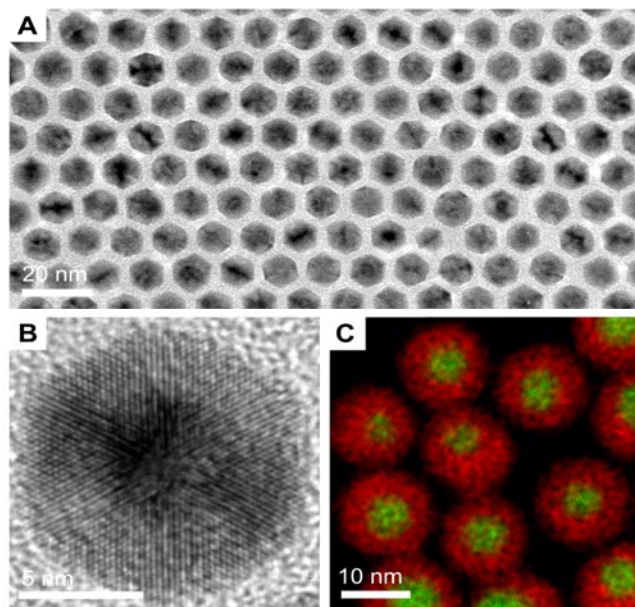


Fig. 1. Faceted Au-Pd core-shell nanocrystals. (A) Bright field TEM image of an ordered array of highly faceted Au-Pd core-shell nanocrystals with an average size of 11.4 nm. (B) High-resolution TEM image of a single Au-Pd core-shell nanocrystal, with contrast difference between the dark core (gold) and lighter shell (palladium). Lattice fringes correspond to an icosahedral structure oriented along  $\langle 111 \rangle$ . (C) STEM-EDX map shown as an overlay of gold and palladium signal, confirming the core-shell structure of the Au-Pd nanocrystals.

**KN012**

## **Colloidal Processing of Porous Adsorbents**

Lennart Bergström, Farid Akhtar

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Porous ceramics are used in numerous applications ranging from catalyst supports and gas sorbents to particulate filters for diesel engines. The use of adsorbents in gas separation processing including post combustion CO<sub>2</sub> capture requires that the microporous adsorbent particles are assembled into strong hierarchically porous macroscopic bodies that allow a rapid uptake and release. We will give examples how the hierarchical porous structure can be controlled by combining colloidal approaches, including sacrificial templating and freeze casting, with the use of novel consolidation methods. The resulting structures have been characterised with a combination of electron microscopy, porosimetry and X-ray tomography and the materials have been evaluated with respect to mechanical strength and chemical durability. Examples on how the pore size distribution can be engineered will be shown together with data on the selectivity and total uptake of carbon dioxide.

### References:

L. Andersson, A. C. Jones, M. A. Knackstedt and L. Bergström, "Permeability, pore connectivity and critical pore throat control of expandable polymeric sphere templated macroporous alumina", *Acta Materialia* 59, 1239-1248, (2011).

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P. Vasiliev, F. Akhtar, J. Grins, J. Mouzon, C. Andersson, J. Hedlund and L. Bergström, "Strong Hierarchically Porous Monoliths by Pulsed Current Processing of Zeolite Powder Assemblies", *ACS Appl. Mater. Interfaces*, 2, 732-737 (2010).

F. Akhtar, Q. Liu, N. Hedin, L. Bergström, "Strong and binder free structured zeolite sorbents with very high CO<sub>2</sub>-over-N<sub>2</sub> selectivities and high capacities to adsorb CO<sub>2</sub> rapidly", *Energy & Environmental Science*, 5, 7664-7673 (2012)



# **Invited Presentations**

IN001

## From Surface Controlled Cavitation to Ultrasonic Surface Treatment

Helmuth Möhwald<sup>1</sup>, Valentina Belova<sup>1</sup>, Ekaterina Skorb<sup>1</sup>, Adam Brotchie<sup>1</sup>, Dmitry Shchukin<sup>1</sup>, Carlos Cairós<sup>2</sup>, Robert Mettin<sup>2</sup>, Marta Krasowska<sup>3</sup>, Dayang Wang<sup>3</sup>, John Ralston<sup>3</sup>

<sup>1</sup>Max Planck Institute of Colloids and Interfaces, Potsdam, Germany, <sup>2</sup>Univ. Göttingen, 3rd Physical Inst., Göttingen, Germany, <sup>3</sup>Ian Wark Inst., Univ. South Australia, Mawson Lakes, Adelaide, Australia

Ultrasound is increasingly used for surface treatment, but less frequently is the surface itself used to control sonochemistry. This is shown in this contribution where chemical patterning is demonstrated as a means to control cavitation.<sup>1/1</sup> By scanning force microscopy it is shown that nanobubbles are formed predominantly on hydrophobic patches. Highspeed microscopy reveals that microbubbles are formed on these areas, and also that the ensuing violent collapse predominates there. This will be quantified as a function of solvent and sonication time and interpreted within a model of heterogeneous nucleation.

The transient high pressures and temperatures following bubble collapse can be used to form mesoporous surfaces, and for selected solvent composition this holds even for hard materials. This enables loading of drugs and coupling with polymers in one step which in turn leads to responsive and self-repairing coatings.<sup>2,3</sup>

/1/ D.G. Shchukin, E.V. Skorb, V. Belova, and H. Möhwald: Adv. Mater.23 (2011) 1922

/2/ D.V. Andreeva, D.V. Sviridov, A.Masic, H.Möhwald, and E.V. Skorb: Small 8 (2012) 820

/3/ J. Gensel, T.Borke, P.N. Perez, A. Fery, D.V. Andreeva, E. Betthausen, A.H.E. Müller, H. Möhwald, and E.V. Skorb: Adv.Mater.24 (2012) 985

**IN002**

## **Dynamic Wetting with Dilute Polymer Solutions**

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The moving contact line of a dilute polymer solution that advances over, or recedes from a solid substrate, is a fundamental problem of fluid dynamics with important practical applications, including coating and thin film deposition processes, sprays, bio- and micro-fluidics. Experiments show that while the advancing motion proceeds as with Newtonian liquids, recession is severely inhibited. This phenomenon was initially understood as an effect of elongational viscosity, which was believed to cause large energy dissipation in the fluid hence reducing the recoil velocity of the drop on the impact surface. However, independent experiments ruled out elongational viscosity, and suggested this phenomenon is related to the dynamic wetting behaviour of dilute polymer solutions.

Later on, it was proposed that non-Newtonian normal stresses generated near the moving droplet edge represent the true cause of the slowing down of the contact line. However, this approach is against experimental evidence showing that the velocity reduction of the contact line is accompanied by a similar reduction of the apparent contact angle; in fact, the action of normal stresses, perpendicular to the surface, would be expected to increase the contact angle. Despite this conceptual inconsistency, and other flaws, this approach seems to receive a growing consensus within the scientific community.

Here, we report some recent experiments on the behaviour of dilute polymer solution drops impacting on hydrophobic surfaces, with the purpose to shed light on the related dynamic wetting phenomena. In particular, we present systematic investigations of the dynamic contact angle, of the velocity field inside the impacting droplet, and of the polymer dynamics in the vicinity of the contact line, under different experimental conditions.

In the first experiment, the apparent dynamic contact angle during the retraction stage after maximum spreading is measured for water and polymer solution drops at different polymer concentrations. Results show that the additive causes a dramatic reduction of the transient contact angle during drop retraction, even if the difference between the final equilibrium values is almost negligible. This suggests that a transient force is exerted on the contact line, opposing its receding movement.

In the second experiment, the fluid velocity inside the impacting drop is analysed by epifluorescent particle tracking, both during the inertial spreading on the target surface and during the subsequent retraction stage. The comparison between drops of pure water and polymer solution drops shows that the fluid velocity is almost identical, which excludes any elongational viscosity effects in the drop containing the polymer.

Finally, in the third experiment the behaviour of polymer molecules near the contact line of impacting drops is investigated by direct visualisation of fluorescently stained  $\lambda$ -DNA molecules, which exhibit the same qualitative behaviour of synthetic polymers such as PEO, but are large enough to be visualized by optical microscopy. It is shown that as the drop edge sweeps the substrate, molecules at the contact line are stretched in a manner similar to other DNA stretching methods such as molecular combing or air blowing techniques. This suggests that the entropic resistance to extension and the hydrodynamic drag of water molecules associated with the polymer chains resist the retraction, slowing the motion of the drop edge.

IN003

## Shedding of Drops in Freezing Conditions from Superhydrophobic Surfaces

Thomas Bauer<sup>2</sup>, Alidad Amirfazli<sup>1,2</sup>

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Shedding of water drops placed on superhydrophobic surfaces (surface temperature  $-8^{\circ}\text{C}$ ) inside a wind tunnel (air temperature  $-4^{\circ}\text{C}$ ) was studied by means of high-speed imaging. Six different superhydrophobic surfaces were used in this investigation (the surfaces ranged from commercially available coatings to various coatings produced in-house). After placing the drops on a cold surface, the air speed was increased and the shedding of the drops was observed to determine the air speed at which the drop will shed. Also, contact angles at the upstream (minimum/receding contact angle) and downstream (maximum/advancing contact angle) positions were measured. Baseline experiments were also conducted (identical protocol) where neither the surface nor air was cooled, i.e. room temperature condition. It was found that in room condition, drops shed very easily at air velocities between 0.7 and 7 m/s, depending on the surface tested (this conforms to our results from an earlier study as well, i.e. A.J.B. Milne and A. Amirfazli, "Drop shedding by shear flow for hydrophilic to superhydrophobic surfaces", *Langmuir*, 25, 14155–14164, 2009). However, in freezing conditions the required shedding air velocities rose for all surfaces investigated; depending on the surface, the air speed increased between 1.5 and 6 times the velocity for room temperature conditions. Both minimum and maximum contact angles were measured to decrease as well for all surfaces in cold compared to room temperature conditions (minimum/receding contact angle decreased from 7 to 60%; whereas maximum/advancing contact angle decreased from 4 to 30%). Also, not all drops shed from cold surfaces, some were stuck and froze. Timing of drop placement did not appear to have a major influence on whether a drop might shed, as in some cases the drop with the shortest time on the cold surface would be the only one to freeze. Surface conditions (condensation and ice creation on the surfaces) as well as airflow seem to have a larger influence.

IN004

## Kinetics of evaporation of sessile droplets: pure liquids, surfactant solutions, nanofluids

Victor Starov

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We showed that the proportionality of the total evaporation flux to the perimeter of the sessile droplet has nothing to do with the local flux increase in a vicinity of the three phase contact line but is a consequence of properties of governing equations. Computer simulations of the instantaneous flux at evaporation of sessile droplets are carried out in a self consistent way by considering an interconnected problem of vapour transfer, heat transfer in vapour, liquid and solid substrate, and Marangoni convection inside the liquid droplet [1]. The influence of thermal conductivity of the solid support on the evaporation process is evaluated. We present a theory describing the evaporation of sessile water droplets in presence of contact angle hysteresis [2]. Predicted universal dependences curves are validated against available in the literature experimental data. Experiments on evaporation of sessile droplets of water-based solutions of surfactant SILWET L77 are performed for different ambient temperatures, values of relative air humidity in experimental chamber, and surfactant concentrations. Instantaneous heat and mass fluxes in the system are calculated, giving us the information about the evaporation rate,  $J$ , as a function of contact angle,  $\theta$ , and contact line radius,  $L$ . Based on this dependence we modelled the evolution of the droplet's shape for two specific modes of evaporation: (I) pinned droplet; and (II) constant receding contact angle. Results of computer simulations are validated against obtained experimental data. It is observed that if surfactant concentration is above the critical aggregation concentration (CAC), i.e. when the surface tension of the solution does not depend on surfactant concentration, then evaporation proceeds in accordance with above described two regimes of evaporation (I) and (II). If the concentration is below CAC, then stage (II) with constant receding contact angle is not observed. Nanofluids are an ever growing topic in modern research due to their unique properties. The influence of nanoparticles have on the wetting properties of fluids has been the subject of increasing interest recently [3]. One of the interesting observations made is that nanofluids may enhance wetting of a nanosuspension as compared to the pure fluid [4]. However, in spite of the importance the wetting properties of nanofluids to be understood. The influence of nanoparticles on spreading of nanofluids over solid surfaces of variable wettability has been investigated experimentally, using 'drop shape' analysis technique. In our studies we used organic (original and modifies polystyrene latex) and inorganic (titanium, silica, carbon) nanoparticles with a range from 10 to 250 nm. We investigated kinetics of spreading of nanosuspensions over surfaces of different hydrophobicity such as silicon wafers, polypropylene, Teflon. Kinetics of spreading of nanosuspensions was investigated using a pure water and solutions of different ionic strength. Our results show that nanoparticles suspended in water has influence of spreading over difference surfaces as compared to the pure water. **References.** [1] S. Senemov, V.M. Starov, R.G. Rubio, M.G. Velarde. *Colloids&Surfaces A*, (2010) **372** (1-3), 127-134. [2] S. Semenov, V.M. Starov, R.G. Rubio, H. Agogo, M.G. Velarde. *Colloids&Surfaces A*, (2011), submitted for a publication. [3] Khellil Sefiane, Jennifer Skilling, Jamie MacGillivray. Contact line motion and dynamic wetting of nanofluid solutions. *Advances in Colloid and Interface Science* 138 (2008) 101–120. [4] K. Sefiane, R. Bennacer. Nanofluids droplets evaporation kinetics and wetting dynamics on rough heated substrates. *Advances in Colloid and Interface Science* 147–148 (2009) 263–271.

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IN005

## From Dewetting Liquids to Sticking Geckos: Insight into the Power of van der Waals

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The stability of thin liquid films, the unspecific adsorption of molecules or cells to a wall as well as the adhesion of bacteria or geckos - these diverse systems have in common that they are governed by the interplay of short- and long-range (van der Waals) forces.

For an effective control, however, a thorough understanding of the fundamentals is necessary. Is it for instance of importance, whether a liquid beads off of a silicon wafer with a thin or a thick silicon oxide layer? If e.g. an antibacterial coating of some nanometer thickness is prepared on different substrates, will it always be antibacterial? In other words, is only the surface of two adhering bodies responsible for the adhesive strength?

Our studies show that also the subsurface compositions of the interacting materials play an important role (1-6). To separate the surface from the subsurface effect and to allow for a controlled variation, we performed experiments with tailored Si wafers (variable Si dioxide layer thickness, variable surface coating) as substrates (4). Adhesion measurements were e.g. conducted by scanning probe microscopy (SPM) in force spectroscopy mode (2). Protein adsorption was monitored by ellipsometry, X-ray and neutron reflectometry (3). For the dewetting studies (6), the SPM was used.



In the various set-ups and the different systems, the same trend is recorded: The long-range van der Waals forces, which make up for the subsurface force contribution, have to be taken into account. Therefore - adhesion is not only superficial!

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**IN006**

## **Adsorption layers, foam films and foams stabilized by protein/surfactant mixtures**

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Foams appear in everyday life in many situations, such as at the sea side or in rivers, on top of a beer, during dish washing. Food and beverages provide extra pleasure when aerated, and frothed milk and cappuccino are popular examples. Foams are hierarchical systems, consisting of foam bubbles in contact with each other. In the contact regions, foam films are formed and play the dominating role for the existence of foam. In turn, foam films (lamellae) consist mainly of surfaces. The two sides of a foam film, the two adsorption layers of the stabilizing surfactant, polymers, or their mixtures, are separated by a thin liquid layer. In contrast to adsorption layers, in such foam films normal forces act in addition to lateral forces along the surface.

The state of art in this scientific field is such that there is good basic knowledge on each of the hierarchical levels, however, relationships in between these levels are in a rather immature state. A question on the properties a surfactant should have to form a stable foam film cannot be answered easily. There is also no simple correlation between the properties of foam films and the stability of real foams. And although it is one of the most frequently asked questions – with which surfactant we can produce foam of desired properties – it cannot be answered in a general way.

The presentation will deal with the state of art of characterizing adsorption layers, foam films, and foams, and possible correlations between them. The focus will be on the experimental possibilities for such studies. For adsorption layers the experimental methods are mainly based on single drops and bubbles [1]. The dynamics and thermodynamics of adsorption layers and their mechanical interfacial behaviour can be measured by drop/bubble profile and capillary pressure tensiometry and provide a broad data basis for a comprehensive characterization of the interfacial layers. Tools for studies of foam films are much more sophisticated and are mainly performed with interferometric methods. Since recently, also an instrument for the quantitative investigation of two bubbles in direct contact is available (Drop Bubble Micro Manipulator DBMM) which, combined with a fast video technique, can provide new information on the breakdown of films and even the dynamic aspects can be analyzed quantitatively [2]. Finally, foams can be formed and studied in many different ways. There are even historical well defined protocols like the Ross-Miles Test still in practice. The data resulting from such standard methods unfortunately do not provide sufficient information for a direct correlation with film or even adsorption layer properties, so that new tools for foam characterization are required.

In addition to the experimental tools also the theoretical side of the scientific problems have recently been dealt with intensively. Besides phenomenological models, quantitative thermodynamic theories were developed, essentially for surfactant and mixed protein/surfactant solutions. Great progress was made also by various types of simulations, including molecular dynamics (MD) and computational fluid dynamics (CFD), leading to a more accurate understanding of interfacial properties, relevant for the given target – improvement of the understanding of the many, typically very dynamic elementary processes in foams and their interrelations.

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## Formation of N719 Dye Multilayers on Dye Sensitized Solar Cell Photoelectrode Surfaces

Gunther Andersson<sup>1</sup>, Lilian Ellis-Gibblings<sup>1</sup>, Viktor Johansson<sup>2</sup>, Rick Walsh<sup>3</sup>, Lars Kloo<sup>2</sup>, Jamie Quinton<sup>1</sup>

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<sup>3</sup>The Australian National University, Canberra, ACT, Australia

The structure of the dye layer adsorbed on the titania substrate in a dye-sensitized solar cell is of fundamental importance for the function of the cell, since it strongly influences the injection of photoelectrons from the excited dye molecules into the titania substrate. The adsorption isotherms of the N719 ruthenium-based dye were both determined with a direct method using the depth profiling technique Neutral Impact Collision Ion Scattering Spectroscopy (NICISS) and with the standard indirect solution depletion method. It is found that the dye layer adsorbed on the titania surface is laterally inhomogeneous in thickness and growth already from low coverage levels involving a combination of monolayers and multilayers as shown in the concentration depth profile in figure 1. It is also found that the amount of N719 adsorbed on the substrate depends on the titania structure, i.e. is different for nanoporous titania and atomic layer deposited (ALD) titania. The present results show that dye molecules in dye-sensitized solar cells are not, as presumed, necessarily adsorbed as self-assembled monolayer on the substrate.

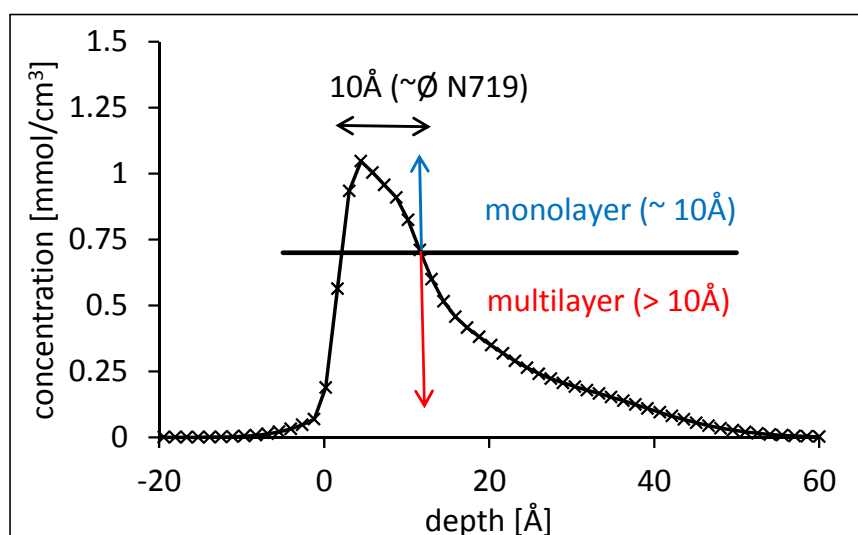


Figure 1: The figure shows the concentration depth profile of the sample immersed into the 0.3 mM N719 dye solution. The measured profile is deconvoluted and corrected for the spherical nature of the substrate. The profile shows that a fraction of the surface is covered with a monolayer of the dye (region with a thickness  $< 10 \text{ \AA}$ , fraction indicated with the upper arrow) and a region with multilayers (region with a thickness  $> 10 \text{ \AA}$ , fraction indicated with the lower arrow). The choice of  $10 \text{ \AA}$  for separating mono- and multilayer is to some degree arbitrary.



**Role of Ions on Silica Surfaces in nano-Friction and nano-Wear**

Ko Higashitani

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Molecular-scale understandings of the normal and lateral interactions between colloidal surfaces and the corresponding wear in electrolyte solutions are fundamentally important not only from the scientific point of view, but also in the development of the leading-edge technologies used for advanced materials, such as the technology to achieve the molecular-scale flatness in the chemical mechanical polishing (CMP). We have carried out a series of experiments of the normal and lateral force interactions and the nano-

wear of silica surfaces in various electrolyte solutions of mono-, di- and tri-valent cations by using an atomic force microscope (AFM), and tried to clarify the mechanism where all the data are systematically correlated to each other. This is the overview of our results on the effects of the type of electrolytes and the solution pH on the normal and lateral force interactions and the nano-wear, and how they are correlated with the nano-structure of silica surface in solutions. As for the friction, it is found that the characteristics can be classified into four types, as shown in Figure 1. The details will be discussed in the presentation. The specific effects of  $\text{CaCl}_2$  and anions will be also discussed.

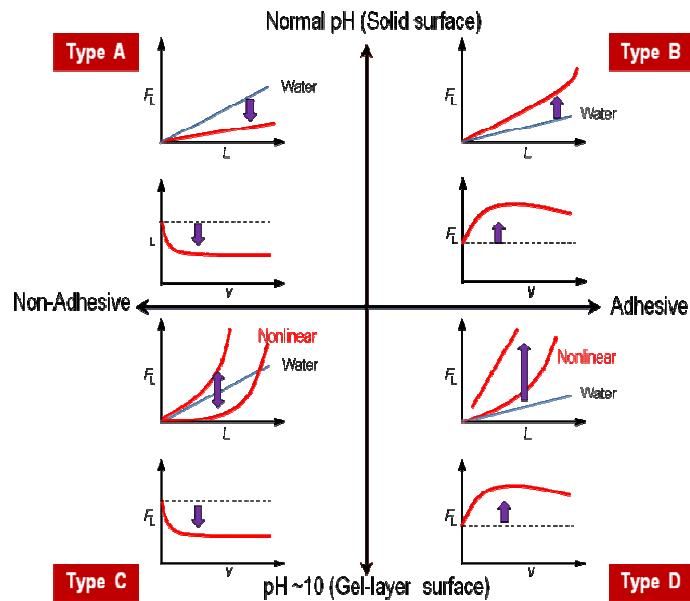


Fig. 1 Classification of types of lateral (friction) force characteristics

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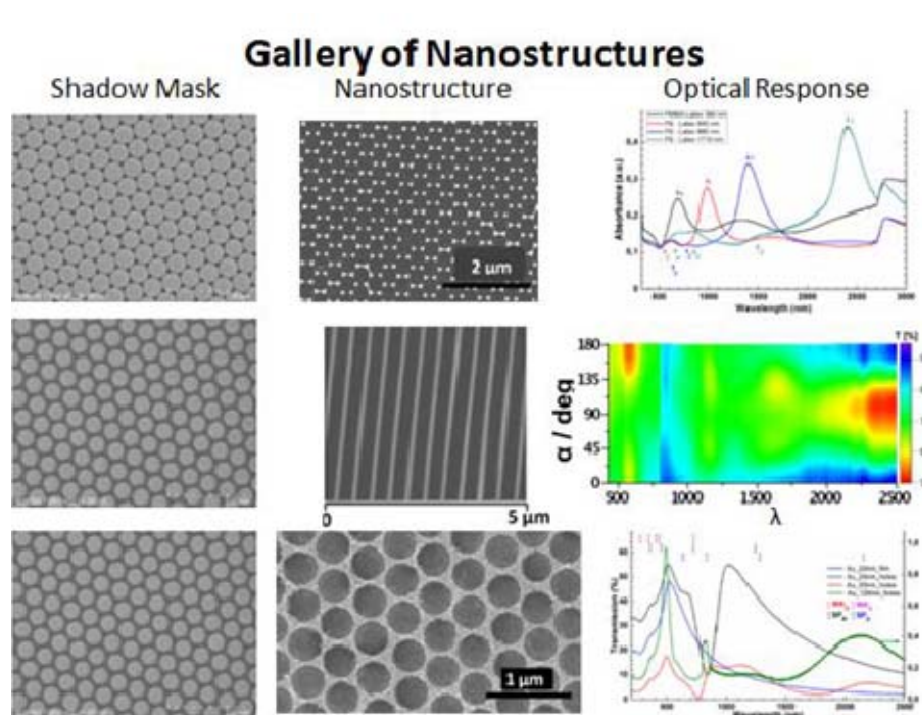
## IN009

### Electromagnetic waves interaction with various metallic nanomaterials

Michael Giersig

Freie University Berli, Brlin, Germany

In the last decade the possibility of active interaction of light with the nanosized plasmonic materials has seen tremendously growth. The metallic nanoparticles can effectively confine the radiation to nanoscale in the proximity of Plasmon resonance whereby the position of this resonance is controlled by the morphology (size and shape) of the nanostructures. In this lecture we will discussed the physical and chemical preparations methods of various nanostructures and their structural and optical characterization.



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# **Oral Presentations**

**OC101**

**Spreading Films, Fingering Instabilities and Soliton-Like Wave Propagation Triggered by High Frequency Surface Vibration**

Amgad Rezk, Ofer Manor, James Friend, Leslie Yeo

*RMIT University, Melbourne, VIC, Australia*

We unravel the mechanisms underpinning a collection of wetting phenomena recently observed in which a thin viscous film, with thickness on the order of 10 microns, is drawn out from a sessile drop by Rayleigh waves propagating on a piezoelectric substrate in the form of 10 MHz order surface acoustic waves. Quite peculiarly, the thin film advances in a direction opposing that of the surface wave propagation. The film subsequently suffers from a transverse instability to form fingering patterns above which soliton-like wave pulses are observed to grow and translate in the opposing direction. In addition to deriving a dynamic spreading model, we show the competing influence of the various acoustic streaming mechanisms at different length scales that are responsible for the flow reversal observed by the advancing film front and the solitary wave pulses.

**Drop Impacts on Dry Surfaces: Wettability and Microstructure**Geoff Willmott<sup>1,2</sup>, Michael Taylor<sup>3</sup>

<sup>1</sup>Industrial Research Limited, Wellington, New Zealand, <sup>2</sup>The MacDiarmid Institute for Advanced Materials and Nanotechnology, Wellington, New Zealand, <sup>3</sup>Institute of Environmental Science and Research, Christchurch, New Zealand

The beautiful and ubiquitous drop impact phenomenon has a long and rich scientific history. Like many other traditional fields, there has been renewed interest of late, driven by the prospect of fine control using materials that are physically and chemically engineered on micro- and nanoscales. This work can be viewed as an extension of microfluidic drop manipulation to higher Weber and Reynolds numbers.

Studies of impacts onto dry surfaces have usually ignored the influence of the surface itself, either because inertial motion initially dominates the dynamics of a spreading lamella, or because inhomogeneities give rise to complex spreading, splashing and deposition behaviours that can preclude fundamental understanding. In the course of recent complex surface research [1], impacts onto very water-repellent superhydrophobic surfaces (SHSs) have gained prominence. SHSs combine microstructural roughness with chemical hydrophobicity, and they can additionally be ordered, hierarchical and/or biological in origin.

In this presentation, the role of wettability in drop impacts will be discussed, particularly in the context of SHSs. High speed-photography experiments using synthetic and biological SHSs will be presented, with consideration of theory pertaining to drop dynamics on SHSs. Non-wetting substrates impart relatively low viscous losses to the spreading lamella. Contact line adhesion is dependent on pinning at surface asperities, and therefore brings both microstructure and dynamic contact angle hysteresis into play. These properties give rise to a particularly wide range of drop retraction and bouncing behaviours, including recent observations of drop symmetry-breaking [2].



Figure: A drop falling and bouncing on a thiolated copper-silver superhydrophobic surface, with time labelled in ms.

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## Design of Nanoparticle Assemblies with Hierarchical Roughness to Produce Superhydrophobic Surfaces

Andrew M. Telford<sup>1</sup>, Brian S. Hawkett<sup>1</sup>, Christopher H. Such<sup>2</sup>, Chiara Neto<sup>1</sup>

<sup>1</sup>The University of Sydney, NSW, Australia, <sup>2</sup>Dulux Group, VIC, Australia

**Introduction:** In this work, we propose to assemble and covalently bind polymeric particles of two different sizes to produce raspberry-like constructs, to be used as a base for superhydrophobic coatings with high roughness.[1] Raspberry particles have been employed before to produce surface with very low wettability,[2] but the focus of this work is on the preparation of the hierarchical particles from scratch, through polymerization and self-assembly. Due to this universal approach, our novel platform is very versatile and potentially up-scalable.

**Methods:** Polystyrene microparticles, approx. 1  $\mu\text{m}$  in diameter, were obtained by surfactant-free emulsion polymerization, while polystyrene nanoparticles, approx. 100 nm in diameter, were prepared by conventional emulsion polymerization. 4-4' azobis(cyanovaleric acid) (V501) was used to obtain charged carboxylic acid residues on the surface of the particles. The particles were characterized by dynamic light scattering (DLS), and transmission and scanning electron microscopy (TEM and SEM). EDC (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide) coupling was used to covalently bind the carboxylic acid residues on the nanoparticles to the residues on the polystyrene microparticles, via linkers with multiple amine groups.

**Results:** Polystyrene particles of approx. 1  $\mu\text{m}$  and 100 nm, with narrow size distribution and bearing carboxylic acid groups, were successfully synthesised, as confirmed by DLS, SEM, TEM and surface acid-base titration. Two different linkers were employed to assemble raspberry-like particles: the short 2,2'-(ethylenedioxy)bis(ethylamine) and the polymeric poly(allylamine) hydrochloride (PAH). In the first step, the microparticles were functionalized with the amine linker. Electrokinetic measurements and IR spectroscopy confirmed the functionalization, showing a charge reversal on the surface of the particles, and the presence of amine groups. In the second step, the amino-functionalized microparticles were coupled with the carboxylated nanoparticles using EDC coupling. The successful assembly of raspberry-like particles was confirmed by SEM (Fig. 1). Thin films of the synthesised raspberry-like particles exhibited high water contact angles, up to 150°, yet the water droplet would remain adhered to the surface upon up to 180° inversion.

**Conclusions:** We introduce a novel approach to obtain superhydrophobic surfaces with hierarchical roughness, exhibiting high water droplet adhesion. The properties of the films can be tailored by preparing particles with different size, by changing the experimental conditions of the emulsion polymerizations used. This approach is substrate-independent, up-scalable, and versatile, as it potentially allows the use of any particle bearing carboxylate surface groups.

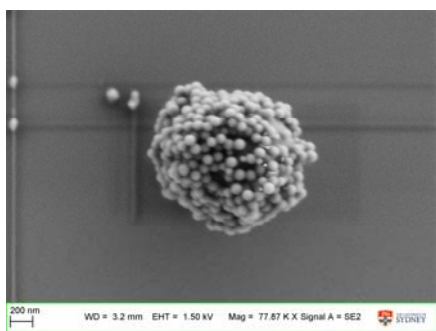


Figure 1. SEM image of a raspberry-like particle composed of 1  $\mu\text{m}$  core particle and 100 nm corona particles.

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**Thin Film Drainage between Micro-drops and Micro-bubbles under Applied Cyclical Drives to Mimic Micro-fluidic Pumping Scenarios**

Raymond Dagastine<sup>1,4</sup>, Rico Tabor<sup>2,1</sup>, Chu Wu<sup>1</sup>, Franz Grieser<sup>1</sup>, Derek Y.C. Chan<sup>1,3</sup>

<sup>1</sup>*Particulate Fluids Processing Centre, University of Melbourne, Parkville, Victoria, Australia,* <sup>2</sup>*School of Chemistry, Monash University, Clayton, Victoria, Australia,* <sup>3</sup>*School of Life and Social Sciences, Swinburne University of Technology, Hawthorn, Victoria, Australia,* <sup>4</sup>*Melbourne Centre for Nanofabrication, Clayton, Victoria, Australia*

Our research has focused on the development of innovative methods to quantitatively study the nano-scale thin films between micro-drops(1) or micro-bubbles(2) during their collision and coalescence. The forces that control these collisions are crucial for understanding applications as wide ranging as purification steps in mineral and pharmaceutical processing to emulsion and foam stability in food and personal care products as well as micro-fluidic devices. Previously, we have developed experimental and theoretical methods developed to study the dynamic interactions between two drops or bubbles using Atomic Force Microscopy (AFM) for single collisions. The agreement between experimental measurements and the quantitative modelling of the thin film drainage between deformable drops and bubbles has shown that the governing physics is dependent on a combination of equilibrium surface forces, hydrodynamic drainage forces and interfacial deformation at a wide range of collision speeds and varied solution conditions. Both experimental measurements and quantitative modelling have been able to shed light on behaviour as diverse as the charging mechanism for drops and bubbles to counter-intuitive observations in micro-fluidic devices such as coalescence of drops on separation.

This talk will focus on what we can learn from the direct force measurement of sequential collisions of pairs of micro-drops or micro-bubbles in order to mimic pumping conditions in micro-fluidic devices. A number of diverse velocity drive profiles were used to drive to drops together with repeated collisions including waveforms for sinusoidal, peristaltic and diaphragm pumping. In most cases, it was shown that when equilibrium interactions of the drops were in a meta-stable state, small perturbations in pumping conditions could cause drop coalescence. This was further probed through using simple constant velocity approach and retract cycles where the approach and retract velocities were varied independently. Agreement between quantitative modeling of these collisions and the experimental measurements allows for visualization of the thin film and pressure profiles during these processes. In addition, the validated model was then used to produce drop stability maps as a function of pumping condition parameters.

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## Probing Biomolecular – Polymer Interactions under Electrical Control using AFM

Amy Gelmi<sup>1</sup>, Peter Knittel<sup>1,2</sup>, Christine Kranz<sup>1,2</sup>, Gordon Wallace<sup>1</sup>, [Michael Higgins<sup>1</sup>](#)

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**Introduction:** To effectively communicate with single living cells, we need to interface, or “plug-in”, the artificial circuitry to molecular components of the cell such as lipid membranes, ion channels and protein-receptors. This will require a deep understanding of the cellular–electrode interface. A way forward will be to use nanometer-sized probes to measure the electrical signals, chemical interactions, and forces responsible for transmitting information at the interface. With organic conductors such as graphene and conducting polymers emerging as electrode materials in biological environments, the prospect of interrogating their interactions with living cells at nanoscale and molecular dimensions is very exciting. The presentation will highlight the design and fabrication of protein functionalized probes and nanoelectrodes integrated into Atomic Force Microscopy (AFM) tips, which have been used to resolve sub-molecular interactions at the bio-electrical interface.

**Methods: Atomic Force Microscopy: Single Protein Molecule – Polymer Interactions under Electrical Control.** To understand the interaction of fibronectin with conducting polymers, we have functionalized AFM probes to directly measure the interaction forces between fibronectin and conducting polymer electrodes with incorporated extracellular matrix components such as hyaluronic acid and chondroitin sulfate. These measurements have been performed using *in situ* electrochemical AFM to study the fibronectin-polymer interaction in response to changes in the surface charge and surface energy of the polymer electrode upon electrical stimulation.

**Design and Fabrication of Integrated Electrode AFM Probes.** The presentation will also highlight the design and fabrication of conducting polymer nanoelectrodes integrated into AFM tips, which are used to directly probe the surface of single living cells. We will discuss the use of Focused Ion Beam for exposing different nano-sized gold electrode designs that provide a template for electropolymerization of novel conducting polymer structures.

**Results:** The presentation will highlight several major findings including the ability to resolve single fibronectin protein interactions with the polymer. For example, differences in the conformation, unfolding force profiles and binding probabilities of the protein as a function of the surface chemistries of the polymers and electrical stimulation are observed in the force spectroscopy experiments. In regards to work carried out with integrated nanoscale electrode AFM probes, we will demonstrate how these AFM tips are brought into contact with substrates and single living cells to directly measure the interaction forces at the electrode-cell interface. Importantly, the effect of electrical signals applied through the AFM tip on the interaction (adhesive) forces and cellular response will be shown.

**Discussion:** This work opens up the possibility to explore a range of protein and cellular interactions with conducting polymer materials at the single molecule level. This will be important as the interaction of proteins and cell receptors with conducting polymer surfaces determines the level of performance attainable in their diverse areas of application including biosensors, bioelectronics, neuro-nanotechnology applications and biomedical implants.



**The organization of the polysaccharide capsule is a key factor for biofilm formation**

Huabin Wang<sup>1</sup>, Jonathan Wilksch<sup>2</sup>, Richard Strugnell<sup>2</sup>, Michelle Gee<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Melbourne, Parkville, Victoria, Australia,* <sup>2</sup>*Department of Microbiology and Immunology, University of Melbourne, Parkville, Victoria, Australia*

The ability of bacterium through its cell surface components such as polysaccharide capsule and/or fimbriae to form biofilms on a substratum such as a medical device surface plays a major role in nosocomial infections [1]. Although it is well recognized that the capsule is one of the key components for biofilm formation, little knowledge is available on the underlying biophysical mechanism. The present study aimed to determine the biophysical mechanism by which the polysaccharide capsule contributes to biofilm formation using Atomic force microscopy (AFM), a powerful tool enabling probe the physical properties of cell interactions in physiological-related environment [2].

We performed experiments on encapsulated wild-type, type 3 fimbriae-deficient, type 3 fimbriae over-expressed, and capsule-deficient *Klebsiella pneumoniae* AJ218 (serotype K54) *in situ* by using an AFM tip to nano-indent live cells in aqueous conditions. *Klebsiella pneumoniae* is an important opportunistic pathogen involved in a variety of hospital-acquired.<sup>3</sup> The obtained AFM force profiles were well modeled by using a combination of the double layer theory of charged interfaces, the Pincus theory of polymer brush compression, Hertz model of elastic deformation and Hooke's law [2,3]. From the analysis, the organization of the surface structure and the mechanical response of the bacteria can be provided. The ability of these four types of bacteria in biofilm formation was determined using the static microtiter plate assay [4].

AFM results show that for encapsulated bacterial cell types (wild-type, type 3 fimbriae-deficient and type 3 fimbriae over-expressed) the absence of type 3 fimbriae leads to a significant reduction in capsule brush thickness (202nm compared with 282nm and 286nm for wild-type and the type 3 fimbriae over-expressed, respectively). This trend is also reflected in the elastic moduli of the compressed capsules of each cell type. The reduction in effective brush thickness of the type 3 fimbriae-deficient bacteria was concomitant with a stiffening of the capsule, compared with wild-type and type 3 fimbriae over-expressed. Static microtiter plate assays show that the biofilm formation of the type 3 fimbriae-deficient bacteria is ten folds lower than the wild-type while that of type 3 fimbriae over-expressed bacteria is about 40% lower than the wild-type.

These results imply that type 3 fimbriae impart fluidity to the polysaccharides that comprise the bacterial capsule. The absence of type 3 fimbriae allows a greater degree of intermolecular interaction, predominately hydrogen bonding, between polysaccharide segments, resulting in more molecular order and so higher rigidity of the capsule. This has important implications in bacterial cell adhesion, since the more ordered and so less fluid the capsular polysaccharides, the less able they are to form strong points of adhesion to a substrate. The over-expression of type 3 fimbriae can physically interfere with the capsule to attach to a substrate. Therefore, the organization of capsule can greatly influence the biofilm formation.

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**Load Bearing and Nano-Friction Behaviour of Salivary Proteins Complexes**

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Saliva has the ability to decrease friction at least two orders of magnitude when in between hydrophobic surfaces. It is known that proteins can provide electrostatic and steric barriers that facilitate lubrication. However, saliva's lubrication properties are unique, and saliva is able to reduce friction by an order of magnitude lower relative to e.g. serum albumin. This ability to lubricate is key for oral health, food processing, taste and mouthfeel perception. Yet, molecular mechanisms of saliva lubrication remain unclear. Recently, it was shown that the surface architecture of adsorbed salivary pellicle appears to be key for enabling such low friction [1]. When adsorbed, salivary proteins form a composite layer that comprises a layer of tightly adsorbed low molecular weight proteins and a highly hydrated layer with extended conformations of high molecular weight heavily glycosylated mucins [1].

Here we attempt to disentangle contributions of major groups of salivary proteins to the formation of the lubricious layer. Using gel filtration column chromatography we have isolated different fractions of salivary proteins and examined their surface force and lubrications behaviour via colloid probe AFM force spectroscopy.

Two fractions were found to behave in a similar fashion to saliva. First such fraction comprised a mixture of mucins and proline rich proteins, with surface force profile characterised by a long range repulsive barrier similar to that of whole saliva. The second fraction was enriched with glycosylated proline rich proteins, and was characterised by a shorter ranged repulsive barrier. It was concluded that a hydrated layer formed by glycosylated species is a key driver of low friction between surfaces modified with adsorbed salivary pellicle. Further, the role of low molecular weight proteins was interpreted in favour of anchoring functionality that facilitates mucin adsorption on the surfaces without compromising layer hydration. Surface force data also indicated that such co-adsorption reduces bridging adhesion that was observed for pure salivary mucins and was pinpointed as a cause of their poor load-bearing capacity.

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**OC108**

**A synthetic tribological system that mimics the lubrication and wear prevention processes of articular cartilage**

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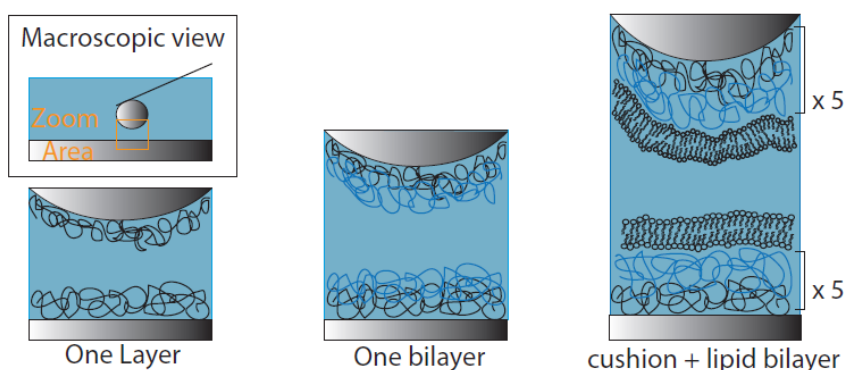
Articular cartilage is a truly amazing tribological system and an example of a highly efficacious water-based, natural lubrication system that is optimized to provide low friction and wear protection at both low and high loads (pressures) and sliding velocities. Not surprisingly, cartilage is a tantalizing model for biomimetic study. Using a reconstituted nanofiber cellulose network that has been chemically modified with adsorbed biopolymers, we have recreated many of the structural, mechanical, and chemical properties of cartilage to produce a synthetic system that exhibits the same lubrication mechanisms, time dependent friction response, and superior wear resistance as natural cartilage tissue. Friction and wear studies demonstrate how the properties of the nanofiber cellulose network can be used to control and optimize the lubrication and wear resistance of the material' surfaces.

## Force Measurements in Cushioned Lipid Bilayer Systems

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Supported lipid bilayers are key tools to investigate cellular membranes, and are novel systems for studies of biolubrication. While solid-supported lipid bilayers are most widely used, bilayers assembled on soft polymer cushions show more potential to mimic in-vivo membranes. Understanding the behaviour of such systems is intimately linked to the question of their structure, which depends on several parameters such as the formation conditions (pH, ionic strength) and lipid bilayer packing. In this study, lipid bilayers on soft polymer cushions were built and characterized by AFM (Atomic Force Microscopy) force measurements in a liquid environment. The components of the cushion were chosen to be bio-polymers (polysaccharides), negatively charged hyaluronic acid and positively charged chitosan, that were assembled using the Layer By Layer (LBL) method. On this cushion, a DOPC (1,2-Dioleoyl-sn-glycero-3-Phosphatidylcholine) bilayer was formed by vesicle fusion. The whole building process, exponential growth of the polysaccharide bilayers [1,2] and fusion of the vesicles on the bilayers' cushion [3], was followed with QCM-D (Quartz Crystal Microbalance with Dissipation) and spectroscopic ellipsometry. The formation process was then repeated in the same conditions in the liquid cell of the AFM (Multimode 8, Bruker) in order to perform force measurements. Force measurements on polymer supported lipid bilayers have been previously reported, for example SFA (Surface Force Apparatus) studies [4]. We instead coated the substrate, a silicon wafer, and the silicon colloid probe at the same time and performed normal and lateral force measurements after the formation of each layer. This research brings new insights into the forces at play during and after the formation of a system in bio-compatible, hydrated, conditions.



**Figure 1:** Principle of AFM force measurements. Polysaccharides bilayers are built at the same time on the probe and on the silicon substrate. Force curves are taken after the formation of each layer in a background electrolyte solution (blue on the drawing).

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## Dynamics of liquid-liquid displacement on nanorough surfaces

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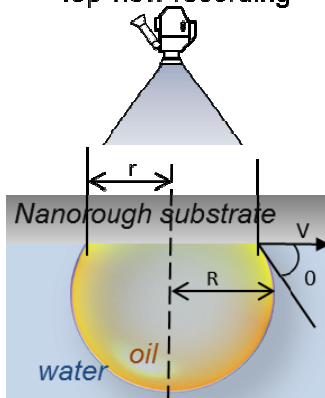
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In microfluidics and coatings, the *motion* of a complex liquid front over nano-textured surfaces controls the fate of the processes. However our knowledge of the impact of nano-heterogeneities on static and dynamic wetting is still limited. The specific effect of nano-roughness on the displacement of a liquid by another immiscible liquid is therefore the focus of this investigation.

Comparison of the dynamics of a water/dodecane and a water/air interface on smooth hydrophobic surfaces revealed that regardless of whether the water is displaced by another liquid or vapour, the spreading data are captured by the molecular kinetic theory<sup>1</sup> for velocities below 0.02m/s. We have developed a new model for contact line friction which accounts for the viscosity of both fluids. This has shown that the three phase contact line (TPCL) motion occurs via the concerted movement of clusters of molecules or contact line segments, rather than through individual molecular displacements.

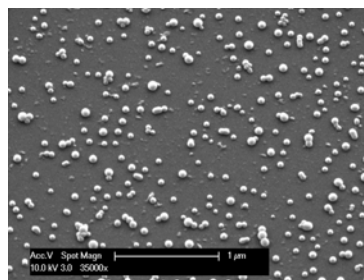
In order to identify the key mechanisms involved in liquid-liquid displacement on nanorough surfaces, the spreading of a dodecane droplet on a range of nano-textured substrates surrounded by water has been studied. The liquid-liquid displacement is investigated by means of optical high speed video microscopy [fig.a]. While the inherent wettability of the substrates was kept constant, their topographic profile was modified in a controlled fashion by decorating the surface with nano-scale features varying in size, spatial density and shape, [fig b]. Surface roughness was found to influence the substrate static and dynamic wettability for root mean square roughnesses below 7 nm. The kinetics of liquid-liquid displacement are substantially slowed down by nano-roughness. Although contact line motion is thermally activated for all surfaces investigated, nanoroughness influences the energy dissipation mechanisms occurring at the TPLC: *both* adsorption-desorption processes and contact line pinning on nano-defects play significant roles. A derivation of the Joanny and de Gennes<sup>2</sup> model for the hysteresis energy was used to evaluate the effect of topographical features on the wetting activation free energy,  $\Delta g_w$ . For low nano-defect densities both solid-liquid interactions and surface pinning strength contribute to the energy barriers hindering the TPCL motion. The activation free energy of wetting can be expressed as a sum of both surface wettability and surface topography contributions, thus providing a direct link between contact line dynamics and roughness parameters.

a) Top view recording

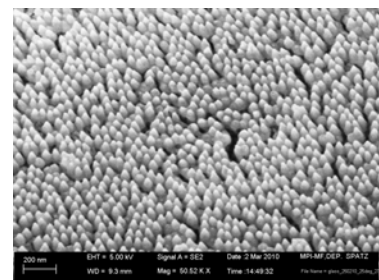


b) SEM images of nano features on smooth glass

Spheres 50nm



Cones 70nm



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## Reversible Patterning of Wettability for Controlling Capillary-Driven Flow in Closed Channels

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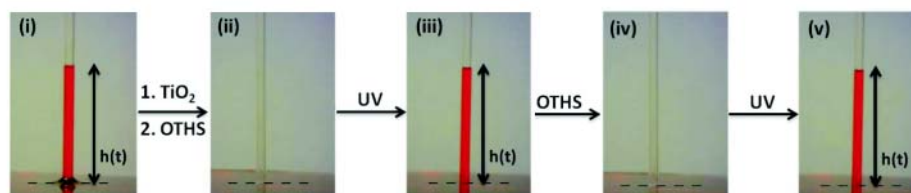
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Capillary driven wetting has received significant attention since the time when the first consistent theoretical description was provided by Washburn [1]. The dynamics of capillary driven flow is rather well understood for smooth, chemically and physically homogeneous systems [2]. However, everyday solids are generally far from being ideal; they are rather rough and chemically heterogeneous [3]. Furthermore, technological developments in the area of microfluidics have generated new interest in the role of non-ideal surfaces. New questions are being asked, such as that of a dynamic contact angle that is dependent on the velocity of the three-phase contact line, or what is the influence on capillary driven flow of heterogeneous (e.g. chemically and/or topographically patterned) walls [4].

Therefore, understanding the dynamics of capillary filling in microchannels or capillaries with heterogeneous walls is important for achieving controlled wetting and liquid flow.

In this study, we combined photocatalytic wettability tuning and photomasking techniques to demonstrate an in-situ method for chemical patterning of capillaries. This allows us to achieve patterns of tuned (on demand) wettability in a wide range (from hydrophobic to complete wetting), as well as the ability to draw, erase and then re-draw these patterns (Fig 1). Using this method we gain a better understanding of the dynamics of capillary filling in microchannels or capillaries with heterogeneous walls which is an important aspect for achieving controlled wetting and liquid flow [5].

Using optical methods we determined the capillary rise dynamics in homogeneous hydrophobic/hydrophilic and chemically patterned capillaries with mm-scale patterns. We observed significant qualitative changes in the capillary rise of typical liquid (in this case glycerol) with respect to that in untreated capillaries with homogeneous inner walls, including the occurrence of a "stick-slip" like behavior. The capillary rise determined experimentally was compared with the classic Washburn Equation and with a modified form. We anticipate that this modulation of flow velocity using chemical patterns will prove useful in autonomous (pump-free) microfluidic applications.



**Figure 1** Images of a cycle of reversible wettability (hydrophilic/hydrophobic switching) of the capillaries by alternating between UV irradiation and OTHS (octadecyltrihydrosilane, hydrophobizing agent) coating. Capillary rise (red liquid) is indicative of a wettable surface.

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OC112

**Hydrophobic entropies are the direct result of dispersion forces**

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The hydrophobic effect drives the organisation of living matter into complex structures like membranes and organelles. Proteins must fold to shield their hydrophobic groups from surrounding waters, and misfolding causes debilitating disease. The same force is also responsible for the formation of surface films, micelles, and other complex biological and interface structures. I describe tests of a new explanation for the hydrophobic effect, and show that the principles behind this explanation hold in any solvent. Collective correlations significantly amplify the strength of dispersion interactions between rotating permanent dipoles in a dense liquid of polar molecules such as water. This attraction between correlated polar molecules contributes largely to the entropy and so we call it entropic dispersion. Simple estimates of the entropic dispersion contribution to the solvation thermodynamics of small hydrophobes are in remarkably good agreement with experiment, as are predictions for the solubilities and conformations of polymers, and polar solvents' deviations from Trouton's rule.

## Microfluidic Devices with Carbon Nanotube Interfaces for Open Circuit Electron Transfer Applications

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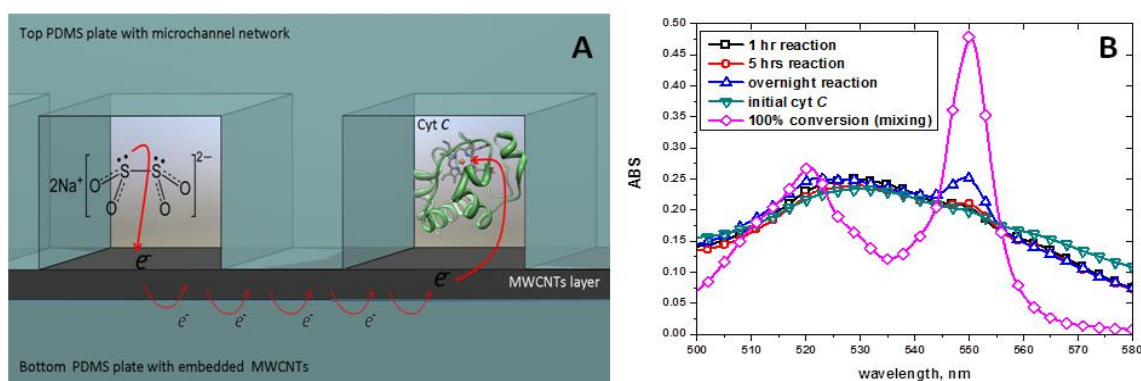
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The integration of carbon nanotubes (CNTs) into elastomeric materials, such as poly(dimethylsiloxane) (PDMS), make them amenable for application in microfluidic devices. This potentially provides devices with enhanced properties such as thermal and electrical conductivity and mechanical strength, all a direct result of the inclusion of the CNTs into the polymer matrix. As a result these materials are ideally suited to a large variety of modern advanced microfluidic technologies which require high performance microfluidic device components. These components include active microvalves, heaters, sorters, pumps, pressure and electrochemical sensors.<sup>1-3</sup>

Here we demonstrate the development of a PDMS microfluidic device with an interface layer made of multi-walled CNTs (MWCNTs). The MWCNT layer provides an “electrical connection” between two microfluidic channels (Figure 1A) which allows contactless biochemical RedOx reactions to be performed between reagents passing through two microchannels that are physically separated.

As a proof-of-concept, the device was successfully used to demonstrate the open circuit electron transfer reaction between an electron donor inorganic molecule (reductant, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> - sodium dithionite) and an electron acceptor protein (oxidiser, cytochrome C). A detectible degree of cytochrome C reduction was observed after 1 hr of reaction (Figure 1B, black trace). This indicates that these MWCNTs have potential in the development of miniaturised contactless



biochemical reactors where purification of the final products is not required.

Figure 1 (A) Illustration of a contactless biochemical RedOx microfluidic device (not to scale) and (B) cytochrome C conversion kinetics from the oxidised state (Fe<sup>3+</sup>) to the reduced state (Fe<sup>2+</sup>). The peak appearing at 550 nm corresponds to the reduced cytochrome C.

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## OC114

### Effect of the number and length of the alkyl chains in lipids on their interactions with model cell membranes

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Hyperlipidemia occurs when there is an abnormally high amount of [lipids](#) in the [blood](#). Its cause is considered to be related to the aggregation of cells in the blood flow. The presence of triglycerides has been observed to give cell aggregation, whereas cell aggregation has not been observed by monoglycerides. This difference can be thought to be due to a difference in the interaction and mixing of triglycerides and monoglycerides with the molecules in a cell membrane. Although macroscopic information is known about how the presence of glycerides affect the cell aggregation, information on the interactions of glycerides with the molecules in a cell membrane is not known on a molecular level and/or on a micro-scale. This information is, however, required in order to learn how to control and change the interaction of glycerides with the molecules in a cell membrane, and therefore needed if we are to eliminate the cell aggregation that contributes to hyperlipidemia. In this study, we aimed to determine the difference in the mixing of the different glycerides (mono-, di-, and tri-) with the molecules in a model cell membrane by using physico-chemical methods.

A Langmuir trough and a Fluorescence microscope were used to investigate the effect of the number and length of the alkyl chains in lipids on their mixing ability with a model cell membrane, a monolayer of 1, 2-Dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) at an air/water interface. The effect of the number of chains was determined by studying the change in the surface pressure ( $\Pi$ )- area per molecule ( $A$ ) isotherms and fluorescence images of mixed monolayers of DPPC and the glycerides (mono-, di-, and tri-). The  $\Pi$ - $A$  isotherms showed that monoglycerides (Palmitin), diglycerides (Dipalmitin) and triglycerides (Tripalmitin) mixed with DPPC to give only partial miscibility, where the mixing was seen to worsen as the number of alkyl chains increased. Fluorescence microscopy revealed partial mixing without aggregation for monoglyceride, but the presence of lipid aggregation for diglyceride and triglyceride. The effect of decreasing the change-length of the glycerides was observed to improve the mixing of the lipids with the DPPC molecules.

The structure of the lipid was concluded to be the determining factor in the mixing ability of the lipids with the molecules in the model membrane. An increase in the number of alkyl chains in a lipid causes its hydrophobicity to increase, resulting in the aggregation of the lipids and their inability to mix with the molecules in the model cell membrane. A decrease in the chain-length of the alkyl chain of the lipid causes its mixing with the molecules in the model cell membrane to improve, due to the smaller size of the lipid molecule and its reduced hydrophobicity.

**Controlled Free Radical Surface-initiated Polymerisation: Biomedical Applications of Surface Coatings, Micropatterns and Electrospun Nano-bottlebrushes**

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**Introduction:** The use of surface initiated polymerisation (SIP) has become widespread as a method of modifying surfaces, particularly in the formation of polymer brush coatings and to produce coatings with advanced functionality.<sup>1</sup> In the last six years we have developed and implemented a method of SIP which relies on the use of macro-initiators/iniferter (mi) or macro-chain transfer agents (mCTA) that are covalently bonded to a surface.<sup>2,3</sup> The method is particularly useful for controlled or living polymerisation mechanisms such as Radical Addition-Fragmentation chain Transfer (RAFT), Atom Transfer Radical Polymerisation (ATRP) and Initiator-Transfer-Termination (Iniferter) and can be applied to a variety of substrate materials with either simple or complex geometries. The use of controlled mechanisms means that sophisticated polymer architectures such as di-, tri-block copolymers, gradient copolymers, star-shaped and hyperbranched polymers can readily be accessed.<sup>4</sup> Cross-links can readily be introduced into coatings for the control of coating material properties such as the elastic modulus.

**Methods:** In this study, we have taken mIs or mCTAs and applied them to form functional coatings from planar solid and porous materials, from electrospun nanofibres and to form dewetted, micropatterned and gradient coatings. mIs and mCTA were synthesised either using either conventional free-radical polymerisation or RAFT polymerisation. Surfaces were characterised using techniques such as X-ray photoelectron spectroscopy, atomic force microscopy and ellipsometry. Standard cell culture techniques were used for the culture of L929 fibroblasts, human mesenchymal stem cells (bone marrow derived) or human embryonic stem cells.

**Results:** We have used mCTAs to form functional coatings for the culture of stem cells *in vitro*. These types of coatings can be used in at least two ways. The use of neutral monomers in the coating provides a surface useful in the formation of cell aggregates prior to a differentiation protocol (for example in the formation of embryoid bodies from pluripotent stem cells). Inclusion of a functional monomer into the coating allowed for the coupling of cell signalling or adhesion molecules which allow long term culture of either adult or pluripotent stem cells on synthetic surfaces in serum-free media. We have used both ATRP and RAFT SIP approaches to form functional coatings on electrospun nanofibres, for example for the reduction of protein adsorption (for filtration, cell culture application) and as a scaffold for potential neural tissue repair. Finally, we have used the dewetting of polymer bilayers and ATRP as a method of fabricating micropatterned polymer brush surfaces. These materials allow for the patterning of cells and can aid our understanding of how the physical and chemical environment can influence the behaviour of cells in small colonies.

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## Tuneable Nano-patterns by the Constrained Dewetting of Polymer Brushes in Molecular Dynamics Simulations

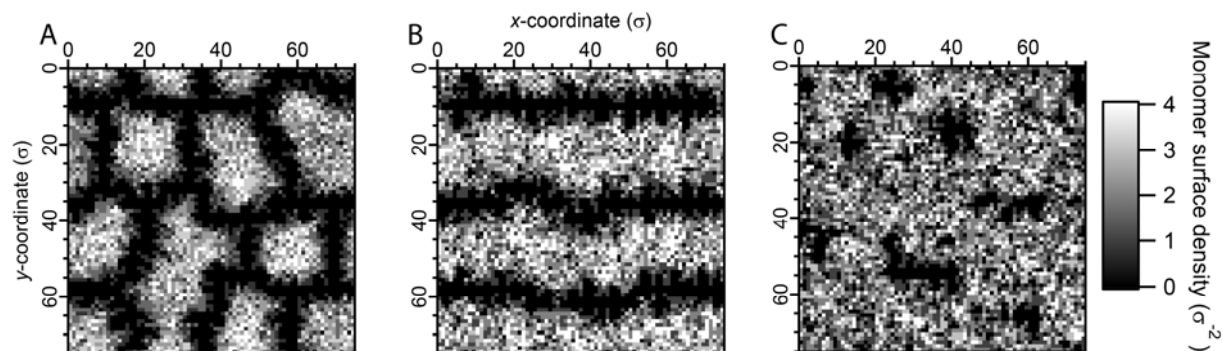
Thomas Lee<sup>1</sup>, Shaun Hendy<sup>2,3</sup>, Chiara Neto<sup>1</sup>

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Polymer brushes, when exposed to a poor solvent, collapse into a compact layer. However, this collapse does not necessarily result in a homogeneous polymer layer. At low to moderate grafting density, polymer brushes collapse into discrete aggregates, with a variety of possible morphologies that depend on the grafting density and interaction with the substrate. This process, known as “constrained dewetting”, is driven by competing factors as the polymer attempts to minimise both the interfacial energy and the stretching of the tethered chains. The result is the formation of nano-sized aggregates, as shown in Figure 1A, including pinned micelles, stripes, and holey layers. Despite the interesting variety of morphologies possible in this system, the phenomenon has received only occasional attention during the past 20 years since it was first observed in molecular simulations.

We have used molecular dynamics simulations to investigate the constrained dewetting process. We have shown the potential for a new method for finely controlling the morphology of the patterns *in situ* by introducing a small amount of solvent that is selective for the polymer, which when adsorbed into the collapsed brush, can change the pattern in the same way as an increase in grafting density. By adsorbing an appropriate amount of solvent to the layer, polymers arranged into a pinned micelle formation may rearrange into a striped or holey layer, as shown in Figure 1B and C.

We have found that constrained dewetting of polymer brushes can be used to create a surface which displays a patterned slip boundary condition.[1] We have achieved this in molecular dynamics simulations by selecting polymer and substrate such that the slip length at the liquid-polymer interface is greater than that at the substrate, causing the liquid to flow at higher velocity over the polymer domains and more slowly over the substrate. This effect could be employed in microfluidic systems to create reversibly switchable mixed boundary condition surfaces, and could potentially be used to create switchable microfluidic mixers.



**Figure 1.** **A.** Aggregation of collapsed polymer brushes into pinned micelles on exposure to a poor solvent. **B** and **C** show the same surface when a small amount of good solvent is added to the system, changing the arrangement of the aggregations to a striped and holey layer respectively.

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OC117

## Flow over polymer brushes: Slippage of a Newtonian liquid

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In macroscopic systems, the traditional assumption of a no-slip boundary condition at liquid/solid interfaces provides a good description of liquid flow. However, on the microscopic scale a finite slip for simple liquids can be detected using high precision nano-scale techniques. The occurrence of interfacial slip is important in all situations where liquid flow is confined, such as in microfluidic systems, porous materials and biological systems [1]. The investigation of the flow of liquids in biological systems in particular requires the design and use of soft interfaces.

In this work the interfacial flow of a simple Newtonian liquid at the interface with a grafted layer of polyethylene glycol was investigated using colloid probe atomic force microscopy (AFM) and quartz crystal microbalance. Different grafting densities were obtained by varying the conditions employed, such as polymer concentration and quality of the solvent. High density polymer brushes were obtained when the polymer in solution was in marginal solvation conditions (near to its cloud point [2]),

In the AFM experiments, hydrodynamic force measurements were performed by bringing together, at different approaching rates and temperatures, a colloidal silica probe and the polymeric brush surface separated by an aqueous solution of sucrose. Characteristic slip lengths were calculated from the force profiles using recently developed experimental and fitting protocols and theoretical models [3-5], and the effect of the conformation of the polymers at the interface is discussed. A quartz crystal microbalance was employed to characterise the polymer brushes, and to perform experiments at higher shear rates than allowed by AFM.

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## Investigations of Peptide Interactions with Biological Membranes Using X-ray and Neutron Reflectometry

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The cellular membrane surrounding the cytoplasm of a cell is a physical boundary that, at the same time works as a functional platform providing diverse biological functions such as signal transduction, and transport of ions or molecules. Increasingly, biomimetic membrane systems are being used to investigate specific biomolecular interactions with a range of cell penetrating peptides of differing structure and function. We report on a number of different peptide / membrane systems where key structural parameters have been studied using either X-ray or neutron reflectometry.

In concert with surface-pressure isotherm and fluorescence microscopy measurements on lipid monolayers, we have shown that the interaction of transcription-activating factor derived peptides TAT-TDPs with cellular membranes is mediated by the presence of heparin acting as a membrane receptor.<sup>[1]</sup> Despite containing large amounts of negative charge, heparin incorporates homogeneously into (zwitterionic) DMPC and (anionic) DPPS lipid monolayers, and improves the adsorption of TAT-TDP molecules. Heparin then associates with the positively charged TAT-TDP molecules and induces insertion into the liquid-expanded phase of the lipid monolayers. X-ray reflectometry shows a heparin/TAT-TDP complex near the headgroups of the lipid monolayer, which resembles the activities of ubiquitous GAG molecules as receptors that promote intracellular transport of cell-penetrating peptides into biological cellular systems.

Antimicrobial peptides such as maculatin 1.1 and aurein 1.2, secreted by the skin of some varieties of Australian tree frogs, have been known for a number of years to be effective agents against antibiotic-resistant bacteria. Yet much remains to be understood about the exact mechanism of how these peptides interact with bacterial and eukaryotic cellular membranes. Neutron reflectometry and a range of other biophysical methods have been used to characterise the interaction of maculatin 1.1 and aurein 1.2 with DMPC and DMPC/PG supported lipid bilayers. The larger peptide maculatin 1.1 was found to bind strongly with the mixed DMPC/PG bilayers in a manner that indicates pore formation as the dominant mechanism of membrane disruption.<sup>[2]</sup> The smaller peptide aurein 1.2 showed behaviours consistent with the carpet mechanism for both the zwitterionic DMPC and the anionic DMPC/PG supported lipid bilayer membranes.<sup>[3]</sup>

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OC119

**Receptor activation at the cell surface-can fluorescence approaches help?**

Andrew Clayton

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The epidermal growth factor receptor (EGFR) is a member of the erbB tyrosine kinase family of receptors. For many years it has been believed that receptor activation occurs via a monomer:dimer transition which is associated with a conformational change to activate the kinase. High resolution structural studies from several laboratories have given us beautiful models of the key components of the EGFR- the extracellular ligand binding domain in tethered and untethered forms, the intracellular kinase domain in symmetric and asymmetric dimers, the juxtamembrane domain and the transmembrane domain. However the way in which these components are dynamically assembled in the context of a full length molecule in a living cell is yet to be determined. In this talk, I will give an overview of my laboratory's efforts in determining the "structure" of the EGFR in solution and in living cells using fluorescence imaging microscopy approaches. The results suggest a need to modify and extend current models of EGFR activation and regulation.

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OC201

**Droplet – Surface Interactions in the Absence and Presence of Adsorbed Polymer Layers**

Piotr Korczyk, Marine Jacquet, Mihail N Popescu, Marta Krasowska, David Beattie

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Oily liquid droplets in aqueous suspension (emulsions) represent a large number of natural and industrial products and materials. The properties of emulsions rely on many physicochemical characteristics, such as oil/water ratio, relative viscosity of the oil and water phases, the presence of polymers and surfactants, and solution properties like pH and ionic strength. These characteristics can be manipulated to produce the desired properties relevant for the target application. Many of the applications of emulsions are dependent on the interaction of the oily droplets with solid surfaces, whether those surfaces are metals, metal oxides, skin, or hair. In spite of the critical nature of this interaction, there are few experimental techniques that can directly probe this interaction, or connect the droplet-solid interaction to the molecular characteristics of the oil/water and water/solid interface. In this work, we have used high speed video microscopy of oil droplet rise and oil droplet collisions with solid surfaces to determine the influence of adsorbed polymer layers on thin film hydrodynamics and droplet attachment. The oil studied was dodecane, and a model hydrophobic surface (thiol-coated gold) has been used as the solid. The measurements provide direct information on thin film drainage and liquid-liquid displacement (droplet spreading) at the solid surface. The dynamic droplet collision data have been acquired in the presence and absence of polymer emulsifiers/surface modifiers (hydrophobically-modified dextrin), either coated on the solid surface, or adsorbed at the droplet-water interface. These adsorbed polymer layers have been characterised by quartz crystal microbalance (for solid surface adsorption) and the oscillating droplet technique (for adsorption to the droplet surface).

**Influence of Surface Charges on Early Spontaneous Spreading of Drops**

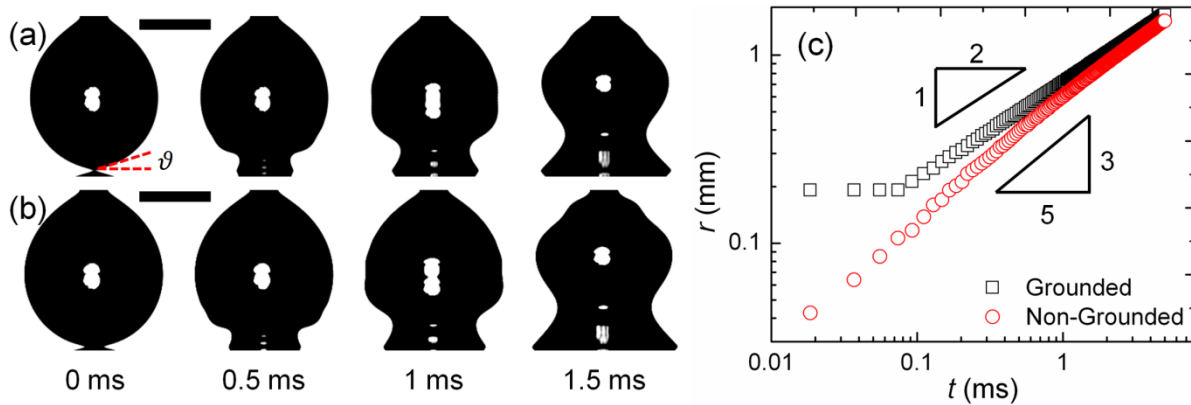
Longquan Chen<sup>1</sup>, Günter Auernhammer<sup>2</sup>, Chunli Li<sup>1</sup>, Nico van der Vegt<sup>1</sup>, Elmar Bonaccorso<sup>1</sup>

<sup>1</sup>Center of Smart Interfaces, Technische Universität Darmstadt, Petersenstr. 17, 64287, Darmstadt, Germany, <sup>2</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz, Germany

The first stage of spontaneous spreading of a liquid drop over a solid surface has attracted much attention recently. Studies focused on effects of surface wettability, softness, or solubility. The general outcome is that this first, fast regime of the spontaneous spreading process is dominated by inertia and capillarity, and follows a power law depending solely on the equilibrium contact angle between liquid and solid,  $\theta_{eq}$ . Only at later stages other surface or liquid properties start playing a role.

We present a study on electrostatic effects on dynamic wetting on both hydrophilic and hydrophobic charged surfaces. We found that the spreading of drops of liquids on charged surfaces follows a power law as well, however spreading on charged surfaces is enhanced with respect to uncharged ones. The speed of spreading grows with surface charge, but also depends on the conductivity and permittivity of the liquid. We provide a semi-qualitative model for explaining our findings and we backup the results by molecular dynamic simulations.

Since charged surfaces are ubiquitous in nature and in technology, our results are certainly relevant for a number of practical applications.



**Figure:** (a) High speed video images of a water droplet spreading on a complete wetting glass surface after standard cleaning. The scale bar is 1 mm. (b) Water droplet spreading on the same surface as in (a), but the surface is grounded. (c) Log-log plots of the spreading radius  $r$  as a function of spreading time  $t$  of the wetting processes in (a) and (b).



**Droplet Actuation Induced by Coalescence: Experimental Evidences and Phenomenological Modelling**

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<sup>1</sup>University of Canterbury, Christchurch, New Zealand, <sup>2</sup>CNRS, Grenoble, France, <sup>3</sup>ENS, Cachan, France

This work considers the interaction between two droplets placed on a substrate in immediate vicinity. We show here that when the two droplets are of different fluids and especially when one of the droplets is highly volatile, a wealth of fascinating phenomena can be observed. In particular, the interaction may result in the actuation of the droplet system, i.e. its displacement over a finite length. In order to control this displacement, we consider droplets confined on a hydrophilic stripe created by plasma-treating a PDMS substrate. This controlled actuation opens up unexplored opportunities in the field of microfluidics. In order to explain the observed actuation phenomenon, we propose a simple phenomenological model based on Newton's second law and a simple balance between the driving force arising from surface energy gradients and the viscous resistive force. This simple model is able to reproduce qualitatively and quantitatively the observed droplet dynamics.

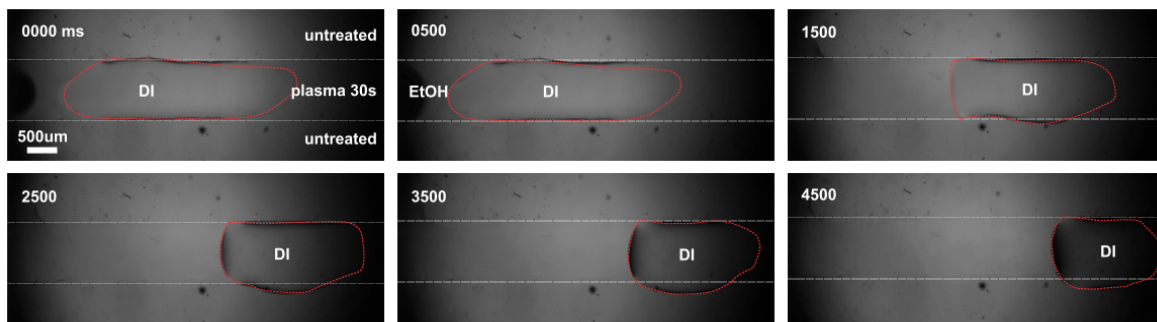


Figure 2: Picture sequence showing from above the actuation of a water droplet by an ethanol droplet on a hydrophilic highway (A side view video of the droplet motion can be seen at <http://www.scivee.tv/node/26233>.)

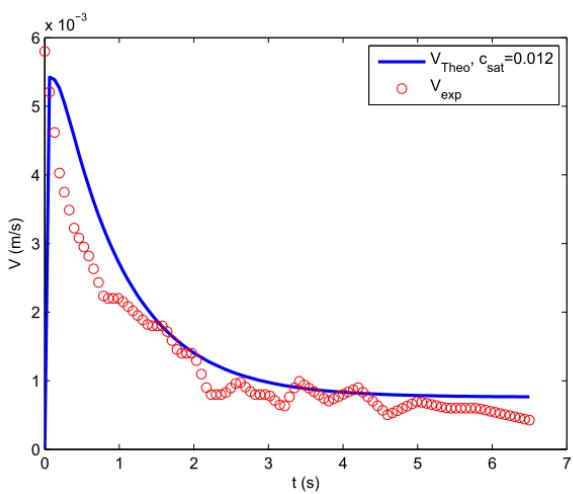
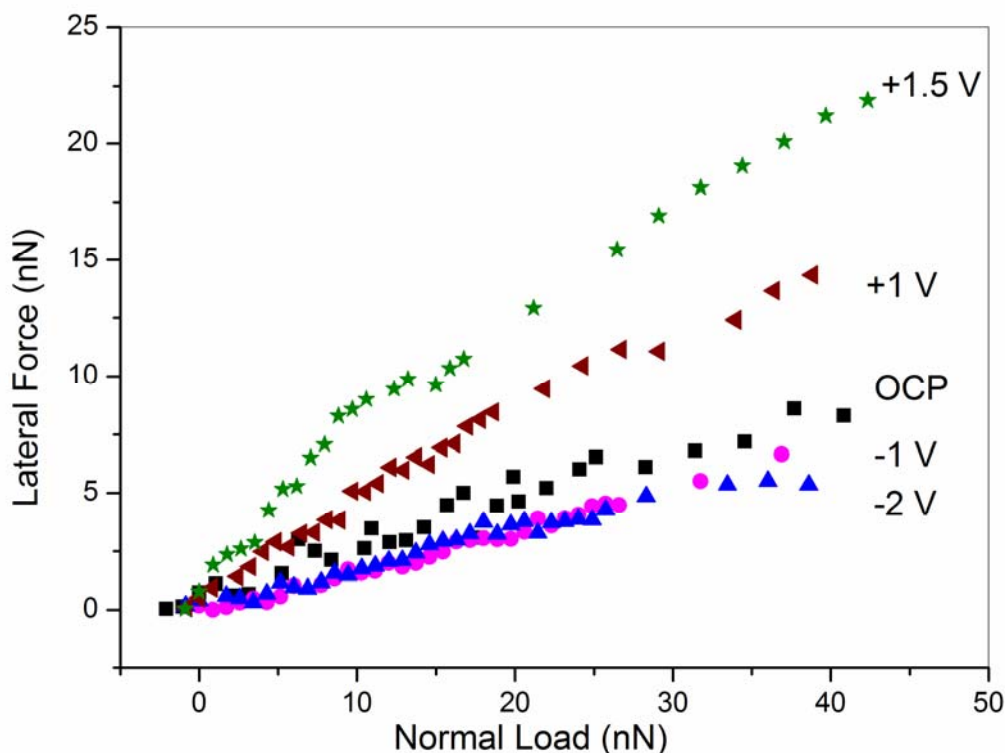


Figure 3: Comparison of the experimentally measured droplet velocity (red dots) and the theoretically predicted one (blue line)

**A Nanotribological Study of the Influences of Potential and Velocity on Ionic Liquid Lubrication**Hua Li<sup>1</sup>, Mark Rutland<sup>2</sup>, Rob Atkin<sup>1</sup><sup>1</sup>University of Newcastle, Newcastle, Australia, <sup>2</sup>Royal Institute of Technology, Stockholm, Sweden

Tribological effects, including friction, adhesion and wear are undesirable as they reduce the energy efficiency of industrial processes and shorten the working life of mechanical parts. Conventional high end lubricants are electrical insulators and subject to decomposition under an applied potential. Ionic liquids nanoscale properties make them potentially excellent lubricants: as the ions interact strongly with oppositely charged surfaces, they resist 'squeeze out' as surfaces are compressed, meaning a lubricating film will remain in place up to higher forces than for a comparable molecular liquid. This work investigates the influence of electrical potential and sliding velocity on the ionic liquid lubrication. Atomic force microscopy is employed to study the frictional behaviour of 1-ethyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate ([EMIM]FAP) confined between a silica colloid probe and an Au(111) substrate. At a given sliding velocity, friction forces vary with the applied potential due to the composition of the ion layer separating the surfaces changing. At the same potential, friction forces increase with the sliding velocity, consistent with a discontinuous sliding process. This study demonstrates ionic liquids can provide an adaptive lubricating mechanism, with lubricity controlled by the applied potential. This result will impact a range of applications, including micro- and nano-electromechanical systems.



**Figure 1.** Lateral force vs normal load for [EMIM] FAP confined between a silica colloid probe and an Au(111) electrode surface at different potentials.

## Flexible Polymeric Material with Metal-Like Conductivity for

### Next Generation Organic Electronic Devices

Drew Evans<sup>1</sup>, Manrico Fabretto<sup>1</sup>, Mischa Mueller<sup>1</sup>, Pejman Hojati-Talemi<sup>1</sup>, Kamil Zuber<sup>1</sup>, Rob Short<sup>1</sup>, Gordon Wallace<sup>2</sup>, Peter Murphy<sup>0</sup>

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Reduced pressure vapour phase polymerisation (VPP) of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) has produced a thin flexible film having ITO equivalent conductivity. This marked increase in conductivity has been achieved by carefully manipulating the characteristics of the thin-film oxidant layer used during the vapour phase polymerisation of the polymer. The resulting film morphology has been transformed from a typical cauliflower-textured surface to one having lamellar-like structure.

The introduction of a tri-block copolymer, and changes in the solvent carrier, not only results in an oxidant thin-film that remains liquid-like under reduced pressure, but one that also induces structured growth during PEDOT film formation. The resulting thin-film is flexible, has conductivity equivalent to commercially available indium tin oxide (ITO), with comparable optical transmission values. PEDOT thin films with a variety of thicknesses have been grown on a range of substrate materials from glass, to plastics, to metals and ceramics, with sheet resistances below  $20\Omega/\square$  for sub-170 nanometre thin-films. For more optically transparent applications the thin-film has been polymerised to a thickness of 65 nanometres, resulting in a sheet resistance as low as  $45\Omega/\square$  and greater than 80% optical transmission in the visible region. Such a result compares favourably to ITO and the currently touted replacements.

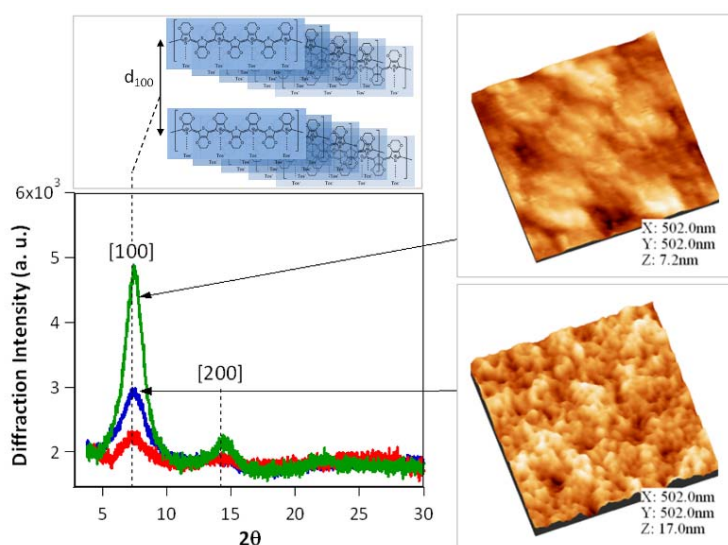


Figure: XRD shows the increase in the “ordered-structure” for the conducting polymer PEDOT. The accompanying AFM images highlight the change in the polymer’s surface texture from cauliflower to lamellar.

**OC206**

**Preparation and Application of Carbon Nanotube Based Nanostructured Hybrid Films**

Aimin Yu

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Carbon nanotubes (CNTs) have been the focus of intense research since their discovery in 1991.<sup>1</sup> Their high mechanical strength and chemical stability, excellent electrical conductivity and electrocatalytic activity have made CNT a promising material for various applications. This work will present our recent research work on fabrication of carbon nanotube based hybrid films using the solution based layer-by-layer self-assembly technique.<sup>2-4</sup> The incorporation of other nanomaterials such as gold, silver nanoparticles and quantum dots brings new properties to the CNT films. The techniques used to disperse CNT in water; the electrochemical, photoelectrical and antibacterial properties of the resulting hybrid films and their application are discussed in detail.

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**OC207**

**Elastic Properties of Liquid Marbles**

Samuel Asare-Asher, Jason Connor, Rossen Sedev

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Jason Connor<sup>1</sup>, Le Woei Ng<sup>1,2</sup>, Catherine Fung<sup>1</sup>, Yung Ngothai<sup>2</sup>, David Druskovich<sup>3</sup> and Rossen Sedev<sup>1</sup>

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*2 School of Chemical Engineering, University of Adelaide, Adelaide, S.A., Australia*

*3 Science Engineering and Health, CQUniversity Australia, Rockhampton, Qld., Australia*

Liquid marbles are liquid droplets covered completely with small particles. They exhibit hydrophobic properties even on hydrophilic surfaces. They roll off easily, bounce and deform. Their behaviour is closely related to the Cassie wetting state and the phenomenon of superhydrophobicity. Typical liquid marbles are of millimetre size but their properties are analogous to smaller capsules and droplets of Pickering emulsions.

In this work we assess the elastic properties of liquid marbles. The water marbles are covered with an uneven and complex multiparticle coating of PE particles as revealed by ESEM imaging. The liquid marbles are highly elastic and can sustain up to 20-30% deformation. Upon further compression their elasticity increases. The modulus of elasticity measured experimentally is essentially identical to that expected for bare liquid droplets. At a critical threshold the liquid marbles are destroyed. We speculate on the mechanism of these processes and specifically the role of the liquid surface and the network of particles.

## Ionic tuning of wettability

Davide Vanzo, Alenka Luzar, [Dusan Bratko](#)

Virginia Commonwealth University, Richmond, VA, USA

We perform atomistic MD simulations to investigate the wetting regimes at the nanoscale on molecular-brush coated graphene surfaces [1]. We tune hydrophilicity by covering the surface with a mixture of covalently bonded butyl and potassium butyrate (or propylammonium chloride) chains at different surface densities and distribution patterns of ionizing groups. In contrast to the Lipmann-like quadratic dependence of the cosine of contact angle on electrode charge, discrete, ionically screened charges at a regular distribution contribute in an additive manner reminiscent of the Cassie-Baxter relation (Fig. 1) [2]. In analogy with functionalization by neutral polar groups, ionic functionalization is most effective with regular surface patterns that maximize the separation between adjacent ionic sites [3]. The findings provide guidance for the design of ionically nanopatterned materials with tailored hydrophilicity at preserved material structure and minimal chemical modification (Supported by U.S. DOE).

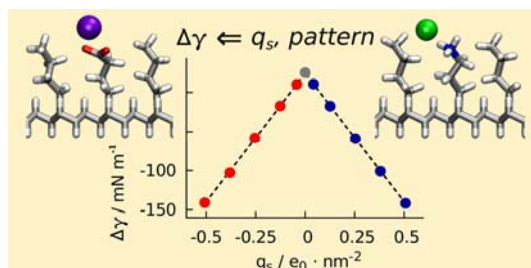


Fig. 1 Reduction in the wetting free energy of functionalized graphene with ionizing –COOK (*left*) or –NH<sub>3</sub>Cl groups (*right*) as a function of surface density for regular pattern of charges.

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OC209

## Colloidal Particle Adsorption at Liquid-Vapour Surfaces

Bruce Law, Sean McBride, Haeng Sub Wi

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Understanding the conditions under which colloidal particles adsorb at liquid-liquid or liquid-vapour surfaces is important in many different industrial, scientific and biophysical processes. For example, in the mining industry the process of flotation (i.e. the attachment of ore particulates to the surface of rising air bubbles) is used extensively to separate mineral-rich ore particulates from non-mineral containing particulates. Colloidal particles at liquid surfaces also act as surfactants with tuneable surface properties (the ligand coating). Scientists have used this surfactant behaviour to self-assemble macroscopic sheets, only a single nanoparticle thick but many millimeters wide, possessing unusual mechanical, electronic and optical properties. Liquid-liquid colloidal particle self-assembly, around droplets, has also been used to create porous drug encapsulation shells of interest to the medical community for the slow release of drugs over time. Despite this extensive interest in colloidal particles at liquid surfaces, the physics of this colloidal particle adsorption process is poorly understood.

In this talk we examine the adsorption of spherical colloidal particles at the liquid-vapour surface. For sufficiently large particles (i.e. particles where the gravitational potential energy dominates the thermal energy), this adsorption process depends upon the particle wettability and line tension where the particle is in mechanical equilibrium at the surface, as described by the modified Young's equation. We use Atomic Force Microscopy to test these concepts by examining dodecyltrichlorosilane coated silica particles adsorbed at the polystyrene-air surface [1]. For sufficiently small particles, particles adsorbed at the liquid-vapour surface will also be in thermodynamic equilibrium with particles suspended in the bulk liquid solution. Thus, the adsorption of small particles is influenced by the particle wettability, line tension, mechanical equilibrium, as well as, surface-to-bulk thermodynamic equilibrium. We use surface tension measurements to test these concepts by examining dodecanethiol ligated gold nanoparticles adsorbing at the air-liquid surface for a homologous series of n-alkane liquids from n-nonane through to n-octadecane [2].

As far as we are aware these are the first studies that systematically account for colloidal particle wettability, line tension, mechanical equilibrium, as well as, thermodynamic equilibrium.

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**OC210**

**Reactive Wetting on a Corroding Mild Steel Surface**

Catherine Fung, Rossen Sedev, Jason Connor

*Ian Wark Research Institute, University of South Australia, Mawson Lakes, S.A., Australia*

There are many instances where liquid drops react with the surface they contact. An important example is salt spray on metal surfaces in relation to the corrosion of engineered structures. When this occurs, drop wetting and spreading are complicated by the reactions taking place at the solid-liquid interface. In time the chemical reactions affect the composition and the wettability in the three-phase system. The relation between chemical kinetics and interfacial energetics is further complicated by the effects of mass transport. We present a set of spreading experiments that demonstrate the diverse wetting behaviour on a corroding mild steel surface. In particular, we discuss the secondary spreading of the droplet, the crystallisation of the electrolyte and the role of wetting in corrosion.



OC211

## Lab on a Particle: Molecular Machines and Molecular Transducers on the Surface of Colloidal Particles

Matt Trau

*University of Queensland, Brisbane, QLD, Australia*

The development of low cost, point of care, molecular-based diagnostics that can detect diseases while they are still curable, represents one of the most promising approaches to reducing the growing disease burden of mankind. Numerous advances in DNA sequencing and proteomic technologies have now given rise to tens of thousands of potentially useful genetic, epigenetic and protein based biomarkers for potential application in cancer and infectious disease. A current bottleneck is the availability of accurate, quantitative, inexpensive, multi-species technologies which can be used either in a “high-throughput” (plug-and-play) pathology setting, or at point-of care. In this presentation, a range of “Lab-on-a-particle” approaches recently developed within our lab for genetic, epigenetic and proteomic molecular read-outs will be presented<sup>(1-7)</sup>. Each of these approaches involves building molecular machinery on the surface of bar-coded colloidal particles which act as molecular transducers to capture, amplify and quantitatively display a variety of analytes that are then read via conventional optical, electronic, or paper-based devices.

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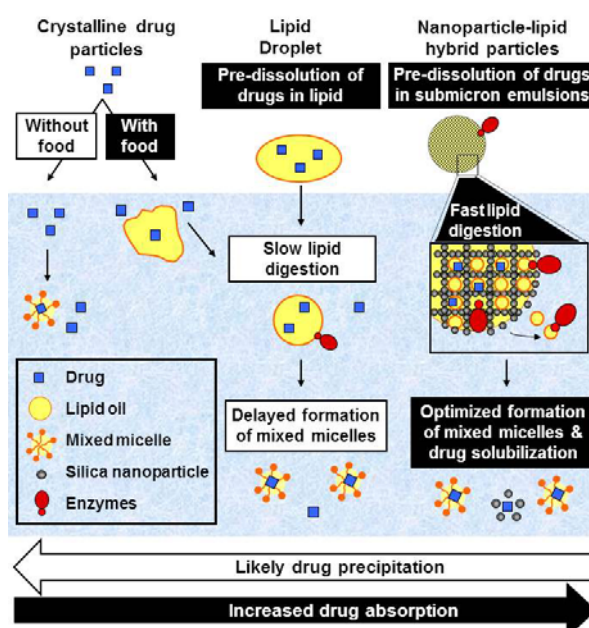
## Hybrid nano-biomaterials engineered from nanoparticle stabilized lipid colloids and their drug delivery applications.

Clive Prestidge, Angel Tan

The Wark, University of South Australia, Mawson Lakes, SA, Australia

Lipid colloids are widely used as drug delivery systems, but often suffer from physical instabilities and non-ideal drug encapsulation and delivery performance. Layers of silica nanoparticles have been engineered to enhance the physical stability of submicron lipid emulsions and liposomes, stabilize encapsulated active ingredients against chemical degradation, control molecular transport and improve the dermal and oral delivery characteristics, *i.e.* increase absorption, bioavailability and facilitate targeted delivery [1]. Hybrid nanomaterials composed of nanoparticles and colloidal lipids are effective encapsulation and delivery systems for both poorly soluble drugs and biological drugs.

Here we report on the synthesis of hybrid nano-biomaterials based on 3-dimensional assembly of lipid emulsions and nanoparticles, and their physicochemical and biopharmaceutical characterization. Specifically we show the importance of nanoparticle type, lipid-nanoparticle ratio and the processing methodology (e.g. drying method) in controlling the internal porous structure of the hybrid microparticles and their performance in controlling the enzymatic digestion of the encapsulated lipids. Further, we show that these materials are highly effective drug delivery systems for poorly soluble drugs, *i.e.* by mimicking and optimising the pharmaceutical food effect they can enhance the gastrointestinal solubilization and increase the oral absorption/bioavailability [2]. Such materials are in clinical development and have potential as the next generation of nanomedicines.



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## Synthesis of enzyme-active organic-inorganic composite particles

Frances Neville, Harley Cheers, Erica Wanless

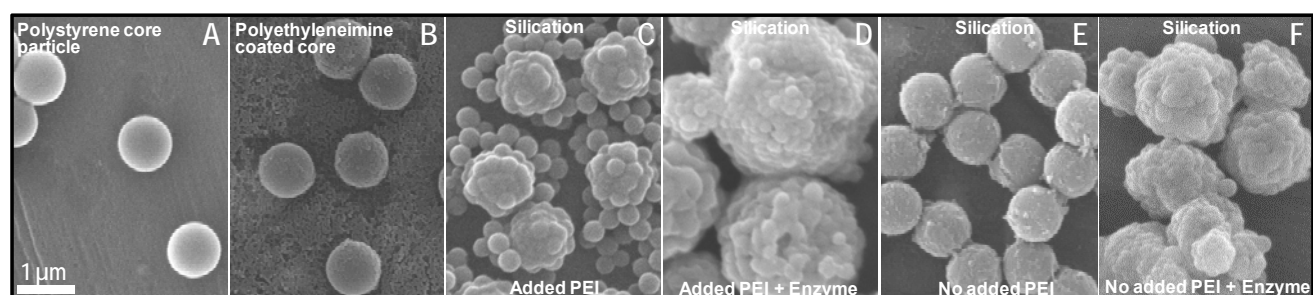
*The University of Newcastle, Callaghan, NSW, Australia*

During the last two decades much research has focussed on organic-inorganic composite particles for their superior optical, mechanical, electrical and catalytic properties [1-2] for use in many fields of science, engineering and medicine.

Here we describe the synthesis of organic-inorganic composite particles where the core is polystyrene covered with an inorganic/organic layer of silica made using the biomimetic polymer polyethyleneimine [3-5]. Furthermore, glucose oxidase enzyme was entrapped within the silica layer adding bioactivity to the composite particles. The combination of functional polymers and enzyme activity has produced composite particles with physical and biochemical activity, which may be used in a number of applications including biosensors, biocatalysis and antifouling coatings.

Carboxylate-modified polystyrene (PS) core particles (Fig. A) were covalently modified with polyethyleneimine (PEI) via the use of a carbodiimide (Fig. B). Subsequently the PS-PEI particles (in the presence and absence of enzyme) were silicated using a one-pot method with and without further PEI added. Trimethoxymethylsilane was used as the silica source and the reaction was carried out in the presence of pH 7.0 sodium phosphate buffer.

SEM images show that when more PEI was added during the silication reaction, primary silica particles formed and bound to the PS-PEI core, producing an organic-inorganic particle with a raspberry-like structure (Fig. C). However, when only the PEI attached to the PS core was present, the silica coverage of the PS particles was much smoother (Fig. E). Nevertheless, whether or not further PEI was added during silication, the composite particles containing enzyme were of similar morphology (Figs D & F respectively), with a rough surface consisting of smaller primary particles than those formed without enzyme (Fig. C).



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**OC214**

**Text-Reporting Paper Blood Typing Assay**

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Our recent studies have focused on the use of paper- and thread-based devices for rapid blood typing assay. These studies found that red blood cells undergo agglutination when they interact with the corresponding antibodies in fibre matrix of paper and thread, and become immobilized in the fibre matrix. This process provides the basis for a new class of blood typing devices to be built. In this work we show the development of a new and user-friendly blood typing assay-reporting concept and prototype – paper-based blood typing device that reports patient's blood type in written text. Paper text patterns are designed and fabricated to allow interactions between grouping antibodies and red blood cells; composite text patterns consisting of bioactive and non-bioactive sections are used to form the letters and symbols for the display of the testing report. This paper-based blood typing device rapidly reports patient's blood type in unambiguous written text.

**Loading and Release of Curcumin from Polyelectrolyte Multilayer Films Studied with In Situ ATR FTIR Spectroscopy**

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The storage and release of small therapeutic molecules from surfaces and colloidal systems is a key goal of many drug delivery studies. Polyelectrolyte multilayers (PEMs) represent a very attractive class of surface treatments that can be used for this purpose, in for example, implants and dermal patches. Such films can be made to be biocompatible, non-fouling, and lubricious. We report on the loading and release of curcumin (a molecule with anti-inflammatory and anti-bacterial properties) from polyelectrolyte multilayers composed of poly(diallyl dimethyl-ammonium chloride) (PDADMAC) and poly(4-styrene sulfonate) (PSS). The loading of curcumin in such PEMs has been studied previously by other researchers using ex situ UV-visible spectroscopy<sup>1</sup>. In our work, we have used the technique of in situ attenuated total reflectance (ATR) FTIR spectroscopy to study directly the formation of the PEM and the incorporation of curcumin. More importantly, we have used the same methodology to study the release kinetics of the curcumin as a function of time, and with variation in salt concentration of the solution above the curcumin/PEM film. The release of curcumin is seen to take many hours, and to be dependent on the ionic strength of the solution into which the curcumin is being released. These observations have implications for the use of PEM films as drug loading media in dermal patches. The FTIR measurements are complemented by quartz crystal microbalance measurements of PEM formation and PEM response to solutions of varying salt content, and with ex situ studies of curcumin release using UV-visible spectroscopy.

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OC216

## New Generation Ceramic Membranes For Water Treatment Sustainability Advancement

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As drinking water is becoming more scarce in Australia due to drought and changes in rainfall patterns, the demand for new sources and the use of recycled water for replacement of potable water has greatly increased. Polymer membranes are currently used industrially in water treatment however they have high fouling tendency caused by the deposition of contaminants such as natural organic matters, a major disadvantages for producing high quality drinking water. Ceramic membranes, which are also used industrially, upon surface modification provide the opportunity for industrial reuse in addition to providing operational advantages in addressing the high fouling tendency of many industrial effluents. There is therefore an urgent need for new generation, ceramic membranes to overcome the high costs of membrane fouling which are able to withstand more cost effective cleaning methods.

Advanced ceramic membranes have been shown to be capable of providing quality membrane performance while being tolerant to waters which readily foul polymer membranes and/or can withstand more aggressive cleaning methods. This study investigates the membrane coating chemistry and morphological properties of the advanced ceramic membranes to correlate surface chemistry with membrane performance as a function of pre-treatment and water chemistry. A combination of colloid and surface science and structural techniques has been used. Surface and near-surface analytical spectroscopies and microscopies including X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to probe the coating structure, composition and fouling properties with electrophoresis used to determine the surface charge properties of the ceramic membranes.

OC217

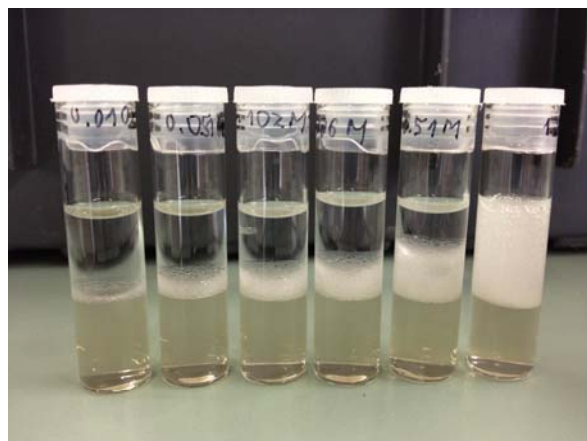
## Stabilisation of emulsions using 2D atomic crystalline materials

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There has been enormous recent interest in 2D materials, the most prominent example being graphene [1], with others such as the transition metal dichalcogenides also having unique properties in the limit of a single layer [2]. Among the methods for producing graphene and other 2D crystalline materials, is the use of ultrasonic exfoliation, particularly in the presence of surfactants in aqueous solution [3]. Aqueous solution processing has significant economic and environmental benefits over the use of organic solvents or ionic liquids [4]. Furthermore, stable aqueous dispersions of 2D particles allow for subsequent use in many applications. Due to their intermediate wettability, graphene and materials such as MoS<sub>2</sub> and WS<sub>2</sub> are highly suited for stabilisation of the oil/water interface.

Emulsions with high stability can be created through the adsorption of particles at the droplet interface, a phenomenon first noted by Pickering. These particles stabilised emulsions are of great interest in many applications such as drug delivery and the creation of novel materials. This presentation will outline progress in the production of particle stabilised emulsions using graphene and MoS<sub>2</sub> as shown in Figure 1.



**Figure 1.** o/w emulsion stabilised with single layer MoS<sub>2</sub> nanoparticles with increasing salt concentration.

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## Influence of Amine Plasma Polymer Film Aqueous Stability on Humic Acid Removal

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**Introduction:** Contaminated water is a worldwide issue as the majority of water purification techniques are generally only used in highly populated areas of developed countries. Decentralized water treatment however does not require the energy and personnel of centralized water treatment. The development of a decentralized water treatment system via plasma polymerization is being investigated.<sup>1</sup> A plasma reactor with allylamine or ethylenediamine monomers was used to functionalize the surface of quartz particles with amine groups. The addition of amine functional groups produces surfaces with higher isoelectric points which are predominately positively charged in solution thus enabling the removal of anionic humic acid via electrostatic attraction. Humic acid is a common water contaminant which originates from the biodegradation of organic matter, resulting in undesirable colour and taste.

**Experimental:** Plasma polymerization was undertaken using a rotating inductively coupled radio frequency plasma reactor. Plasma power (4-60 W), monomer flow (4-10 sccm) and polymerization time (5-60 minutes) were varied. Surface characterization was carried out using X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS). Humic acid removal by allylamine and ethylenediamine films was investigated by stirring particles in 10 mg/L humic acid at pH 7 for 30 minutes. Solution stability of allylamine and ethylenediamine films was assessed via stirring in pH 7 milli-Q water for 30 minutes. Particles were dried and analysed via XPS.

**Results:** Plasma power, monomer flow rate and polymerization time for both allylamine and ethylenediamine were varied to determine the conditions for optimal humic acid removal. Humic acid removal studies revealed that significantly more humic acid could be removed by allylamine than ethylenediamine films, despite the fact that XPS revealed that plasma polymerized ethylenediamine films produced higher concentrations of nitrogen than allylamine films for the same polymerization times. After aqueous immersion, XPS revealed a decrease in the nitrogen concentration of both films however ethylenediamine films however showed a greater decrease in nitrogen concentration than allylamine films.

**Discussion:** Lower humic acid removal by ethylenediamine films in comparison to allylamine films was attributed to the loss of amine groups from ethylenediamine films in solution. The greater decrease in the nitrogen concentration of ethylenediamine films in comparison to allylamine films is expected to be due to the saturated hydrocarbon structure of ethylenediamine which results in a less stable film in solution. Comparisons between allylamine and ethylenediamine plasma polymerized films demonstrate that while ethylenediamine films have higher nitrogen concentrations, allylamine films perform significantly better in humic acid removal, thus aiding in the development of a decentralized water treatment system.

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**Electrostatically-Driven Particle Engulfment into Liquid Drops**

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The transport of solid particles from a gas phase onto a liquid interface, and the possible complete engulfment into the liquid phase, is interesting from both a fundamental and applied perspective. The emerging field of liquid marbles, including so-called “dry water”, and the widely used granular filtration devices both rely on the interaction between dry solid particles and an air/liquid interface.

Here, we report on experiments where the transport of particles into a liquid drop is driven by an accumulation of electrostatic charge on the particles; the interaction of the particles with the pendent drop allows the charge to flow to earth. Dry silica particles, of size 75 – 90 microns diameter, are spread onto an electrostatically charge substrate. The electrostatic charge is transferred to the particles in the bed. The particle bed is positioned beneath a pendent water droplet (~2 mm diameter) attached to a steel capillary of 1.3 mm outer diameter. The bed is moved upward towards the drop. Video footage of particles transporting to the drop have been recorded and analysed as shown in Figure 1.

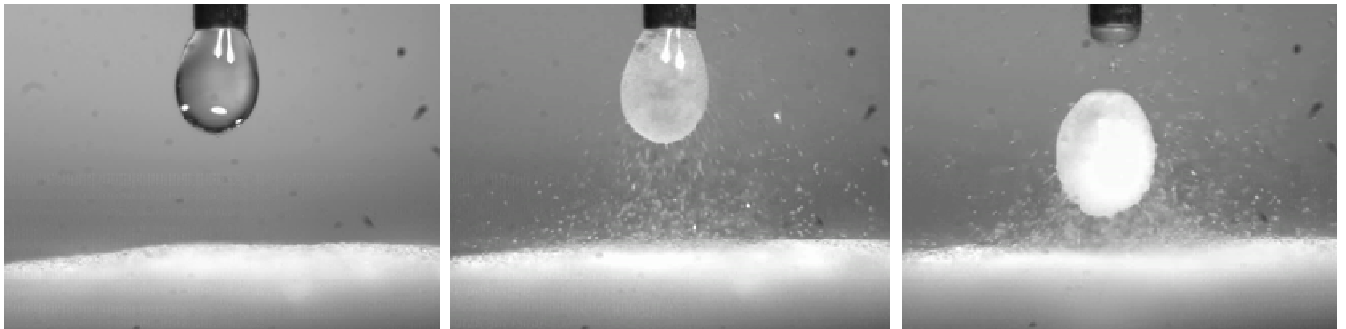


Figure 1: Frames from a high-speed video showing the transport of silica particles from the powder bed to the pendent water droplet, followed by eventual detachment of the drop. Needle outer diameter is 1.3 mm.

From separations as great as 2.5 mm (more 25 times the particle diameter) particles begin to “jump” into the drop. The particles jump from a radial area of the bed some five times greater than the droplet itself, and are observed to follow complex trajectories; some particles enter the drop from above. At a critical separation, a cascade-type event initiates where a rapid transfer of particles to the drop occurs, followed by eventual detachment of the particle-laden drop. The presence of the cascade is observed to be independent on the speed at which the bed is moved but critically dependent on the separation. It is possible to halt the approach after particles have begun to transport to the drop and cease further particles jumping across the gap. The phenomenology of the observed criticality will be discussed in terms of the change in drop volume, and the materials used for both the particle and liquid phases.

**OC220**

**Producing fertilizers from wastewater: the role for colloid and interface science**

Tim Muster

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Wastewater contains significant amounts of water, carbon, nitrogen, phosphorus and other potential resources. However, traditional wastewater treatment has focused on managing its inherent carbonaceous content to ensure against microbiological hazards in the treated effluent and biosolids, and minimal effort has been made to recover any inherent value. The end of the 20<sup>th</sup> century saw legislative demands put in place to reduce the discharge of nitrogen and phosphorus to avoid eutrophication issues in receiving water bodies, and opportunities were exploited to capture biogas and hence cut down on energy costs.

The 21<sup>st</sup> century presents an increasing need to recover more from wastewater, with the primary drivers being the need to recycle water, capture more energy offsets from biogas production and to return phosphorus to agricultural production. Access to phosphorus fertilizer is of growing concern to ensure global food production, due to uncertainty in supply and declining rock phosphate quality. Approximately one fifth of phosphorus fertilizer demand could be potentially available globally in municipal wastewaters, and opportunities exist to simultaneously recover nitrogen as ammonia. Current wastewater treatment processes are now being questioned with regards to their sustainability for nutrient recovery, especially in the light of increasing urbanisation. This paper presents opportunities for colloid and interface science to meet future resource recovery challenges in urban environments.

## Bubble Probe Microscopy: One Step Closer

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The development and characterisation of electrochemically generated hydrogen bubbles for force spectroscopy will be described\*. Bubbles have been grown at the platinised tip of a commercially available atomic force microscopy (AFM) needle probe (exposed electrode  $r < 300$  nm) and monitored by CCD camera (Figure 1). Results show consistent bubble growth in galvanostatic conditions. The utility of the bubble probes in AFM force spectroscopy is demonstrated, showing that interaction forces decay with the bubble radius in ultrapure water.

In summary, we are reporting:

- Controlled hydrogen bubble generation at a nanoelectrode
- Manufacture of first AFM bubble probes with radii under  $20\ \mu\text{m}$
- Dynamic force measurements between hydrogen bubbles of radii less than  $50\ \mu\text{m}$  and solid surfaces

These findings open doors for unprecedented nanoscale studies of gas bubble generation and interaction dynamics as well as for further physical and electrochemical studies at this scale.

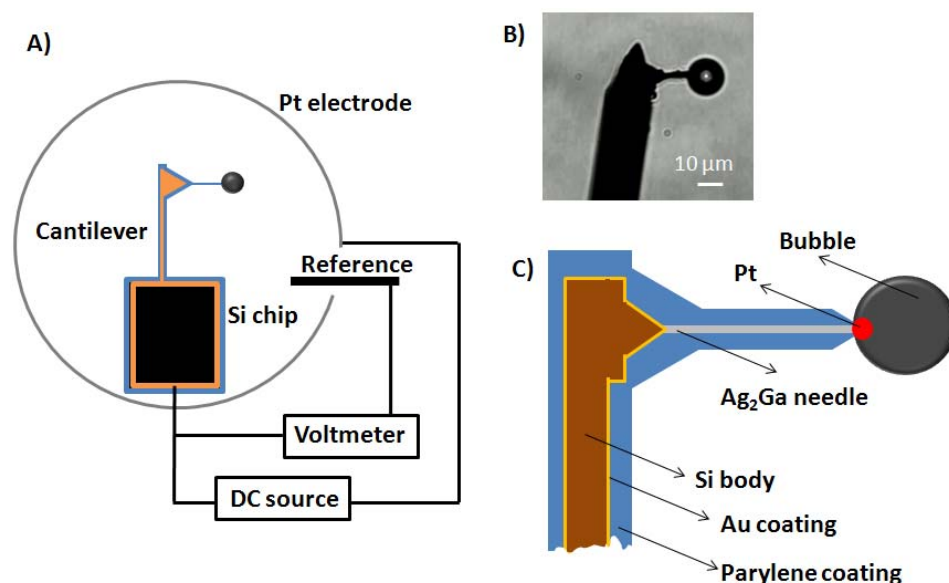


Figure 1. Bubble probe generation setup (A), photograph of a H<sub>2</sub> bubble probe (B) and probe schematic (C)

\*Donose, B.C.; Harnisch, F.; Taran, E. *Electrochemistry Communications* 2012, 24, 21

## Bounds for the surface potential of electrolyte-oil interfaces inferred from a cascade partial coalescence phenomena

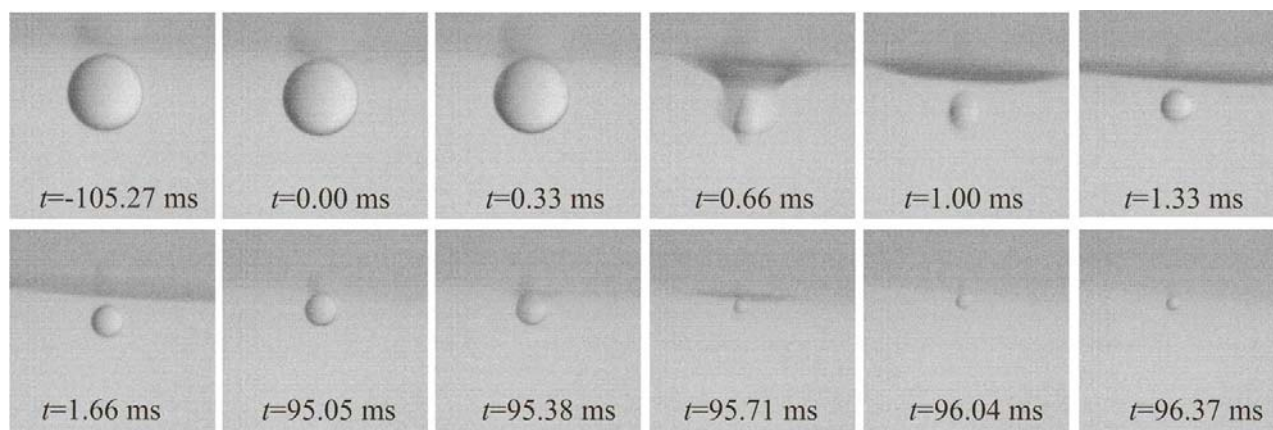
Natalie Kuznicki<sup>1,2</sup>, Pasindu Sellapperumage<sup>2</sup>, Marta Krasowska<sup>2</sup>, Zhenghe Xu<sup>1</sup>, Jacob Masliyah<sup>1</sup>, John Ralston<sup>2</sup>, Mihail N. Popescu<sup>2</sup>

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The value of the surface electric potential (or that of the closely related  $\zeta$ -potential [1]) of a fluid-fluid interface is a crucial parameter for the stability of emulsions, extensively used in the food, cosmetics, or pharmaceutical industries. Because liquid-liquid (i.e., liquid or gas) interfaces are deformable, determining their  $\zeta$ -potential using classic colloid methods designed for solid particles, such as measuring the electrophoretic mobility of drops or bubbles, remains a very challenging task [2].

For a variety of fluids it has been observed that a small drop of a liquid A slowly approaching through an immiscible liquid B a quasi-planar liquid B - liquid A interface may experience a phenomenon of partial coalescence upon colliding with the interface [3-6]. In this process, only a part of the "mother" drop passes through the interface and a smaller "daughter" drop is left behind.

In this work we report experiments that small oil droplets (diameter  $\leq 500 \mu\text{m}$ ) in slow, steady, buoyancy-driven rise through pure or salty water at neutral pH exhibit such a cascade partial-coalescence phenomenon upon the soft collision with a quasi-planar water-oil interface (see Figure below: toluene drop in neutral pH water). For droplets of pure toluene, n-heptane, and various heptol compositions (toluene - n-heptane mixtures) we have observed that the cascade partial-coalescence process stops once a critical size of the droplet has been reached. We infer that this is due to the oil-water interface being electrically charged, in agreement with previous reports [2] and we use it to estimate lower- and upper-bounds for the absolute value of the electrical potential of the interface. We argue that the approach presented here can be developed into a simple method to determine the absolute value of the surface potential for a variety of liquid-liquid interfaces.



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**Bubble-Surface Interactions in the Presence of a Stimulus Responsive Polymer**

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Polymers are used routinely in the mineral processing industry to prevent bubble-particle attachment in flotation. For many years, the common view was that these polymers act by adsorbing to a significant degree and altering the hydrophobicity of the mineral. Recent work from this group has shown that polymers not only affect the static contact angle of a coated mineral, they also affect the thin film drainage and rupture kinetics, and impede the movement of the three phase contact line following bubble-surface attachment<sup>1-3</sup>. These latter two dynamic aspects of polymer modulated bubble-particle attachment raise interesting possibilities for altering flotation outcomes. In this work, we present data on bubble-surface collisions for a hydrophobic mineral surface (talc) with the presence of an adsorbed polymer layer that responds to solution stimuli. Carboxymethylcellulose is a commonly used additive in flotation. It is also stimulus responsive in terms of its adsorbed layer hydration, conformation, and rigidity<sup>4</sup>. Bubble-surface collisions performed as a function of pH illustrate the influence of these polymer layer characteristics on thin film stability and dewetting dynamics. In addition, interferometric AFM (iAFM) experiments were performed for the same system, allowing simultaneous and independent measurement of the force required for film rupture and the thickness of the wetting film prior to rupture.

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## A Water Gradient can be used to Regulate Biophysical Properties of Skin and Mucosa

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We investigate how a gradient in water chemical potential over skin and mucosa can affect barrier structure and function. At normal conditions there is a substantial water gradient over the skin as it separates the water-rich inside of the body from the dry outside and this leads to a variation in the degree of hydration from the inside to the outside. Buccal (oral) and nasal mucosa are less subjected to osmotic stress than skin and the water chemical potential ought to be close to constant over esophageous (gullet) and tracheal (windpipe) mucosa. Furthermore, there is a growing interest for both local and systemic drug delivery via the buccal and nasal routes. Sufficient mucoadhesivity is then a prerequisite, often accomplished through water sorption by the applied drug formulation. Hence, even though the physiological conditions in the mouth and nose are such that the water activity is high, a buccal patch for example could drastically change the local conditions.

In this study we raise the question: How do changes in the water gradient across skin and mucosa affect their permeability? We approach this problem in novel ex vivo diffusion experiments that permit strict control of the gradient in the chemical potential of water and hence well-defined boundary conditions. Model drugs used are budesonide, methyl salicylate, xylometazoline, metronidazole, benzydamine and EDTA. The basic findings are: i) a water gradient can be used to regulate transport of drugs with different lipophilic characteristics across the skin barrier. It is shown that the drug transport across skin increases abruptly at low water gradients, corresponding to high degrees of skin hydration, and that this effect is reversible. ii) buccal and nasal mucosa are orders of magnitude more permeable than skin, but observe the same general response in drug transport rate to a change in the water gradient. iii) The barrier properties of esophageous and trachea, and their response to osmotic stress, closely resemble buccal and nasal mucosa.

This phenomenon is highly relevant to drug delivery applications due to its potential of temporarily open the skin barrier for transdermal drug delivery and then close it after treatment. The results contribute to the understanding of the occlusion effect and indicate the boundary conditions of the water gradient needed to make use of this effect. We have further used X-ray diffraction, DSC, sorption calorimetry, dynamic vapor sorption, confocal Raman spectroscopy and impedance spectroscopy ex vivo to gain better understanding for what happens on a molecular level in the skin when changing the water gradient. We have also performed a clinical proof of concept on skin, using TEWL, corneometry and an irritation test, to verify the ex vivo results described above. Transmucosal drug delivery is seemingly more complex in that it requires sufficient mucoadhesion whereas the same mechanism can hamper drug penetration rate. Thus increased knowledge on how to facilitate both mucoadhesion and drug penetration is a vital future goal.

OC225

**Probing the extent of surface tension additivity on biointerfaces**

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Surface free energy of a chemically heterogeneous surface is often treated as an approximately additive quantity through Cassie equation. However, deviations from additivity are common and molecular interpretations are still lacking. We use molecular simulations to measure the microscopic analogue of contact angle,  $\theta_c$ , of aqueous nanodrops on heterogeneous synthetic and natural surfaces as a function of surface composition. The synthetic surfaces are layers of graphene functionalized with prototypical nonpolar and polar head group: methyl, amino and nitrile. We demonstrate positive as well as negative deviations from the linear additivity. We show the deviations reflect the uneven exposure of mixture components to the solvent and the linear relation is recovered if fractions of solvent accessible surface are used as the measure of composition. As the spatial variations in polarity become of larger amplitude, the linear relation can no more be obtained. Protein surfaces represent such natural patterned surfaces, also characterized by larger patches and roughness. Our calculations reveal strong deviations from linear additivity on a prototypical surface comprising surface fragments of melittin dimer. The deviations reflect the disproportionately strong influence of isolated polar patches, their preferential wetting, and changes in the position of the liquid interface above hydrophobic patches. Since solvent-induced contribution to the free energy of surface association grows as  $\cos\theta_c$ , deviations of  $\cos\theta_c$  from the linear relation directly reflect nonadditive adhesive energies of biosurfaces [1]. (Supported by US NSF and DOE).

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**OC226**

**Liquid Marble as Micro-Bioreactor**

Tina Arbatan, Aswan Al-Abboodi, Fatemeh Sarvi, Lizi Li, Miaosi Li, Junfei Tian, Nan Fu, Peggy Chan, Wei Shen

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Liquid marbles can be used as micro-bioreactors, thanks to their unique properties. On the one hand, the highly porous, non-adhesive, and hydrophobic shell of liquid marbles efficiently inhibits any direct contact between the liquid core of the marble and the surface that supports it, while allowing oxygen and carbon dioxide to pass through. On the other hand, the finite volume of liquid in liquid marbles is capable of containing microorganisms and cells, providing suitable growth conditions for the microorganisms and cells. Moreover, due to their soft and flexible structure, liquid marbles can be manipulated rather easily when required; hence biological reactions or assays inside liquid marbles can be conveniently controlled. The combination of these properties account for the high efficiency of micro-bioreactors made of liquid marbles for applications such as conducting biochemical reactions, microorganism culturing and 3D cell spheroid culturing.



OC227

## Hydrogel Nanoparticles: Surface Properties and Interactions with Living Cells

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Thermosensitive polymer nanospheres based on N,N-diethylacrylamide and 2-hydroxyethyl methacrylate (HEMA) have been prepared and characterized. The polymeric nanoparticles (NPs) had a hydrodynamic diameter of ca. 600-800 nm at 20 degrees in aqueous suspension. Their surface interactions (adhesion and friction) as well as their cellular uptake have been investigated.

Adhesion and friction between two nanoparticle monolayers grafted onto mica surfaces and immersed in water were studied using a surface forces apparatus (SFA). They were irreversibly grafted onto chemically modified mica surfaces at a constant surface coverage. The measured normal forces between two opposing NP monolayers were found to be strongly dependent on the temperature. At temperatures lower than the lower critical solution temperature (LCST), the grafted NPs were swollen, and the normal interaction forces between the two NP monolayers were purely repulsive. Above the LCST, the NPs collapsed, and attractive forces between the NP layers were measured. The swollen NPs exhibit very low friction forces compared to the collapsed ones. The effect of the sliding velocity on the shear stress was investigated, and the results are in agreement with the so-called adhesive friction model developed for rubber friction. Our results suggest that the water content in the contact area and the interdiffusion of polymer chains are important parameters in determining adhesion and friction between hydrogel nanoparticles.

Uptake and intracellular trafficking of hydrogel nanoparticles (NPs) were studied with a RAW 264.7 murine macrophage cell line. Results show that the uptake rate, the mechanism of internalization and the concentration of internalized NPs are correlated to the NP Young modulus. Soft NPs were internalized preferentially via macropinocytosis while the uptake of stiff NPs were mediated by a clathrin-dependent mechanism. NPs with an intermediate Young modulus exhibited multiple uptake mechanisms. The accumulation rate of the NPs into lysosomal compartments of the cell was also dependent on the NP elasticity. Our results suggest that control over the mechanical properties of hydrogel NPs can be used to tailor the cellular uptake mechanism and kinetics of drug delivery.

OC228

**Methane-Propane Mixed Gas Hydrate Film Growth on the Surface of Water and Luvicap EG Solutions**

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We studied the growth rate of methane-propane mixed gas hydrate films on the surface of water and up to 3 wt % aqueous solutions of a kinetic hydrate inhibitor, Luvicap EG, using a High Pressure-Video Cell. The growth rate of the hydrate film on water was found to increase with the system subcooling. Using Mori's heat-transfer limited growth model, we estimated the initial thickness of the hydrate films on water to be between 1.3 and 25  $\mu\text{m}$ . Addition of Luvicap EG inhibited both the nucleation and the growth of the hydrate films, as we observed that the films on Luvicap EG solutions grew at a slower rate, and their nucleation required greater subcoolings, as compared to those on water. Notably, the hydrate films that grew on Luvicap EG solutions were more transparent, and thus thinner, than those on water. The thinner and yet more slowly growing hydrate films on Luvicap EG solutions suggest that the growth mechanisms had changed from that of a heat-transfer limited growth to a mass-transfer limited growth.

## Micro-Patterned High Conductivity Polymer Films and their Application in Organic Electrochromic Devices

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As concerns about our increasing energy usage start to take hold, alternate energy efficient devices and systems have generated intense scientific interest. Devices such as organic solar cells generate electrical power, however complementary to this, devices such as organic electrochromic devices (OECDs) present themselves as candidates for reducing the energy consumption of buildings and/or vehicles. These devices are based upon thin films (< 200 nm) of conducting polymer(s) deposited in a sandwich-like architecture, where their optical properties “switch” between a transparent to a highly attenuated state by means of an externally applied voltage. By utilising their switching behaviour, electrochromic windows can reduce energy consumption within a commercial building through regulation of incoming light, hence reducing cooling and lighting costs. OECDs require only minimal power to switch their optical properties, with little or no further power required to maintain the new switched state. In this study, we have incorporated conjugated polymer thin films such as, poly(3,4-ethylenedioxythiophene) (PEDOT), into several OECDs. The polymers are synthesised using a technique known as vapour phase polymerization (VPP) which results in uniform thin films that can also possess high conductivity. These *in-situ* deposited polymers are then incorporated into devices that can be used as active window tinting.<sup>3</sup> The VPP technique involves depositing an oxidant solution onto a given substrate, upon which the polymer is grown by exposure to a monomer vapour. Of particular interest is the ability to create micro-patterns of the oxidant mixture using inkjet printing which, after exposure to the monomer vapour, results in a patterned polymer. The inkjet printing/VPP synthesis combination has been generalised to a range of different conducting polymers, which to date include: poly(3,4-ethylenedioxythiophene); poly(3,4-ethylenedioxyselelophene); poly(3-hexylthiophene); and polypyrrole, thus demonstrating the wider applicability of the synthesis technique with respect to OECDs for energy efficiency applications.

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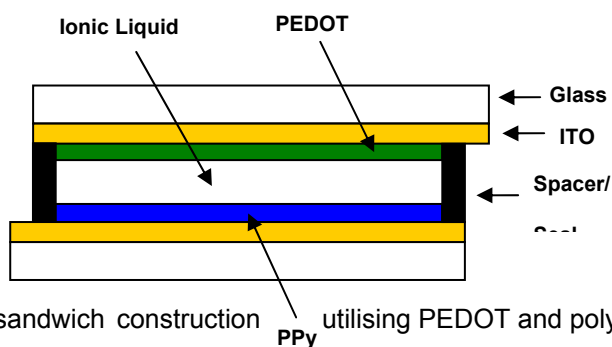


Figure 1: Typical OECD sandwich construction utilising PEDOT and polypyrrole.

**Graphene Oxide as a Novel Colloidal Stabilizer in Dispersed Polymerization Systems**

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Since the discovery of graphene in 2004,<sup>1</sup> there has been intense research devoted to the creation of graphene-polymer composite materials, aimed at exploiting graphene's extraordinary mechanical, electrical and thermal properties.<sup>2-4</sup> Graphene however is incompatible with most polymers and homogeneous composites are difficult to realize. An attractive route to the creation of such composites is the use of graphene oxide (GO), prepared by the treatment of graphite with strong oxidizing agents and acids.<sup>5</sup> GO possesses numerous functional groups for further reaction, and can be readily dispersed in aqueous media. Additionally, GO can be reduced back to graphene post-functionalization using a variety of techniques.

It was recently reported that GO can act as a 'surfactant' to stabilize oil in water (o/w) emulsions,<sup>6,7</sup> which was attributed to the amphiphilic nature of GO (consisting of hydrophobic graphitic regions and hydrophilic and charged oxygen containing functional groups). These Pickering emulsions are extremely stable and are also pH dependent, raising the possibility of switchable systems. Our research focusses on utilizing these surfactant-like properties of GO to create polymer nanoparticles that are 'armoured' with GO sheets, in particular by miniemulsion polymerization. Using precursor graphite nanofibres to ensure a narrow distribution in GO sheet size, miniemulsions of styrene (with 5 % w/w hexadecane) in water have successfully been polymerized with GO as a sole surfactant, the first time that this has been reported.<sup>8</sup> Highly textured, roughened particles with a diameter of approximately 500 nm were formed, the surface morphology due to GO at the interface. The particle size distribution is however relatively broad, with current investigations examining the influence of aqueous phase pH, hydrophilic co-monomers and cross-linking agents. Additional work relating to emulsion polymerization systems stabilized by GO will also be discussed. We consider these methods to be convenient routes towards the creation of polymer-graphene composite materials for a variety of applications.

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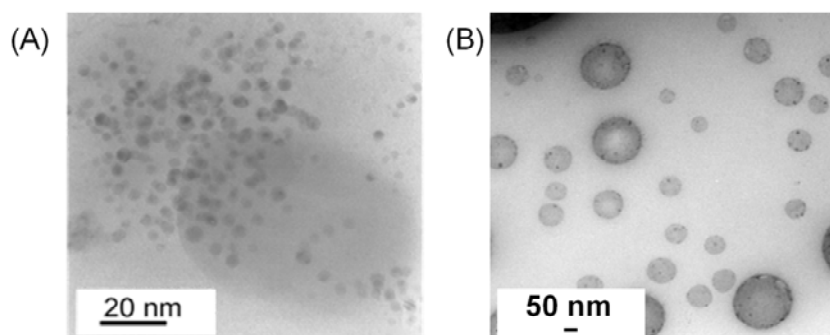
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**Controlled nanoarchitectures for the effective storage of hydrogen**Francois Aguey-Zinsou*The University of New South Wales, Sydney, Australia*

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 effect 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<sup>1</sup> 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 (Fig. 1A) instead of the usual 400 °C required for bulk magnesium. Similarly, core-shell NaBH<sub>4</sub>@Ni nanoparticles (Fig. 1B) demonstrated for the first time the possibility of reversibly storing hydrogen under practical conditions with NaBH<sub>4</sub>, a compound that irreversibly decomposes into its elements at temperatures > 500 °C.



**Fig. 1:** (A) magnesium nanoparticles<sup>2</sup> and (B) core-shell NaBH<sub>4</sub>@Ni<sup>3</sup>

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**Surface Complex Grafted Nanoparticles of Metal Hydroxide as Sunlight Photocatalysts for Selective Oxidation of Alkyl Aromatics**

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We reports a new class of photocatalysts, metal hydroxide nanoparticles grafted with alcohols, which at ambient temperatures when irradiated with light (visible or ultraviolet light or sunlight) have the ability to efficiently oxidize stable compounds such as toluene and xylenes with gaseous oxygen yielding fine chemicals, such as aldehydes, alcohols and acids.

It is very difficult to oxidize the stable alkyl aromatic molecules under moderate conditions. The current commercial approaches can only be conducted under high temperatures and oxygen pressures or require recovery of homogeneous cobalt catalysts. However, improved conversion through increased temperature always significantly decreases product selectivity with runaway reactions giving over-oxidized products (such as CO<sub>2</sub>). The conversion of the commercial toluene oxidation at elevated temperature is limited to  $\leq 15\%$  to guarantee product selectivity. We also found that the well-known titanium dioxide photocatalysts and the photocatalysts of supported gold nanoparticles, are unable to oxidize the stable alkyl aromatic molecules. In this study, the photocatalysts were obtained by simply grafting metal hydroxide nanoparticles with alcohols, they can efficiently catalyse the oxidation of the stable compounds at ambient temperatures when irradiated with light, achieving relatively high conversion and product selectivity. For example toluene can be oxidised with a 23% conversion after 48-hour exposure to sunlight with 85% of the product being benzaldehyde, and only a trace of CO<sub>2</sub>.

The new photocatalysts have several important characteristics:

- (1) New mechanism distinctly different from those of any known photocatalysts. The surface complexes are anchored on the surface of metal hydroxides by chemical bonds and can absorb light generating free radicals on the surface, which then initiate aerobic oxidation of the stable alkyl aromatic molecules.
- (2) Utilizing sunlight to drive production of fine organic chemicals in an efficient and green approach (via utilizing light absorption to generate active radicals that induce reaction).
- (3) High chemoselectivity, for example, only one of the two methyl groups of xylenes is oxidized (for conversions up to 49%) while the other remains intact.
- (4) Enabling synthesis of temperature-sensitive products, which previously would have been prohibited due to their unstable nature at high temperatures.

The results of our research highlight the potential for utilizing sunlight to drive the production of fine chemicals. The findings reported in this paper may inspire further studies in a wide range of organic synthesis driven by sunlight, design of new photocatalyst materials, and development of new reaction processes.

## Graphene Growth and the Carbon-Catalyst Interface: Insights from Non-Equilibrium Molecular Dynamics

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Carbon nanostructures, such as fullerenes, carbon nanotubes and graphene, are currently at the forefront of nanoscale molecular and material sciences. Yet in many cases, a precise, atomistic understanding of how such nanostructures form is currently lacking. Here our recent non-equilibrium molecular dynamics (MD) simulations of graphene formation on transition metal catalysts<sup>1,2</sup> will be presented.

We employ the density functional tight-binding method, an approximate density functional theory (DFT), to simulate these phenomena with an accuracy comparable to that of “true” DFT, but at a cost that is comparable to classical force-field-based methods. Our simulations have recently demonstrated that graphene, contrary to common assumptions, may actually form underneath the catalyst surface before “precipitating” to the surface (Figure 1). Following this sub-surface to surface transition graphene becomes ‘anchored’ in place on the catalyst surface by a surface defect. Our simulations also reveal the precise nature of the catalyst itself – most interestingly, it is not a static, inert structure as is commonly assumed; instead it is a dynamic species that constantly evolves as graphene nucleation proceeds. For the first time these simulations draw into question the nature of the carbon-catalyst interface itself, and its influence on nanoscale self assembly processes such as graphene and carbon nanotube growth.<sup>3</sup> Our simulations show that the carbon-catalyst interface must be accurately modelled if these nanoscale self assembly processes are to be truly understood.

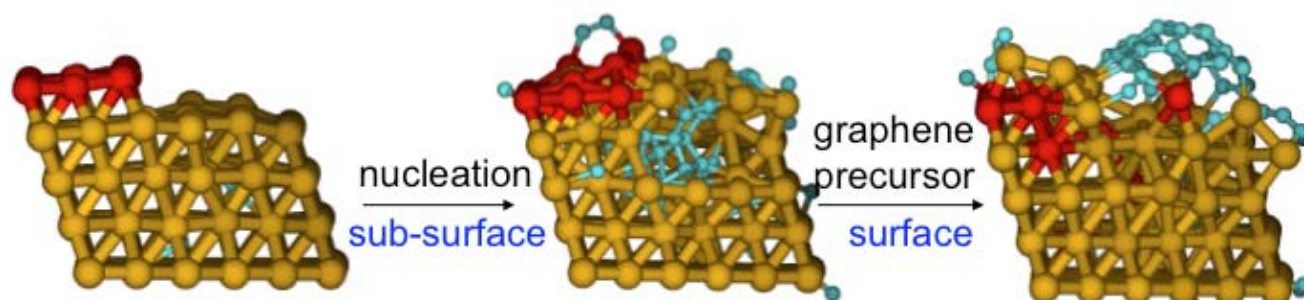


Figure 1. MD simulations show that graphene nucleation may occur in the catalyst subsurface, before precipitating to the surface region.

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**Colloidal Forces Between Bubbles and Drops – Compound Sessile Drops**

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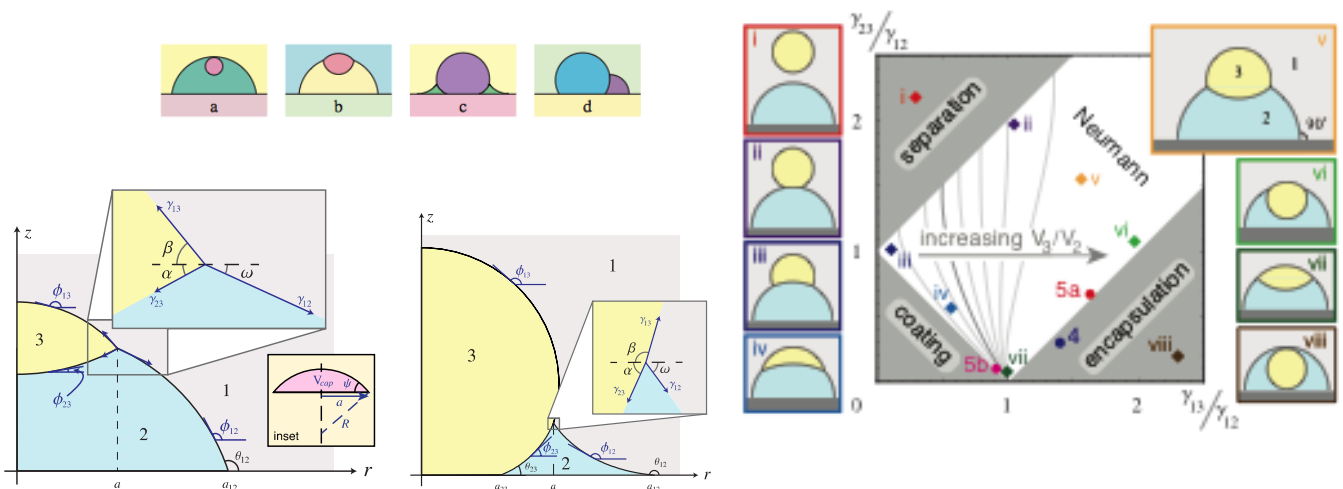
Compound sessile drops arise from the contact of three immiscible fluids and a substrate. Their configurations assume distinct geometries depending on the interfacial energy ratio and the wetting properties of the substrate, see Figure (a)-(d).

For drop sizes that are small compared to the capillary length, the shapes of the interfaces are independent of gravity. However, because of density differences, microgravity effects can still determine the equilibrium configuration. A surface energy diagram can be constructed as an overall design tool to predict the possible shapes of compound sessile drops (see Figure Right).

In certain cases, the drop shapes results from a balance of repulsive van der Waals forces of quantum mechanical origin and (micro) gravitational forces.

Kinetic processes such as the evaporation of one of the phase can facilitate the transition between configurations that correspond to local energy minima.

Such compound sessile drops may prove useful as the first step towards development of functional surfaces in applications such as soft optics, photonics and surface encapsulation (2).



**Figure Left:** Possible configurations of compound sessile with a lens (b), a pendular collar (c) or without symmetry (d). **Right:** Possible compound sessile drops with a lens in an interfacial energy ratio diagram. Characteristic lens shapes in the region are given in the insets (i)–(viii) for the substrate contact angle  $\theta_{12} = 90^\circ$  and volume ratio  $V_3/V_2 = 1/4$ . The contour lines in the Neumann region locate the boundaries where the lens shape changes from concave-convex (iii-iv: to the left) to biconcave (v-vii: to the right) at the volume ratios:  $V_3/V_2 = 0.01, 0.1, 0.25, 0.5, 1, 2, 5$ .

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**Colloidal Forces Between Bubbles and Drops – Interactions and Assembly**

Rico Tabor<sup>1</sup>, Michael J Neeson<sup>2</sup>, Chu Wu<sup>2</sup>, Franz Grieser<sup>2</sup>, Derek YC Chan<sup>2</sup>, Raymond Dagastine<sup>2</sup>

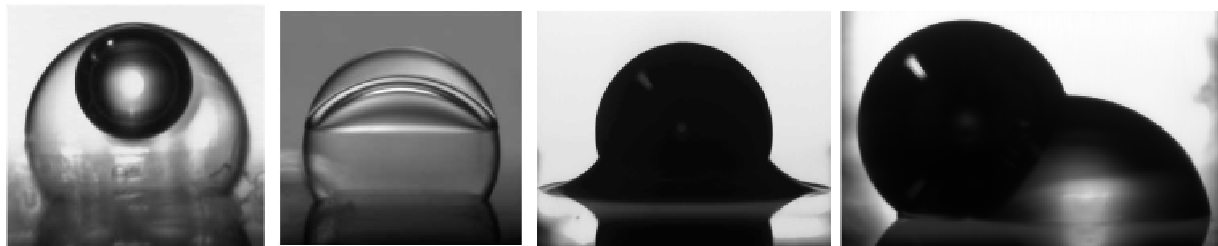
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Understanding the interactions between droplets of oil and gas bubbles is central to tuning the desired properties of foodstuffs such as ice cream and mousse, cosmetics and pharmaceuticals, and in mineral flotation and separation. Fundamentally, the interaction between dissimilar fluid interfaces is an interesting problem, as they may charge and deform to different extents. We have used the atomic force microscope (AFM) to analyse collisions between bubbles and oil droplets - of around 100 microns diameter - in surfactant-free aqueous solutions.<sup>1</sup> This information was used to enable the analysis of complex surface-immobilised compound drops.

Through carefully chosen experiments and quantitative modelling,<sup>2</sup> it was possible to obtain surface potentials for the oil drops and air bubbles. Between like pairs of drops or bubbles, electrical double-layer forces were predictably repulsive, and Van der Waals forces were attractive. However, it was found that within a small pH-range, double-layer forces between dissimilar bodies could be rendered attractive. Similarly, material choice allowed the sign of the Van der Waals force to be selected to be either positive or negative, and ionic strength also has a surprising role via screening when Van der Waals forces are small.

Using the information obtained from force measurements, we produced a range of surface-immobilised compound drops (comprising 2 or more immiscible fluids) and analysed their structures. It was found that systems are broadly controlled by the relative surface energies within the system, but that more subtle Van der Waals and microgravity forces may influence the equilibrium state.

These results give new insight into how coalescence and interactions can be controlled for fluid handling in microfluidics, as well as dispersion and formulation science. Material choice, pH and ionic strength can be used to enhance or avoid coalescence. Significantly, a roadmap is provided which guides the formation of compound drops with specific, designed geometries for surface encapsulation and optical functionalisation.



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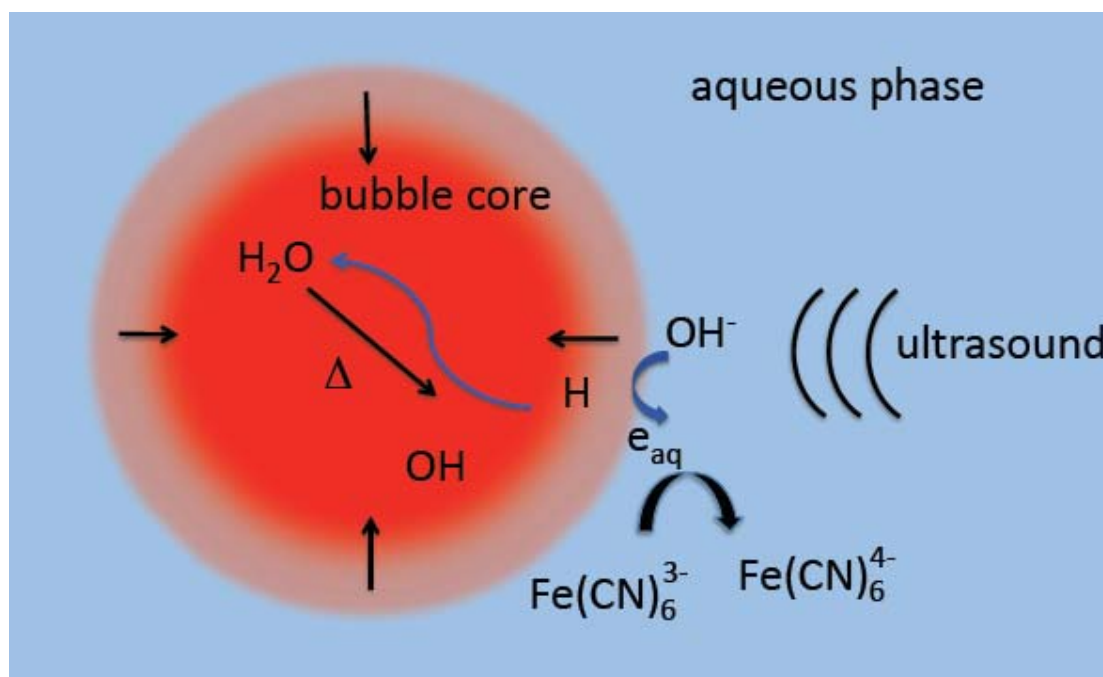
## OC303

### Free Radical Generation and Reactions in the Sonolysis of Aqueous Solutions

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The inertial collapse of bubbles in water can produce transient local “hot spots” with temperatures above 4000 K. Gases trapped in such bubbles are rapidly heated and, depending on the gas in the bubble, produce free radicals. Most of these free radicals recombine within the bubble. However, conditions can exist that lead to further reaction of these radicals with solutes at the bubble solution interface, or in bulk solution. A schematic representing radical generation within a collapsing bubble and some subsequent reactions is shown in the figure below.



The talk will present new information on the generation of radicals in cavitating bubbles created in aqueous solutions exposed to ultrasound, and how both oxidising and reducing radicals can be produced. A special case for generating the hydrated electron will be described. The effect of surface active solutes on inter-bubble effects and on radical yields will also be discussed.

OC304

**Detergent-free microemulsions: “new” formulations for “green” solubilisation or an urban legend?**

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Surfactants are a prime example of molecules that form well-defined aggregates (micelles and liquid crystals) in solution. Hydrotropes are another class of surface active substances, but in contrast to surfactants they do not form structures or only loose and undefined fluctuations.

In the 1970s mysterious so-called “surfactant-free” microemulsions were proposed, but neither convincing investigations of their structure were published nor was given a plausible explanation of the mechanism [1, 2]. Finally, Katz and Vitale [3] showed a way of producing very fine emulsions with small droplets in a liquid phase without surfactants, dispersing agents of mechanical agitation that are remarkably stable in time. We show the precondition of the existence and stability of such “surfactant-free emulsions” is the mixture of two solvents with a solute (can be also a solvent), e.g. anethol, that is highly soluble in one solvent (ethanol), but not in the other one (water). In addition, the two solvents (e.g. water and ethanol) must be miscible, either completely or at least to a large extent. Whereas this two-phase region is widely studied now, we were interested in the monophasic region close to the binodal line, a region that we call here the “pre-Ouzo domain”.

We present a study of the monophasic region of such a surfactant-free ternary system containing water, ethanol and octanol based on dynamic light (DLS), small-angle X-ray (SAXS) and neutron (SANS) scattering. To our surprise, from these experimental results it became evident that well-defined micellar structures and consequently two distinct pseudo-phases exist in these ternary mixtures. To get further information about the partition of ethanol between the pseudo-phases (one is water-rich, the other one rich in octanol) we further considered the partial pressure of ethanol above the liquid medium.

From the experimental results we were able to deduce a model for the driving force of this particular micelle formation that does not require the presence of surfactants. In the present contribution we will introduce this new type of association colloids and show how general it is.

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OC305

## The Theory of Brownian Coagulation

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The theory of Brownian coagulation is 95 years old. In 1916, von Smoluchowski published his theory of *rapid* coagulation in which the rate of depletion of singlet particles in a dispersion that has been destabilised by the removal of repulsive barriers between the particles was calculated by considering the process as the mutual diffusion of the particles towards one another. The theory of *slow* Brownian coagulation was developed by Fuchs in 1934 and later by Verwey and Overbeek in 1948 in which the residual presence of a repulsive barrier to coagulation controlled the mutual diffusion process. The conventionally accepted theory of slow coagulation was developed following the suggestion of Derjaguin in 1966 that the rate of coagulation was significantly affected by the repulsive hydrodynamic drainage forces that each particle exerted on the other during the final stages of approach. This effect was variously treated by invoking the concept that the mutual diffusion coefficient is a strong function of particle separation in the close approach regime. The modern conventional theory relies on the attractive component of the inter-particle pair potential *being infinitely attractive* at contact to counter *the infinite drag* on two approaching particles there and thus ensuring the production of contact doublets. We examine the consequences of the attractive potential being finite at contact and construct a new theory of slow Brownian coagulation which attempts to account for the experimentally observed features of coagulation which are at variance with theoretical prediction. A simple result for the stability of suspensions is derived and discussed with some numerical predictions with respect to the peculiar insensitivity of coagulation rate with particle size observed experimentally.

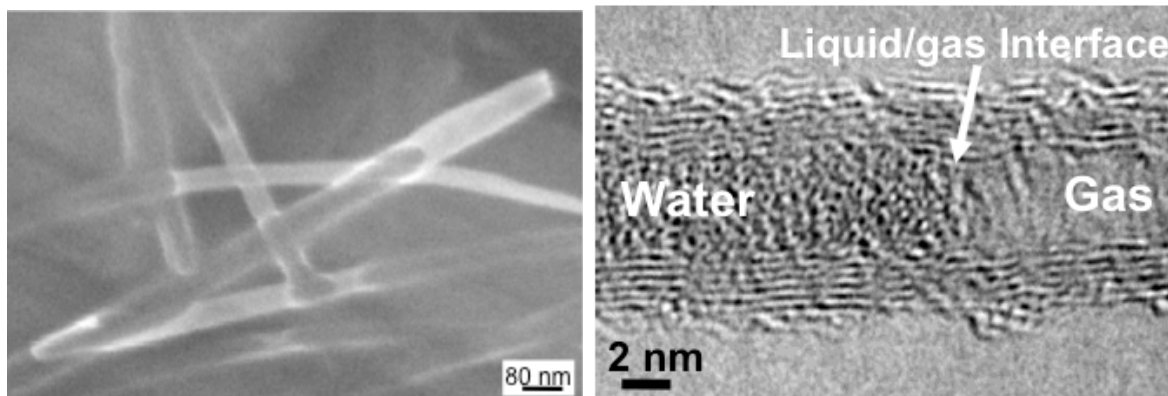
## Beyond the Slip Length – Using Surface Forces to Explain Ultra-high Water Flow in Carbon Nanotubes

Davide Mattia<sup>1</sup>, Francesco Calabrò<sup>1,2</sup>, Kah Peng Lee<sup>1</sup>

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Experimental results of water flow through carbon nanotubes (CNTs),<sup>1</sup> showing orders-of-magnitude higher than expected flow rates, have generated an intense debate about the underlying physical phenomena and whether such flow can be explained within the continuum model on which classical fluid mechanics is based.<sup>2</sup> These results also hold great promise for filtration applications in general and water desalination in particular.

Attempts so far to explain these results have focused on the nature and value of the slip length at the wall and its possible dependency on a wide range of parameters, from contact angle to roughness, viscosity and shear rate. All these solutions are somewhat unsatisfying when slip values in the order of tens of micrometers for CNTs with diameters of only few nanometers are obtained. Moreover, no model has been yet capable of explicitly relating the flow enhancement with solid-liquid molecular interactions occurring at the channel walls.



Water plugs in 40-60 and 2-5 nm diameter carbon nanotubes, respectively.

A different approach is presented here with a model capable of explaining the effect on water flow of the solid-liquid molecular interactions at the channel wall via the work of adhesion.<sup>3</sup> A comparison with published experimental and modelling results showing good agreement will be presented and insight on how to extend this model beyond the specific case of water-CNTs will be offered.<sup>4</sup>

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**OC307**

**Accounting for roughness in surface interactions between non-ideal surfaces**

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A method of incorporating surface roughness into theoretical calculations of surface forces is presented. Surface roughness is represented as a probability distribution of surface heights around an average surface height. A roughness-averaged force is determined by taking an average of the classic flat-surface force, weighing all possible separation distances against the probability distributions of surface heights. A normal distribution may be assumed for the surface probability distribution, characterised by the RMS roughness measured by AFM. Alternatively the probability distribution may be defined by the histogram of heights measured by AFM. Both methods of treating surface roughness are compared against the classic smooth surface calculation and experimental AFM measurement.

The DLVO theory of colloidal stability, developed by Derjaguin and Landau,<sup>1</sup> Verwey and Overbeek,<sup>2</sup> has been of considerable value in understanding surface interactions between colloidal particles. While the limitations of the theory are well known, the theory has nevertheless provided insight across a vast range of fields, including agriculture and food science, mineral and oil extraction, filtration and biology.

One limitation of the theory is that it is built upon the assumption of ideally smooth surfaces. The boundaries between surfaces and solution are taken to be infinitesimally sharp, with the separation distance between surfaces uniquely defined by a single pure value. In practice real surfaces with the exception of mica are typically never atomically smooth but are characterised by a certain roughness, with pits and mounds causing the local surface height to deviate around its average value. Consequently the surface forces between the purely smooth surfaces predicted by DLVO theory do not in general provide the most accurate estimate of the true surface forces. As various locations across the surface rise or fall in accordance with that surface's roughness, the local distance between the two surfaces becomes greater or smaller, perturbing the force felt between surfaces.

Here we describe how the influence of surface roughness on surface forces of any nature can be addressed using real data obtained using the Atomic Force Microscope.

## Structural Details of the Electrical Double Layer Revealed at High Resolution

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The surface charge and the diffuse layer of counterions form an electrical double layer that significantly affects the way surfaces interact in solution. The structure and properties of this solid–liquid interface are of practical and scientific relevance for biological systems, geophysical processes, surface chemistry, weathering mechanisms and electrochemistry.

In this work we directly measure surface forces between surfaces in potassium nitrate (KNO<sub>3</sub>) solution - from very dilute to near saturation. The significantly improved resolution of the extended surface force apparatus (eSFA) allows the distinction of hydration structures and hydrated-ion correlations as never seen before.

Above concentrations of 0.3 mM, hydrated-ion correlations are detected that give rise to oscillatory transitions. Using the much increased resolution of the eSFA we can assign those features to layering of hydrated ion layering. This is in contrast to the traditional idea of water layering. A new picture of the internal structure and associated energies in the electrical double layer emerges.

A single hydrated-ion layer adjacent to the surface (i.e. outer Helmholtz layer) is particularly well defined and plays a distinctive role. It is mobile only at low concentration and can be expelled, or, external mechanical work can be used at slightly higher concentration to partially dehydrate it, resulting in an abrupt increase of surface adhesion. Above 20 mM attractive surface forces are measured in deviation to the DLVO theory – a sign for the prevalence of ion correlation forces.

A 1–3 nm thick ionic layer finally solidifies at the surfaces at concentrations as low as 100 mM, i.e. clearly below bulk saturation of the electrolyte solution. The existence of this crystal-precursor changes our understanding of crystallization in confinement and associated forces, which are important for rock or concrete weathering and biomineralization.

**Direct imaging of single hydrated ions at the solid-liquid interface**Maria Ricci, Kislon Voitchovsky*EPF Lausanne, Lausanne, Switzerland*

The spatial distribution of ions at solid-liquid interfaces is a central problem to fields as diverse as colloidal science, biology, electrochemistry, condensed matter physics, materials science and chemical engineering. Ions dissolved in the liquid tend to accumulate close to the surface of charged solids, forming an electrostatic double layer (EDL). The structure and spatial distribution of the EDL is key to many processes such as colloidal stability, molecular self-assembly, charge diffusion, or protein-protein interactions, and hence has been the object of intense experimental and theoretical research over the last century. To date, most EDL models, such as the widely used Gouy-Chapman-Stern model (GCS) [1] tend to fall short close to the solid (<1nm) especially for highly charged systems. In the Stern layer region, the GCS assumptions of point charge, constant dielectric permittivity and purely coulombic interactions are no longer valid. As a consequence, many important phenomena originating within the Stern layer region cannot be captured by GCS; this is the case for ion correlation effects [2], ion-specific forces [3] or charge inversion [4].

Experimentally, results are typically based on techniques such as diffraction or spectroscopy [5]. These techniques, although very accurate, usually require averaging over large area and hence cannot capture local effects and lateral inhomogeneities in the Stern layer.

Using an approach based on amplitude-modulation atomic force microscopy [6,7], I show that it is possible to resolve individual hydrated ion at the surface of different solids in water. The approach exploits the lateral variations in the hydration structure of the solid induced by adsorbed ions to enhance the resolution, effectively providing atomic-level maps of the Stern layer. The results reveal a surprising complexity even in simple systems such as monovalent metal ions on mica, with ion-specific electrostatic correlation effects.

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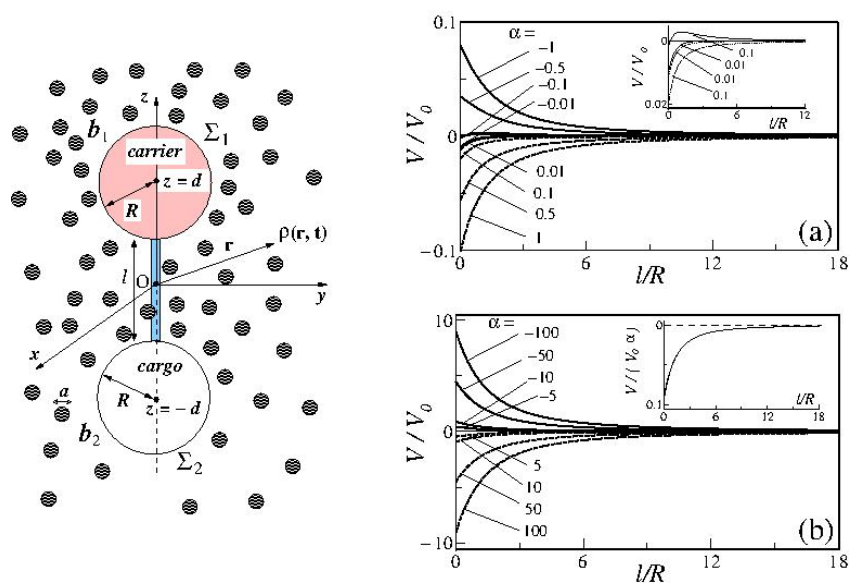


## Chemically Active Colloids as Particle Carriers

Mihail N Popescu<sup>1,2</sup>, Mykola Tasinkevych<sup>1,2</sup>, Siegfried Dietrich<sup>1,2</sup><sup>1</sup>Ian Wark, UniSA, Mawson Lakes, SA, Australia, <sup>2</sup>Max-Planck Institute for Intelligent Systems, Stuttgart, Germany

The reduction in length scales brought about by “lab-on-a-chip” applications has raised a number of challenging issues, such as how to enable small objects to perform autonomous, directional motion (so-called self-propulsion) in a liquid environment [1-3]. One option is that of employing catalytically activated chemical reactions to extract “chemical” free energy from the surrounding liquid environment and to transform it into mechanical energy (motion of microparticles) [1-3].

Self-diffusiophoresis, which is one such mechanism, is achieved by using particles which are partially covered by a catalyst in a well controlled way such that a chemical reaction promoted by the catalyst in the surrounding solution generates gradients of the reaction products along the particle's surface [1-9]. These particles have the potential of acting as carriers at the micro-scale [2,9]. We study a simple model for an active particle – inert carrier composite: a spherical particle with its whole surface being active, which is connected by a thin rigid rod to a chemically inert cargo spherical particle. (This choice emphasizes the subtleties of self-diffusiophoresis in that the composite moves even though each of its components is motionless when isolated.) We derive an exact, analytical solution for the velocity and exploit it to analyse in detail the performance of the composite, as well as the direction of its motion, in the case in which the carrier and the cargo consist of different materials (different effective interactions with the solution) leading to different phoretic mobilities,  $b_1$  and  $b_2 = \alpha \times b_1$ .



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**OC311**

**Stability of Interfacial Nanobubbles**

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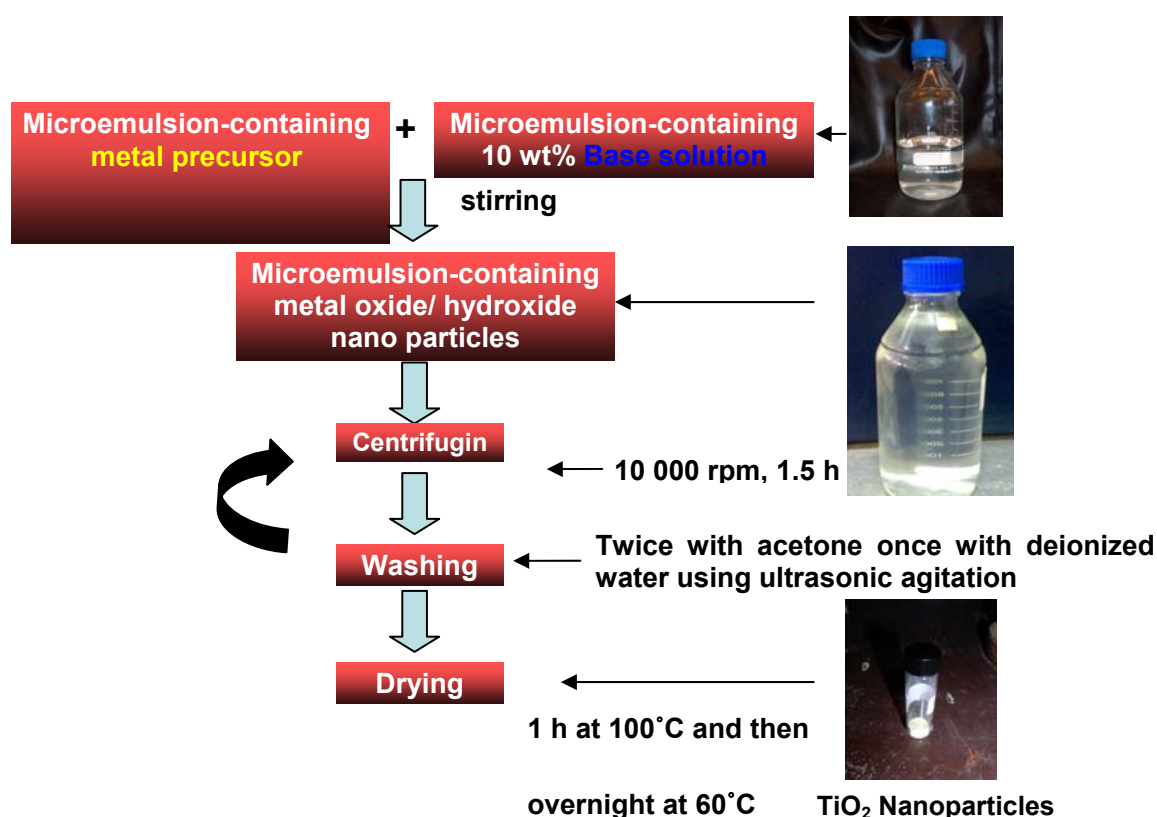
Recently interfacial nanobubbles (INBs) at solid-water interfaces have drawn research interest. Although several theoretical models have been proposed to explain their long lifetime, the underlying mechanism still remains in dispute. In this work, the morphologic evolution of INBs was examined in air-equilibrated and partially-degassed water, respectively. Our results show that INBs can disappear noticeably faster in partially degassed water than in air-equilibrated water, thus underlining a major contribution of the saturation level of the dissolved gas to the long lifetime of the INBs. Our results also indicate that the three-phase-boundary of INBs was pinned during the morphology evolution of INBs, which can significantly slow down the growth and shrinkage kinetics of the INBs according to our newly developed one-dimensional version of the Epstein-Plesset model.

## Salt and Temperature Insensitive Microemulsion Used as Soft Nanoreactors

Ali Bumajdad

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Water-in-*n*-heptane microemulsions stabilized by a mixture of the cationic di-*n*-dodecyldimethylammonium bromide (DDAB) and the non-ionic polyoxyethylene (23) dodecyl ether (Brij®35) (90:10 molar ratio) were proved to be relatively insensitive to both temperature and salt addition and hence can be used a soft nanoreactor to prepare variety of nano-sized metal oxides such as CeO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZnO, MgO and Cr<sub>2</sub>O<sub>3</sub> [1-5]. The phase behavior stability of such microemulsions will be explained and then the bulk and surface properties of some metal oxide nanoparticles prepared in such system will be discussed. The soft nanoreactor droplet size and concentration were controlled by varying the surfactant concentration, *S*, (= 0.05, 0.1, 0.15 and 0.2 M) and the water-to-surfactant molar ratio, *W*, (=20, 35 and 50) and the effect of such variables on the properties of the prepared metal oxides will be explained. The diagram bellow explains, briefly, the metal oxide synthesis procedure.



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OC313

**Bicontinuous cubic phase nanoparticle lipid chemistry affects toxicity in cultured cells**

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Gaining an increased understanding of the toxicity of new lipid nanoparticle formulations such as the class of compounds called cubosomes™ and hexosomes™ is crucial for their development as therapeutic agents. Surprisingly, the literature on the in vitro and in vivo toxicity of cubic and hexagonal phase forming lipid nanoparticles is negligible, despite a rapidly growing number of publications on their potential use in various therapeutic applications. In this work we have developed methods to study the in vitro cytotoxicity of two chemically distinct cubic phase nanoparticle dispersions using the lipids glycerol monooleate and phytantriol respectively. We have found that the toxicity of phytantriol cubosomes is considerably greater than that of glycerol monooleate cubosomes. The increased toxicity of phytantriol appears to result from its greater ability of disrupting the cellular membrane. This finding has significant impact for further research on the use of cubic phase forming lipids for therapeutic and diagnostic applications both in vitro and in vivo.

**Morphological Studies of Nanoscale Thin-Film Optoelectronic Devices Using Neutron Reflectometry**

Michael James<sup>1</sup>, Tamim Darwish<sup>1</sup>, Arthur Smith<sup>2</sup>, Hamish Cavaye<sup>2</sup>, Kwan Lee<sup>2</sup>, Paul Meredith<sup>2</sup>, Ian Gentle<sup>2</sup>, Paul Burn<sup>2</sup>

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The operating efficiencies and lifetimes of thin-film optoelectronics are key performance metrics that require further optimisation before the widespread use of such devices. Organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs) both rely on charge transport in nanoscale thin films. To better understand the morphologies and molecular interactions within nanoscale optoelectronic systems, as-prepared and annealed devices were investigated in a series of experiments using the *Platypus* time-of-flight neutron reflectometer at Australia's OPAL reactor. Scattering contrast between key molecular components of the discrete electronic layers was enhanced in a number of instances using chemical deuteration.<sup>[1]</sup> A purpose built cell allowed *in situ* annealing and simultaneous collection of photoluminescence and neutron reflectivity data. Inter-diffusion processes between electron transport, hole transport and emissive layers in multilayer (OLEDs) were shown to occur after annealing beyond specific critical temperatures. Neutron reflectometry was used to quantify the degree of intermixing and the results correlated with the amount of solid state emission from these devices.<sup>[2,3]</sup> Organic photovoltaic solar cells (OPVs) produced by solution processing methods typically show poor efficiencies in their as-cast state, despite substantial inter-mixing between sequentially processed electron donor (P3HT) and electron acceptor (PCBM) components.<sup>[4]</sup> However, devices annealed at temperatures up to 150 °C show essentially complete inter-diffusion accompanied by substantial increases in their external quantum efficiencies. Importantly, large gains in efficiency seem not to require complete blending of the bilayer structure, but only modest increases in the amount of PCBM acceptor in the largely P3HT donor layers.<sup>[5]</sup> Photovoltaic devices fabricated using this bilayer approach and suitable annealing conditions (including those formed by photocrosslinked P3HT)<sup>[6]</sup> yielded comparable power conversion efficiencies to bulk heterojunction (BHJ) devices made from the same materials.

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**Nanoscale Networks of Self-Assembled Amyloid Fibers for 3D Cell Culture**

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Physical interactions of cells with their local microenvironment (i.e. the extracellular matrix) are of vital importance in maintaining homeostasis and defining cellular phenotype. Furthermore, it is becoming apparent that the addition of a more physiological third dimension to *in vitro* culture platforms can have profound effects on cell fate. Thus, in order to investigate cellular responses to physical interactions in a more physiological manner it is vital for new cell culture platforms to be developed that more accurately mimic the cells microenvironment and allow the influence of added dimensionality to be directly assessed.

Many proteins under specific reaction conditions can self-assemble into amyloid fibers traditionally associated with neurodegenerative disease, however there is a growing body of evidence to suggest that mature amyloids are a non toxic by-product, and the true toxic culprits are smaller soluble protein aggregates. The nanoscale fibrous morphology and mechanical properties of amyloids makes them ideal candidates for the fabrication of new biomaterials that mimic the fibrous proteins that constitute the extracellular matrix. By controlling the reaction conditions used for the *in-vitro* self-assembly of hen egg white lysozyme it is possible to create amyloid fibers with varying morphology and mechanical properties. Here we will present results investigating the kinetic and thermodynamic parameters controlling self-assembly. In turn we show how adjusting these parameters can determine the morphological and mechanical properties of the fibers. Such studies were achieved using a combination of atomic force microscopy, transmission electron microscopy, rheology and synchrotron based small angle x-ray scattering.

Furthermore, we show that at sufficient concentrations, networks of lysozyme fibers form highly hydrated 3D self-supporting gels which mimic the morphology and mechanical properties of the extracellular matrix. By varying the reaction conditions used gels can be fabricated that possess mechanical properties matching various cellular microenvironments present throughout the body. Cells can be cultured either encapsulated within the gels (3D) or on the surface of (2D) amyloid fiber based films. The results of which are used to elucidate the effects of dimensionality on cell fate when cultured in a range of biomimetic microenvironments.

## The Self-Assembly of Tail-type Polysoaps and Polymerized Micelles

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*The University of Sydney, sydney, NSW, Australia*

We have used the RAFT controlled polymerization technique to polymerize the tail-polymerizable surfactant monomer MUTAB (Figure 1) to various degrees of polymerization,  $n$ , to elucidate the influence of the polymeric backbone on the micelle self-assembly and dynamics. At small  $n$  the micelle shape is approximately independent of  $n$  but transitions above a critical value ( $n \sim 60$ ) the micelles undergo elongation. This elongation initially increases as  $n^{0.6}$ , with a transition to  $n^{1.0}$  behaviour when  $n$  becomes sufficiently large that the micelles can support only one polymer chain. Model rod-like micelles were produced by the addition of salicylate. These solutions become more viscous with increasing  $n$  despite the total volume of micelles being constant. The relaxation times are in the range of hundredths to a few seconds – thus demonstrating the rapidly equilibrating nature of the micelle systems – although they are highly dependent on  $n$ , with a transition from scission dominated relaxation (typical for rod-like micelles) to reptation dominated relaxation (typical for polymer systems) at  $n \sim 120$ .

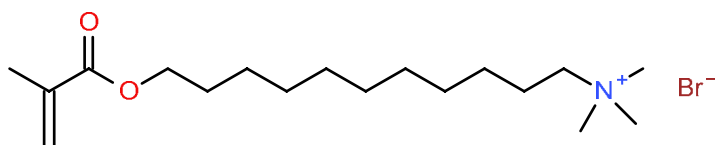


Figure 1. The tail-polymerizable surfmer MUTAB

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**Phase Behavior, Self-Assembly, and Emulsification of Tween 80/Water Mixtures with Limonene and Perfluoromethyldecalin**

Suraj Sharma, Gregory Warr

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Polyoxyethylene nonionic surfactants form micelles in dilute solution above a critical micelle concentration and a wide variety of lyotropic liquid crystalline phases at higher concentrations.<sup>1</sup> These self-assembled structures are strongly influenced by the addition of various types of oils solubilized into the aggregates leading to a rich phase behavior in ternary systems of surfactant, water, and oil. Tween 80 is a biocompatible nonionic surfactant widely used as emulsifier in food, cosmetics, and pharmaceutical industries. Although there are numerous studies on the formulation and characterization of microemulsions using such food grade surfactants like Tweens and cosurfactants, but the structural details of microemulsions formed at high Tween 80/oil ratio is not well understood, and the effect of oil solubilization on the aqueous phase behavior of Tween 80 and its role in the emulsification of lyotropic liquid crystals is likewise relatively unexplored. In this context, we have studied the phase behavior, microstructure, and emulsification characteristics of ternary mixtures of Tween 80 with water and d-limonene (LM) or perfluoromethyldecalin (PFMD) by small-angle X-ray and neutron scattering (SAXS, SANS) and polarizing optical microscopy. In the Tween 80/water binary system, a micellar solution ( $L_1$ ), a hexagonal ( $H_1$ ) phase, and a surfactant liquid or inverted micellar solution ( $L_2$ ) are successively formed at 25 °C. LM can be solubilized into all the phases formed by Tween 80/water mixtures, whereas no solubilization of PFMD occurs. The  $L_2$  phase was found by SANS to be bicontinuous with low interfacial curvature. Added water swells and amplifies the pre-existing amphiphilic structure. A Tween 80/water hexagonal liquid crystal can be used to emulsify a large amount of PFMD, yielding stable liquid crystal emulsions similar to those reported in a nonaqueous ionic liquid system.<sup>2</sup> Emulsification of LM with Tween 80/water fails due to the loss of mechanical strength as the hexagonal phase is swollen by LM and transforms into a lamellar phase.<sup>3</sup>

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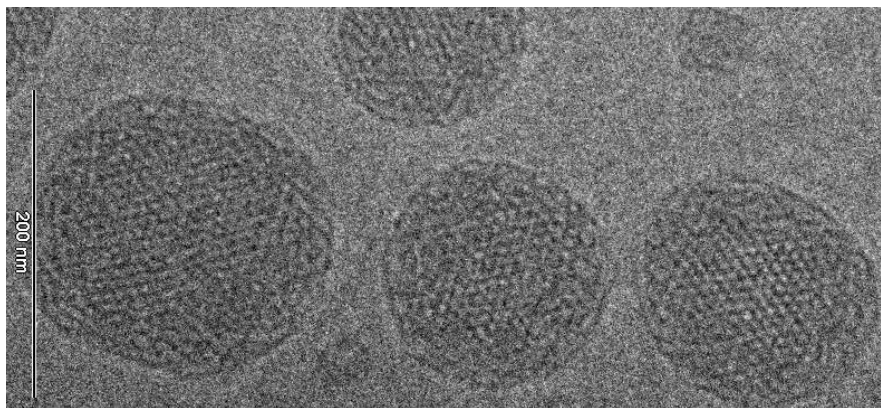
OC318

## What was old is new again: new and old stabilizers for nanostructured lipid-based drug delivery systems

Ben Boyd

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There is increasing interest in lipid-based delivery systems for pharmaceuticals and nutraceuticals due to their biocompatibility and versatility in structure. Cubosomes, particles possessing internal nanostructure (figure below) are emerging as potential alternatives to liposomes, although they require steric stabilization to prevent agglomeration. Cubosomes were first reported in the 1980's using  $\beta$ -casein as the stabiliser, however since then these particles have been stabilized almost exclusively using a synthetic polymeric stabilizer, Pluronic F127. Pluronic F127 is known to disrupt cubosome internal structure [1]. We have a growing interest in the potential use of alternative stabilisers for cubosomes from a biocompatibility and functionality perspective.



In this presentation our recent efforts at revisiting old, and finding and designing new stabilizers for cubosomes are described. We have revisited  $\beta$ -casein as a stabiliser for cubosomes [2], establishing its capability to stabilise cubosomes prepared from different lipids. We have also investigated alternative Pluronics [3] and other steric stabilizers [4], as well as new custom polymeric stabilizers for these systems using high throughput methods to determine structure-property relationships in these systems. The studies highlight  $\beta$ -casein, alternative steric stabilizers and new custom polymers as a suite of new stabilizers with advantages over F127 for use in these systems.

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## A High-Throughput Approach to Develop Self-Assembling Glycosolated Materials for Biomedical Applications

George Feast, Oliver Hutt, Xavier Mulet, Charlotte Conn, Calum Drummond, G. Paul Savage

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Carbohydrate based drugs are underrepresented in the field of therapeutics despite the discovery of numerous carbohydrate binding proteins.<sup>1</sup> Examples are found in the treatment of diabetes (eg miglitol), thrombosis (eg fondaparinux) and influenza (zanamivir and oseltamivir). The major obstacle for drug-development in this area is the high polarity of sugars which restricts their ability to cross the enterocyte layer in the small intestine, thus reducing bioavailability. Moreover, when administered intravenously carbohydrates suffer from fast renal excretion. It is anticipated that by formulating carbohydrates as self-assembled nanoparticles, we can increase the lifetime of such molecules *in vivo* and therefore open up a whole new area of drug discovery.

Utilising the copper catalysed azide-alkyne cycloaddition (CuAAC) 'click' reaction between azide-tethered sugars and alkyne substituted hydrophobic tails, we have synthesised a library of glycosolated amphiphiles with systematic variations in headgroups, chain lengths and chain unsaturation in a high-throughput manner (Fig. 1). After the addition of water these compounds self-assemble, and the resultant liquid-crystalline phases were characterised using a high-throughput technique, developed within our group, at the SAXS beamline at the Australian Synchrotron.<sup>2</sup>

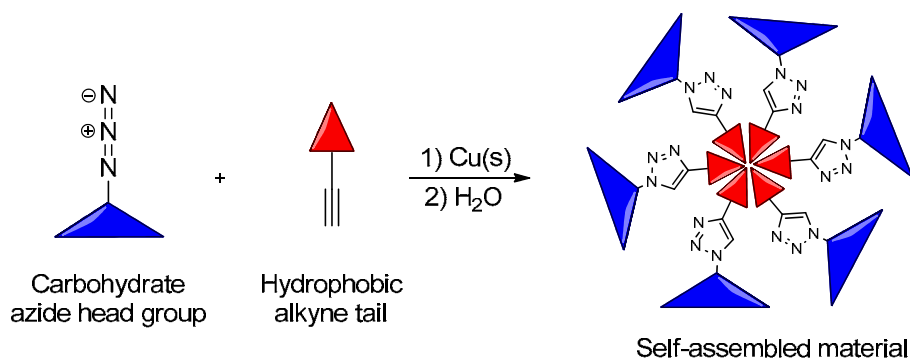


Figure 1: Synthesis of amphiphiles

From this initial screen we determined which amphiphiles were likely to have interesting phase behaviour across a range of water concentrations. These amphiphiles were then synthesised on a large scale and subjected to full phase characterisation. With this data we can construct structure-property relationships for the phase behaviour of glycosolated amphiphiles, and use this in the quest to synthesise new nanomedicines.

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## pH-Responsive Polymer Brushes Grafted from Planar Substrates

Erica Wanless<sup>1</sup>, Timothy Murdoch<sup>1</sup>, Emelyn Smith<sup>1</sup>, Benjamin Cheesman<sup>1</sup>, Steve Edmondson<sup>2</sup>, Grant Webber<sup>1</sup>

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Modification of substrates with stimulus responsive polymer brushes is a flexible route to novel functional surfaces. We have used a macroinitiator approach to impart suitable initiator functionality to oxidised silicon substrates, and subsequently grown brushes of poly(2-(diethylamino)ethyl methacrylate) (poly(DEA)) by surface-initiated activators regenerated by electron transfer atom transfer radical polymerisation (SI-ARGET ATRP). SI-ARGET ATRP is a recent, oxygen tolerant variant of ATRP which requires lower copper catalyst concentrations (down to ppm levels). Polymer brush layers of different thickness have been produced by controlling the brush growth time, and the growth conditions have been optimised via judicious control of solvent composition and reaction temperature.

Due to the weak polybasic nature of poly(DEA), the subsequent polymer brush layers display pH-responsive behaviour. The brushes reversibly swell and uptake water in acidic environments, as the brush 'arms' become protonated and neighbouring chains repel each other, and collapse at pH values above the  $pK_a$  of the surface-bound polymer.

We have studied these swelling transitions by both quartz crystal microbalance (QCM) and fluid cell ellipsometry measurements by growing comparable polymer brush layers on both silica-coated QCM crystals and oxidised silicon wafer. The QCM studies enable us to monitor the combined mass of the polymer brush and solvent as the latter changes in response to solution pH. Complementary *in situ* fluid cell ellipsometry studies on the brush-modified wafers allow us to follow the evolution of brush thickness and composition as a function of pH, see Figure 1.

With appropriate monomer selection, polymer brushes may be designed to either be nonresponsive (e.g. permanently hydrophilic) or respond reversibly to other external stimuli. The living nature of ATRP allows the formation of diblock copolymer brushes and an area of particular interest is the combination of blocks with different responsive natures.

We have also studied the growth of similar polymer brushes from curved, particulate surfaces, creating pH-responsive polymer-particle hybrids which will be discussed in a separate presentation at this Conference.

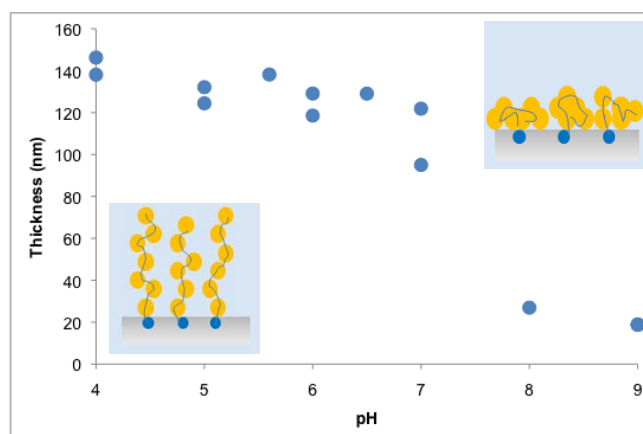


Figure 1: *In situ* ellipsometric thickness as a function of pH for a poly(DEA) brush grown on a silicon wafer using SI-ARGET ATRP.

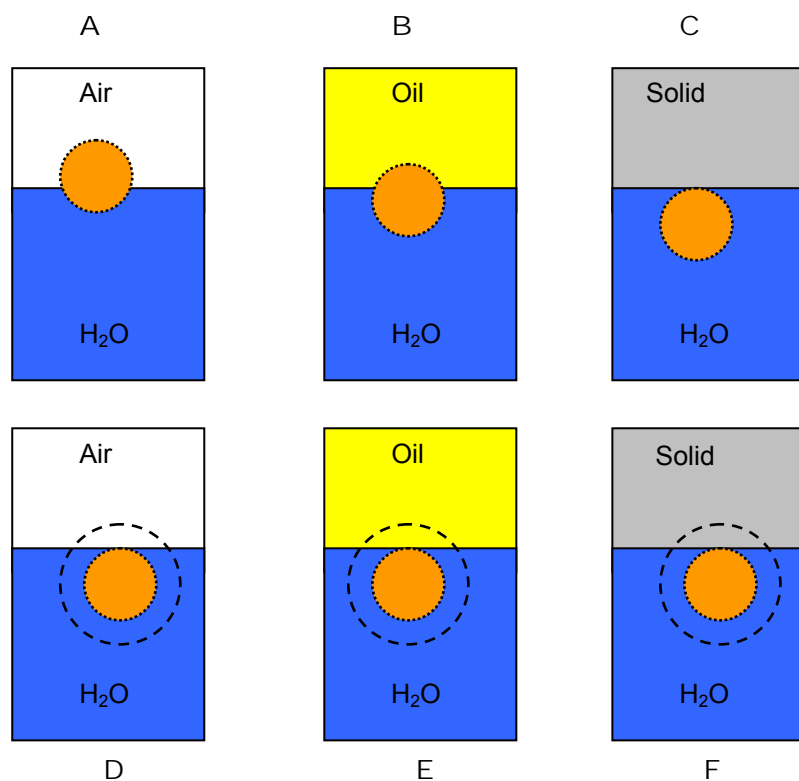
## A New Model of Hydrophobic Hydration of Ions

James Beattie, Alex Djerdjev

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The presently accepted description of the hydrophobic hydration of ions is flawed. Both the European group of Horinek, Netz *et al.*<sup>1</sup> and the Berkeley school of Geissler, Saykally *et al.*<sup>2</sup> describe as the essential feature the partial emergence of the ion at the air/water interface into the vapour phase. **(A)**

This reduces the unfavourable energy required to create a cavity in the water to accommodate the ion.



The model would predict that the surface affinity of the ion at the oil/water interface **(B)** would be smaller, because now a cavity must be created in the oil to accommodate part of the ion volume. And at a solid hydrophobic surface **(C)** there should be little surface affinity, because no cavity can be formed in the solid. These implications of the model are not addressed. Furthermore, the evidence that the hydroxide ion surface affinities, as reflected in the zeta potentials, are very similar for all three phases is ignored.

In contrast, the model we have proposed to account for the preferential adsorption of hydroxide at hydrophobic/water interfaces does not require the emergence of the ion out of

the aqueous phase.<sup>3</sup> Rather, as the ion approaches the interface, the number of water molecules affected by the absence of correlations with the hydration waters is reduced by the same amount, regardless of whether the hydrophobic phase is gas, liquid or solid **(D, E or F)**. The effect is common with any low dielectric hydrophobic medium.

We are now testing this explanation with measurements of the surface and interfacial tensions and surface adsorption of other 'hydrophobic' ions such as the tetrabutylammonium cation.

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## pH-Responsive Polymer Brush-Modified Hybrid Particles

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Surface modification of particles, for example by growing polymer brushes, can have a large effect on their colloidal behaviour. With appropriate monomer selection, the resulting brush-modified hybrid particles can be designed to respond reversibly to external stimuli, e.g. temperature, solvent or pH.

We recently reported the first surface-initiated activators regenerated by electron transfer atom transfer radical polymerisation (SI-ARGET ATRP) of poly(2-(diethylamino)ethyl methacrylate) (poly(DEA))<sup>1</sup> growing brushes on 120 nm diameter silica particles. We employ an electrostatically adsorbed macroinitiator<sup>2</sup> to add initiator functionality to the interface; a flexible technique that can be used to introduce comparable functionality to both particulate and planar substrates. Controlling the brush growth time produces brushes of different length, and changing the silica particle size has allowed the effect of surface curvature to be investigated. The ARGET variant of ATRP requires low copper catalyst concentrations, and the living nature of ATRP allows the formation of diblock copolymer brushes - an area of particular interest is the combination of blocks with different responsive natures.

Due to the weak polybasic nature of poly(DEA) the hydrodynamic diameters of the resulting hybrid particles are pH-dependent (Figure 1). As the pH is decreased below the  $pK_a$  of poly(DEA) at pH ~7.5, the hydrodynamic diameter increases as a consequence of protonation and swelling of the polyelectrolyte brush. Substantial volume increases of up to 200% have been seen and the swelling is reversible when the solution pH is cycled between pH 4 & 7 (Figure 2).

The scale of our volumetric swelling is notably larger than the ~50% increase previously reported.<sup>2</sup> An area of ongoing investigation is the potential application of the hybrid particles as *in situ* switchable rheology modifiers.

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<sup>2</sup> X. Y. Chen et al. *Langmuir*, 2004, 20, 587.

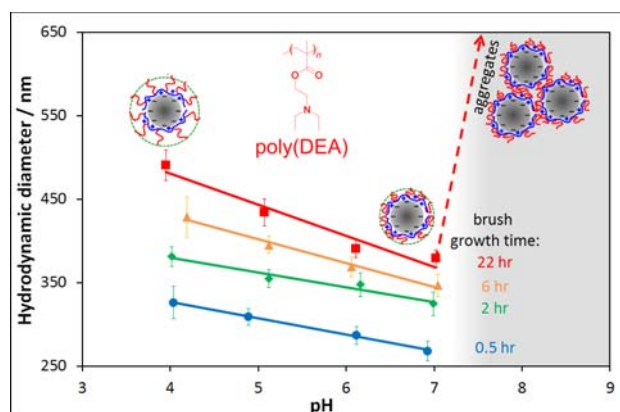


Figure 1 - Hydrodynamic diameter ( $D_{hyd}$ ) of poly(DEA) brush-modified particles as a function of pH. The shaded area denotes particle aggregation. Unmodified silica  $D_{hyd} = 124 \pm 4$  nm.

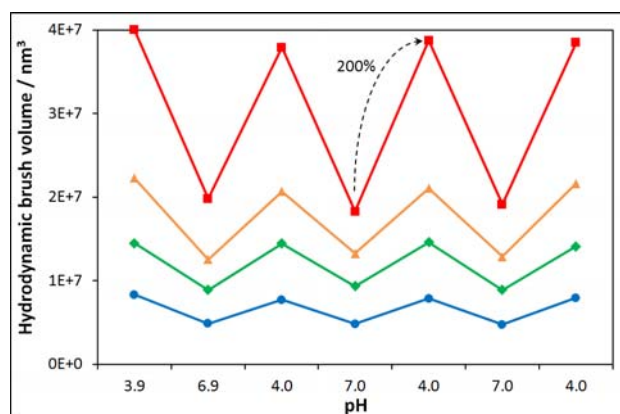


Figure 2 - Hydrodynamic brush volume of poly(DEA) brush-modified particles as the pH was cycled between 4 and 7 demonstrating the highly reversible & reproducible nature of the swelling.

## Vapour Layers Stability on Superhydrophobic Surfaces

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We investigate the effect of wettability and surface roughness on the heat-transfer and boiling on a heated solid surface in contact with water. Four types of surface finish were compared: textured superhydrophilic, smooth hydrophilic, smooth hydrophobic and textured superhydrophobic surfaces.

We found that surface roughness and wettability can alter dramatically the onset of the nucleate boiling regime and the transition temperature to film boiling or Leidenfrost regime. Using a series of cooling (Fig. 1) and controlled heating experiments we demonstrate that on textured superhydrophobic surfaces the nucleate boiling phase could be completely eliminated<sup>1</sup>, that is, a stable Leidenfrost vapour layer can be sustained at all surface temperatures.

The development of textured superhydrophobic coating has been of growing industrial interest for the last decade because of their water-repellent and self-cleaning properties. The effects on the thermal exchange demonstrated in our study could open new applications possibilities, ranging from efficient heat-exchange devices to technologies for drag reduction<sup>2</sup>.

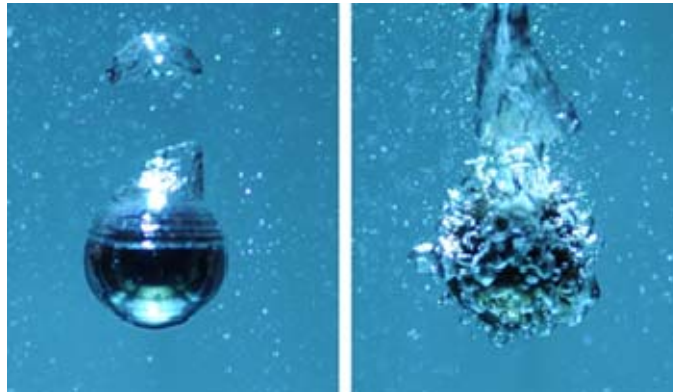


Figure 1. A heated steel sphere being quenched in water in the Leidenfrost regime (left image) and after transition to the nucleate boiling regime (right image).

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## ZnO Nanowires Synthesized by a Direct Ultraviolet Decomposition

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In this work, a low temperature (~178°C) ultraviolet (UV, 1000W) decomposition process was employed to fabricate ZnO nanowires on a flexible PET substrate in ambient air. The zinc acetylacetonate hydrate acted as a single precursor. HRTEM images revealed that the *nanowires* consisted of single crystalline ZnO nanoparticles. The nanoparticle size as determined by the Debye-Scherrer equation was ~6-9nm. The nanowires had a diameter of ~50-100 nm and a length of up to several hundred or thousand microns. An X-ray diffraction pattern revealed that the nanowires exhibit a single phase of crystalline structures and belong to hexagonal (wurtzite) ZnO with lattice constants  $a = 0.325$  nm and  $c = 0.52$  nm. The growth mechanism of the ZnO nanoparticles is oriented to a self-assembling attachment process.<sup>1</sup> This work reveals that there is a high contrast ratio of photocurrent to dark.<sup>2</sup>

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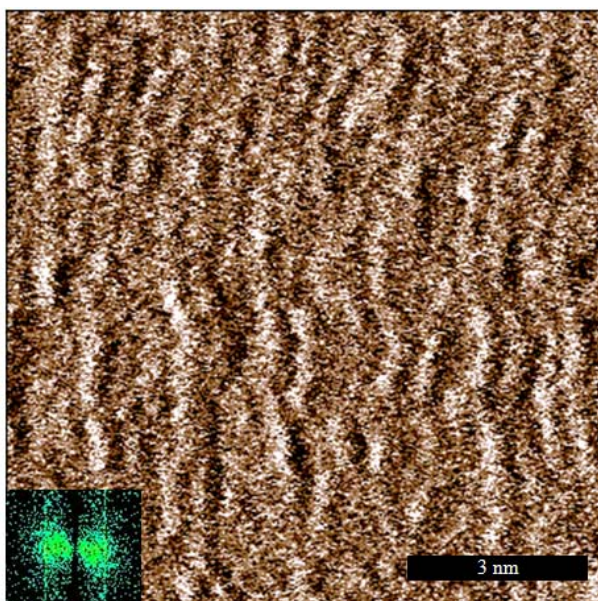
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**Adsorbed and Near Surface Structure of Ionic Liquids at Solid Interfaces**

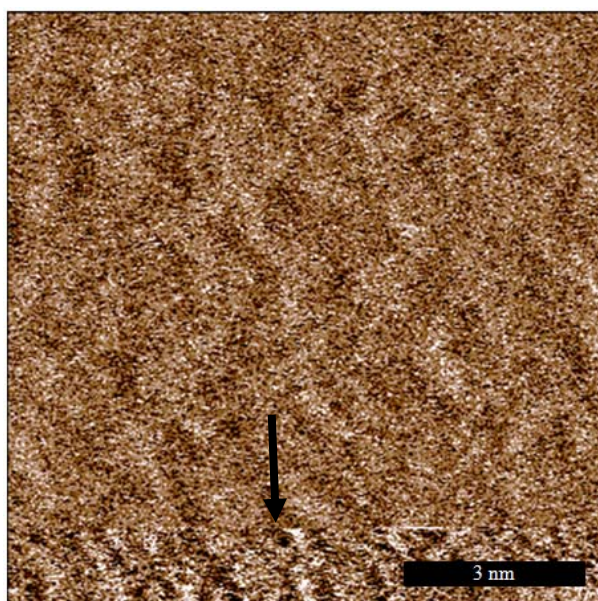
Rob Atkin<sup>1</sup>, Juan Jose Segura<sup>3</sup>, Aaron Elbourne<sup>1</sup>, Erica Wanless<sup>1</sup>, Gregory Warr<sup>2</sup>, Kislon Voitchovsky<sup>3</sup>

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Atomic force microscope (AFM) imaging has been used to elucidate the structure of ionic liquids adsorbed to mica, and the morphology of the layer of ions next to the surface. Results for two ionic liquids will be presented: the protic ionic liquid ethylammonium nitrate (EAN) and the aprotic ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm TFSI), using soft contact and phase imaging modes respectively. In the bulk liquid, EAN's charged and uncharged groups form a disordered sponge phase, similar to a bicontinuous microemulsion, but with a domain size of only 1 nm. At the mica surface, the ethylammonium ions adsorb to charge sites with cation ethyl groups facing away from the surface, and the substrate crystallinity leads to the formation of worm-like structures (Figure 1). When the imaging force is slightly reduced, the tip moves out of contact with the surface adsorbed ion layer, and probes the morphology of the layer next nearest to the substrate (Figure 2). In this layer, the wormlike morphology is replaced with a more disordered structure with features that are broadly consistent with an aligned sponge. The surface adsorbed structure for EMIm TFSI is less pronounced than for EAN, consistent with reduced bulk structure. However, the level of structure in the near surface layer is similar to that noted for EAN. Phase images of subsequent solvent layers have been obtained for EMIm TFSI and show the degree of order decays with distance from the surface.



**Figure 1.** Soft contact AFM image of EAN adsorbed to the mica surface.



**Figure 2.** AFM image of EAN layer above the surface adsorbed layer. The arrow in the image indicates where the force acting on the tip is reduced, and the tip moves from the surface bound ions to near surface layer.



## Natural Bactericidal Surface: Mechanical Rupture of Bacterial Cells by Cicada Wings

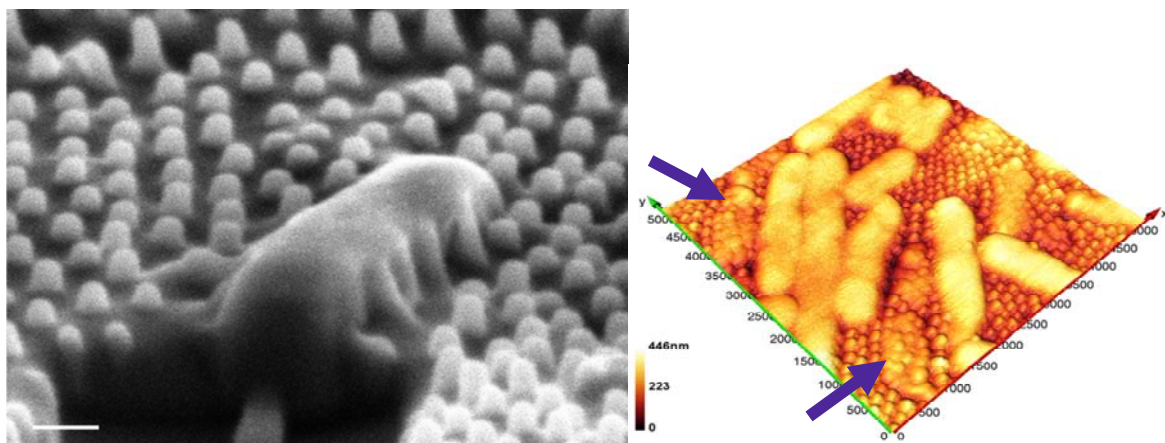
Elena Ivanova<sup>1</sup>, Jafar Hasan<sup>1</sup>, Hayden Webb<sup>1</sup>, Vi Khanh Truong<sup>1</sup>, Gregory Watson<sup>2</sup>, Jolanta Watson<sup>2</sup>, Vladimir Baulin<sup>3</sup>, Sergey Pogodin<sup>3</sup>, James Wang<sup>1</sup>, Mark Tobin<sup>4</sup>, Christian L bbs<sup>5</sup>, Russell Crawford<sup>1</sup>

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Many insects have evolved to possess super-hydrophobic surfaces. These are thought to limit bacterial contamination through a self-cleaning action. While investigating the adhesion of *Pseudomonas aeruginosa* cells on the wings of a species of cicada (*Psaltoda claripennis*), the wing surfaces were shown to be lethal to the cells. SEM showed nano-pillars on the surface penetrating the cells, which were killed by this action. The killing effect was fast, with individual cells killed within approximately 3 minutes. The bactericidal effect appears to be based on the physical surface structure; significant alteration of the surface chemistry of the wing through a gold coating also resulted in cell death. The cicada wings were able to maintain a clean surface via a continuous cleansing process through bactericidal action, rather than by repelling bacterial cells. Surfaces that inhibit bacterial contamination via their physical structure represent a novel approach for the development of antibacterial surfaces.

Due to the nature of their environments, many insects have a requirement to minimize their contamination by foreign particles in order to retain functionality. These foreign particles may be dust or dirt, or bacterial cells that may seek to colonize and infect the insect. As such, these insects have evolved various strategies or mechanisms for coping with contamination. Several have evolved to possess super-hydrophobic surfaces, particularly on their wings, which not only enable them to remain dry and minimize weight, but also bestow a self-cleaning effect. Adhesion of water droplets that contact the surface is so low that they easily slide and roll across the surface, sweeping off contaminating particles such as dust. It is thought that the same mechanism may also be responsible for the ability of these insects to limit bacterial contamination, i.e., that there may be a direct relationship between self-cleaning and anti-biofouling.

In this research, we have investigated the anti-biofouling ability of the surfaces of cicada (*Psaltoda claripennis*) wings. Cicada wings are generally highly hydrophobic and possess excellent self-cleaning properties. While it is thought that there may be a direct relationship between self-cleaning and anti-biofouling, it has not yet been properly explored. To address this, the initial adhesion behavior of *Pseudomonas aeruginosa* ATCC 9027 cells on cicada wing surfaces was assessed and characterised, in order to determine the propensity of the wings for resisting bacterial contamination.



OC327

## Effect of Water on the Wetting and Spreading of Imidazolium-based Ionic Liquids

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The study of ionic liquids (ILs) interacting with solid surfaces has received increasing interest due to their promising applications in industry [1]. One key consideration is the influence of water impurity on the interfacial behavior of ILs [2]. In this study, using various techniques including sessile drop methods, AFM and ToFSIMS, we investigated how water in the ILs or in the ambient vapour influences the wetting behaviour of two groups of imidazolium-based ILs (with anion TFSI<sup>-</sup> or BF<sub>4</sub><sup>-</sup>) on freshly cleaved mica. For the TFSI<sup>-</sup>-group, their contact angle relaxed over several hours, and the final contact angle (after relaxation) was dependent on the ambient humidity (RH) and the water content of the IL. The contact angle relaxation of the BF<sub>4</sub><sup>-</sup>-group is not notable in comparison. Our results indicate that the final contact angles of all ILs studied decrease with increasing RH, which is confirmed to be a result of water adsorption on mica. However, in contrast, increasing the water content of ILs decreases the final contact angle of [bmim][BF<sub>4</sub>] but increases the final contact angle of [bmim][TFSI] on mica at fixed RH (40%). The experimental results demonstrate that even trace amounts of water may have a significant impact on static and dynamic wetting, depending on the nature of the specific IL and the solid surface.

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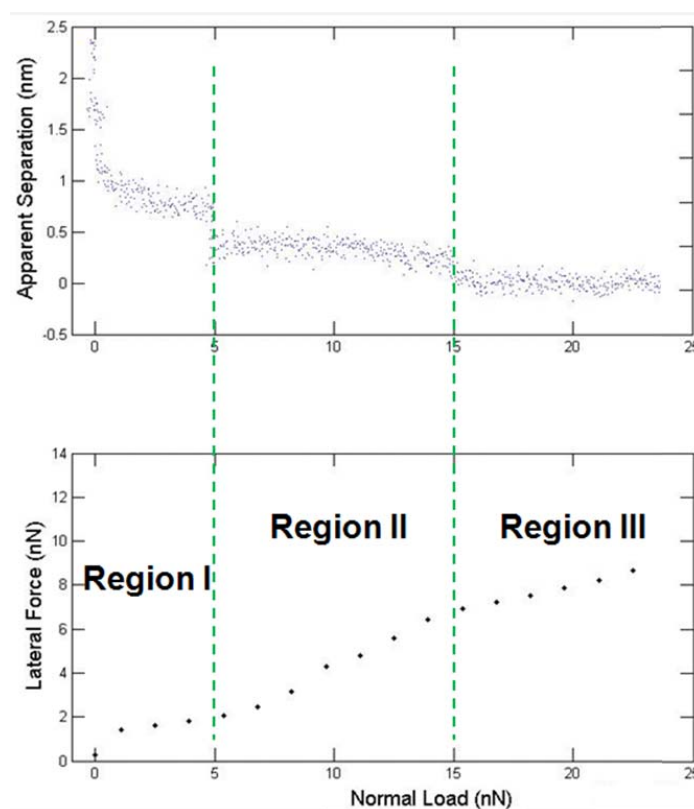
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## Ionic Liquid Lubrication: the Impact of Molecular Structure and Temperature on Friction in Protic Ionic Liquid Systems

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Colloid probe Atomic Force Microscopy (AFM) has been used to study the nanotribological properties of the Ionic Liquid (IL) ethanlammonium nitrate (EtAN) confined between a mica surface and a silica colloidal probe. Normal force curve measurements (Figure 1 top) reveal a series of steps at separations that are consistent with the size of an EtAN ion pair ( $\sim 0.5$  nm) due to displacement of structured solvent layers as the two surfaces are brought together. Lateral force measurements (Figure 1 bottom) show that friction depends on the number of ion pair layers confined between the colloid probe and the surface. Three regions in the friction vs. normal load plot can be identified, delineated by a change in the gradient. At low loads, when more than a single layer is confined between the surfaces, the friction force increases linearly and is independent of tip velocity. A sharp transition between low friction and high friction occurs at  $\sim 8$  nN. This transition corresponds to the tip displacing an ion layer as the surfaces move closer together. At higher loads, a single layer of cations strongly adsorbed to the mica substrate remains. Under these conditions, the friction increases linearly but with a steep gradient. These results will be compared to those obtained previously for ethylammonium nitrate (EAN) elucidating the effect of EtAN's alcohol group on lubricity. New data for the effect of increased temperature on lubrication for EAN will also be presented.



**Figure 1.** Normal and lateral force curve data for EtAN confined between a silica colloid probe and mica. In both graphs the normal load is plotted on the x-axis, which allows the correlation between push through force in the normal data and changes in slope for lateral data to be identified.

### Star-Polyphile Self-Assembly: News from the Experimental Front

Liliana de Campo<sup>1</sup>, Mino J Moghaddam<sup>2</sup>, Trond Varslot<sup>1</sup>, Rainer Mittelbach<sup>1</sup>, Toen Castle<sup>1</sup>, Nigel Kirby<sup>3</sup>, Chris Garvey<sup>4</sup>, Stephen Hyde<sup>1</sup>

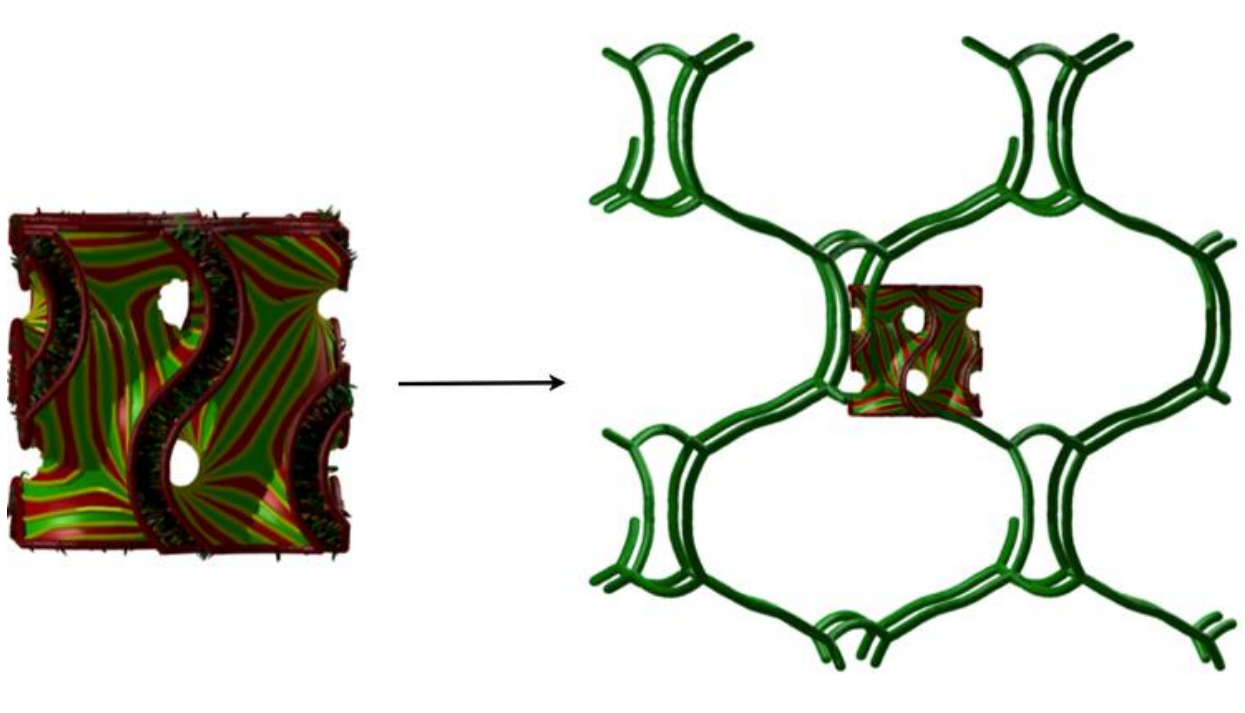
<sup>1</sup>ANU, Canberra, ACT, Australia, <sup>2</sup>CSIRO, North Ryde, NSW, Australia, <sup>3</sup>Australian Synchrotron, Melbourne, Vic, Australia, <sup>4</sup>ANSTO, Lucas Heights, NSW, Australia

Star-Polyphiles are small molecules with three mutually immiscible chains attached to a common center [1,2]. In the work presented here these consist of a hydrophilic (oligoethyleneglycol), oleophilic (hydrocarbon) and fluorophilic (perfluorocarbon) chain.

In contact with water these star-polyphiles self-assemble to a variety of different liquid crystalline structures, most of which structurally resemble those found in conventional surfactants, like lamellar and type-2 bicontinuous cubic, micellar cubic and hexagonal phases. However, the hydrophobic region is split into completely separate hydrocarbon and fluorocarbon nanodomains [2].

It has been a particular challenge for us to elucidate how these hydrocarbon and fluorocarbon domains are arranged within the hydrophobic matrix of the bicontinuous cubic phases. But now we have models in place that emerge from theoretical considerations [see S.T. Hyde's presentation, 3]. These models are in good agreement with the molecular dimensions, the strong constraints imposed by the star-geometry of the molecules, and with our experimental data (SAXS and SANS).

Apart from common sense, all evidence strongly points towards the fact that at certain water contents, the hydrocarbon and fluorocarbon domains are highly periodic, forming a "superstructure" superimposed on the (hydrophilic/hydrophobic) periodicity of the bicontinuous cubic phases. An example of one of these highly complex structures, a perfectly "striped" gyroid structure, is shown below: the fluorocarbons (green) form networks, while the hydrocarbons (red) form filaments that separate the green networks.



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[3] Evans M. E., Robins V., Hyde S.T., *submitted*

## Supramolecular Nano-Assemblies of Chelating Amphiphiles and their Mn or Gd Complexes for MRI imaging

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<sup>1</sup>CSIRO, North Ryde, NSW, Australia, <sup>2</sup>ANU, Canberra, ACT, Australia, <sup>3</sup>CSIRO, Parkeville, VIC, Australia, <sup>4</sup>CSIRO, Clayton South, VIC, Australia

The development of selective systems for cancer diagnosis and therapy is one of the key areas of current cancer research. We have focused our research activities on the synthesis, physicochemical characterisation and biological activity of novel chelating amphiphile molecules that can sequester a variety of metal ions such as transition metal ions, paramagnetic metal ions and radio-metal ions and their potential application as smart contrast agents (CAs) for a range of imaging modalities, including MRI.(1-3)

Here we report on novel chelating amphiphiles with ethylene diamine tetraacetic acid (EDTA) and diethylene triamine pentaacetic acid (DTPA) headgroups. Some prototype molecules of DTPA conjugates are shown in Figure 1.

The nanoassemblies (NAs) formed by the dispersion of the chelating amphiphiles were then complexed with a variety of metal ions including Mn and Gd. The NAs formed by complexation of Gd or Mn with various chelating amphiphiles displayed a broad range of structures from tubular micelles to liposomes, cubosomes and hexosomes, multilayered nanospheres and multiwalled nanotubes. These NAs were identified by synchrotron small angle X-ray Scattering (SAXS) and cryo-TEM.

The relaxivity values of a range of NAs displayed several fold increase in relaxivity ( $r_1$  values) over Magnevist, a commercially available agent. The superior relaxivity values combined with several order of magnitude higher payloads of the paramagnetic metal ions sequestered within the supramolecular NAs suggests high promises towards superior contrast agents for MRI.

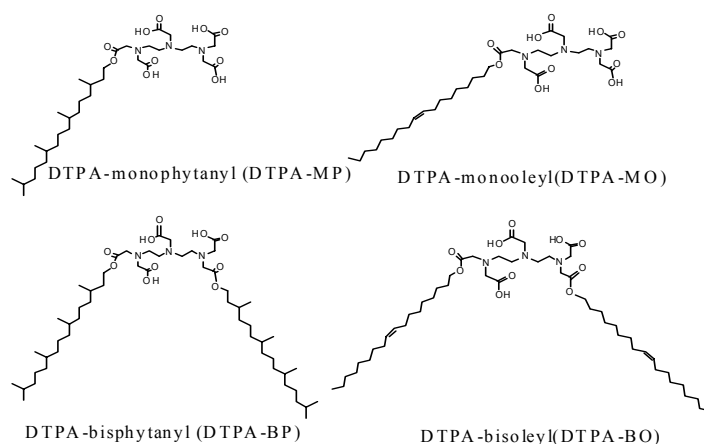


Figure 1 Prototype chelating amphiphile molecules

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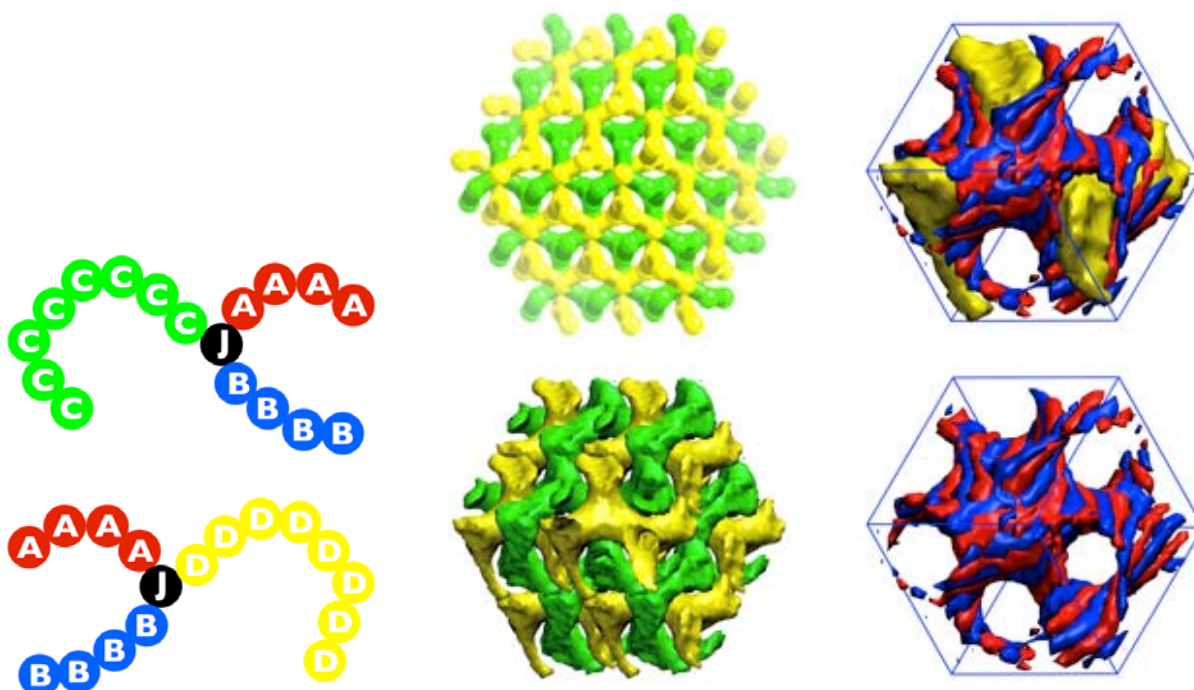
### New three-arm star polyphile self-assemblies..... frustration and more frustration

Stephen Hyde<sup>1</sup>, Liliana De Campo<sup>1</sup>, Jacob Kirkensgaard<sup>1,2</sup>, Myfanwy Evans<sup>1,3</sup>

<sup>1</sup>Australian National University, Canberra, Australia, <sup>2</sup>Copenhagen University, Copenhagen, Denmark,

<sup>3</sup>Erlangen-Nürnberg University, Erlangen, Germany

A theoretical analysis of the simplest possible 3D domain patterns of three-arm star polyphile liquid crystals and related copolymer phases is a fascinating, and non-trivial, exercise in non-euclidean 2D geometry, and then differential geometry. Both simulations and experiments have revealed some of the most complex liquid crystal morphologies known, combining chirality and polycontinuity. A simulation snapshot of assembly of two three-arm polyphiles is shown below.



The patterns that emerge can be coherently described as minimally frustrated structures that grow via a two-step assembly process: one that minimises curvature variations of a warped membrane in space, and the other that maintains as far as possible uniform stripe dimensions within the curved membrane.

This principle leads inexorably to extraordinarily convoluted morphologies for these novel liquid crystalline mesophases, combining in some cases 1-periodic, 2-periodic and 3-periodic domains, all interwoven in a mesoscale fabric made of three chemically distinct species. These are the observed three-phase analogues of bicontinuous mesophases, reported by Liliana De Campo.

OC401

## Building Plasmonic Nanocolloid Superlattice Sheets with Soft Ligands

Wenlong Cheng

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Lipid and polymer are classic building units to be used in natural and artificial 2D material systems, respectively. In contrast, recently there is burgeoning interest in constructing new class of 2D materials from nanoscale optoelectronic building blocks. In particular, it is possible to fabricate free-standing periodic nanoparticle arrays (superlattices) which behave as mechanically strong nanomembranes with Young's moduli of several GPa. Such superlattice nanomembranes differ from solid-supported superlattice films in that they exist as free-standing, isolated forms in their final stage of growth or processing. This constitutes an exciting route to integrate unique properties of optoelectronic nanomaterials with striking mechanical robustness and flexibility into a single tailorable multifunctional system, leading to lightweight metamaterials and devices with new functions for novel applications in optoelectronics, electrocatalysis, and ultrafiltration.

In this talk, I will discuss our recent success in constructing monolayered nanoparticle superlattice sheets/membranes from plasmonic nanospheres, nanorods, nanocubes, and nanowires. Soft ligands, DNA, polymer and surfactants were used to functionalize these nanocolloids as well as facilitate the formation of 2D superlattice membranes. The fundamental soft-hard interactions were revealed by Synchrotron-based small-angle X-ray scattering, allowing us to propose entropic spring model to interpret the ligand-mediated self-assembly process. In conjunction with top-down lithography, we are able to shape these superlattice membranes into the desired structures. In addition, we thoroughly investigated the mechanical properties of our nanoparticle superlattice sheets by nanoindentation by an atomic force microscope, and were able to derive Young's moduli and breaking strength. We also investigated plasmonic properties of individual nanoparticles as well as the superlattice sheets. The experimental results were compared with the theoretical modelling by DDA simulation.

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OC402

## Irreversible Bidirectional Nanoparticle Crossing Oil-Water Interfaces

Ge Su, Dayang Wang

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The present talk will highlight our recent study of nanoparticle crossing oil/water interfaces. In order to deliberately engineer their interactions with both oil and water phases, Au nanoparticles (NPs) were coated with stimuli-responsive polymer brushes. We have experimentally and theoretically demonstrated that the resulting NPs can readily transfer from oil to salty water across the planar interfaces when the environmental temperature is reduced below 5 °C, while they transfer from salty water to oil when the environmental temperature returns to room temperature. This bidirectional NP phase transfer across oil/salty water interfaces is actually not driven solely by the temperature. The water-to-oil particle transfer after warming is dictated by the ionic strength of the aqueous phase, which is directly associated with the ionic strength response of the polymer brushes anchored on the NPs. In contrast, the temperature onset for the oil-to-water NP transfer after cooling is weakly correlated with the transition temperature of the polymer brushes in either of the bulk phases. We have developed a preliminary thermodynamic model to rationalize this transfer mechanism disparity. Furthermore, we have also demonstrated that when the environmental temperature is below 5 degree nanoparticles can be transferred back to and well dispersed in salty water with ionic strength as high as 0.5 M, in which the nanoparticles tend to agglomerate and precipitate at room temperature. This implies that cold water (< 5 degree) can provide a better (re-) hydration. which should provoke a number of experimental and theoretical interest in temperature effect on the structural stability, hydration, denaturing, and re-activation of biological molecules.

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2. Mao, Z.; Gao, J.; Bai, S.; Nguyen, T.-L.; Xia, H.; Huang, Y.; Mulvaney, P.; Wang, D.; *Angew. Chem. Int. Ed.* **2009**, *48*, 4953.
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**Droplets on Liquids and their Long Way into Equilibrium**

Stefan Bommer<sup>1</sup>, Sebastian Jachalski<sup>2</sup>, Dirk Peschka<sup>2</sup>, Barbara Wagner<sup>2,3</sup>, Ralf Seemann<sup>1,4</sup>

<sup>1</sup>Saarland University, Experimental Physics, 66123 Saarbrücken, Germany, <sup>2</sup>Weierstrass Institute, 10117 Berlin, Germany, <sup>3</sup>Institute of Mathematics, Technische Universität Berlin, 10623 Berlin, Germany, <sup>4</sup>Max Planck Institute for Dynamics and Self-Organization, 37073 Göttingen, Germany

In recent years a thorough understanding of thin film dewetting from solid substrates was developed. However, the understanding of a thin liquid film dewetting from another liquid remained scarce. By *in situ* AFM studies we explore the dewetting dynamics and morphologies of liquid polystyrene (PS) dewetting from liquid polymethyl-methacrylate (PMMA). Using a selective solvent allows to remove the dewetted PS layer and to image the liquid/liquid interface at selected times. Combining the PS/air and the PS/PMMA interfaces we obtain the full three dimensional shape of the dewetting morphologies. The characteristic shapes of the rim profiles, the equilibrating droplets and their dewetting dynamics depend not only on the ratios of viscosity and surface tension of the two liquids but also on the relative film height of the underlying liquid. The latter originates from the flow field of the dewetting liquid which penetrates surprisingly deep into the lower liquid it is dewetting from.

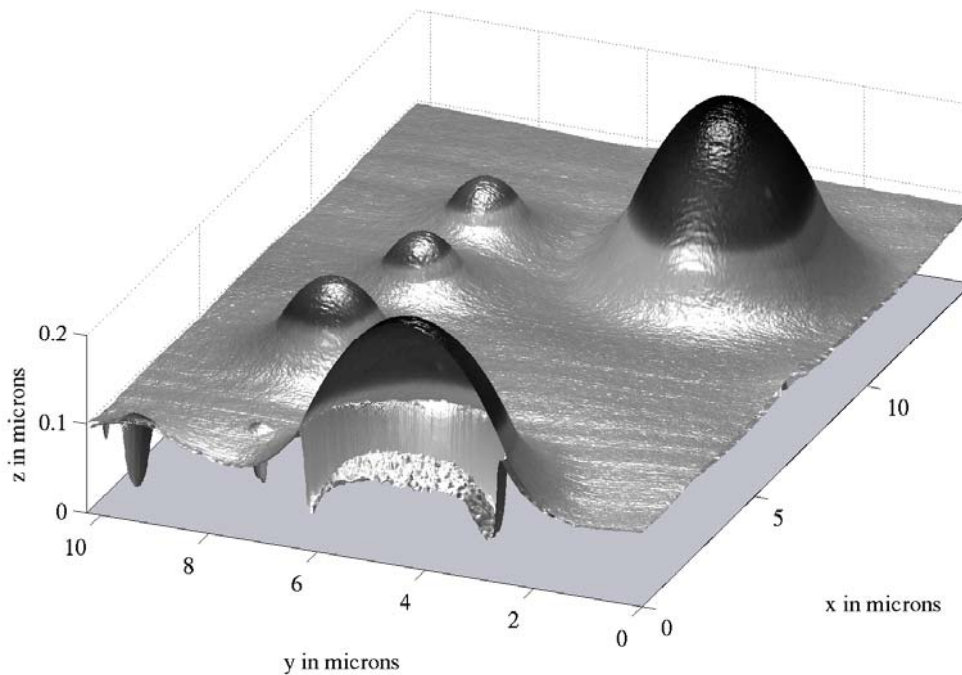


Figure 4: not equilibrated polystyrene droplets swimming in a liquid polymethylmetacrylate layer.

**Nanocrystal Solar Cells - One Solution to Photovoltaics**

Paul Mulvaney

*University of Melbourne, Victoria, Australia*

Semiconductor nanocrystals or quantum dots were proposed as tunable lumophores for a wide range of applications in the late 1990s: including biolabelling, single photon emitters, tunable LEDs and solar cells. However challenges in synthesizing these materials has led to only slow success in the development of devices.

In this talk we present results demonstrating that, with careful optimization, p-n junctions can be fabricated from nanocrystal inks using solution processing. Annealing converts the inks into continuous semiconductor films with well-defined optical and electrical properties. Unlike the case for PbS(Se) based PV devices, quantum size effects are not beneficial for tuning the film band gap of CdTe PV systems. The goal of the solution processing is to convert the small crystals into a bulk semiconductor film.

The main advantages of nanocrystal inks in this case are: (i) solution processing is scalable and avoids expensive vacuum processing steps. (ii) The annealing can be carried out at low temperatures, that enable deposition onto polymer and other soft surfaces for flexible electronics. We show how devices with efficiencies up to 10% may be fabricated at a fraction of the cost of conventional PV devices. We discuss the advantages and disadvantages of this approach [1,2].

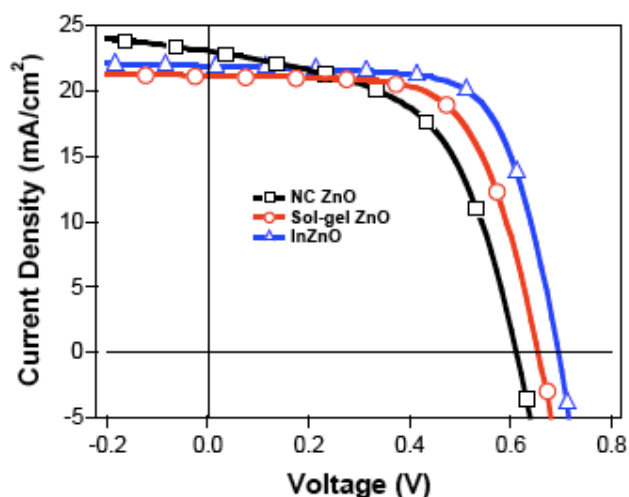


Figure 1: I-V curves under AM1.5 showing the effects of the ZnO on the open circuit voltage and short circuit current.

**References**

- [1]. J. Jasieniak, B. Macdonald, S. Watkins, P. Mulvaney, *Nano Letters*, 11, 2856-64 (2011).
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## Ligand Ordering on Nanorods and Nano-Patterned Surfaces and its Effect on Their Interaction in Solution

Asaph Widmer-Cooper<sup>1</sup>, Phillip Geissler<sup>2</sup>

<sup>1</sup>University of Sydney, Sydney, NSW, Australia, <sup>2</sup>UC Berkeley, Berkeley, CA, USA

Inorganic nanoparticles are often covered with surfactant-like ligands that play an important role in stabilizing the particles from random aggregation in solution. Here we show that on nanorods (Fig. 1a) such ligands can undergo an ordering transition near room temperature that has strong similarity to the one commonly observed for macroscopic self-assembled monolayers (SAMs).

Using large-scale molecular dynamics simulations with explicit ligand and solvent molecules, we explore the effect of changing the temperature, the facet dimensions, and the density of ligand coverage on the ligand order and on the ordering of the solvent molecules near the particle surface (Fig. 1b). In particular, we consider the case of CdS nanorods and nano-patterned surfaces covered in strongly-bound octadecyl ligands in *n*-hexane solvent.

By calculating the potential of mean force between such surfaces, we also show that changes in the ligand and solvent ordering can induce dramatic changes in how nanoparticles interact in solution, with the capability to switch the interaction from purely repulsive to strongly attractive (Fig. 1c). This change in interaction will, in turn, have important consequences for whether the particles remain suspended in solution, randomly aggregate, or undergo controlled self-assembly into large-scale ordered structures. More generally, this work demonstrates that fluctuations and ordering phenomena on multiple scales can be strongly coupled in nanoscale colloidal systems.

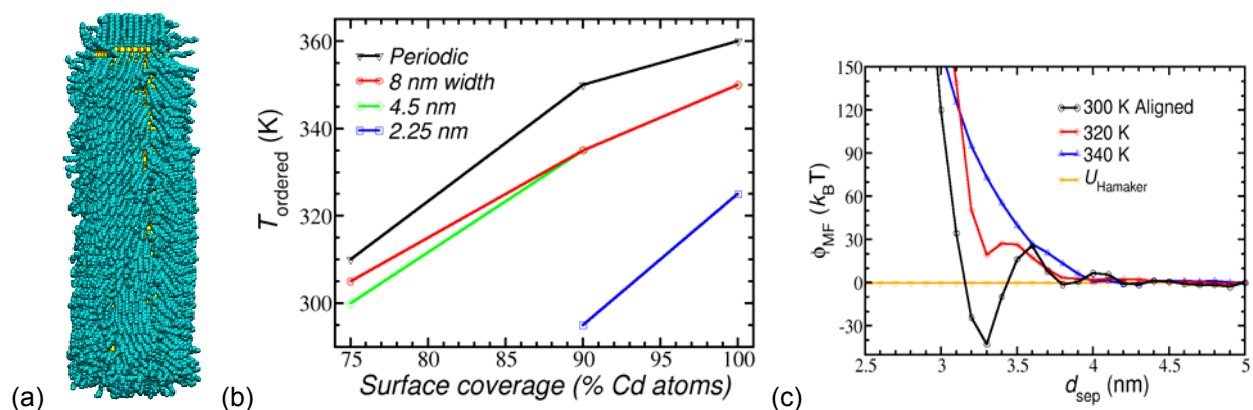


Fig. 1. (a) Ordered ligands on a 4x20 nm CdS nanorod in *n*-hexane at 300 K. (b) The maximum temperature at which ligands are highly ordered ( $T_{\text{ordered}}$ ) as a function of the ligand surface coverage and facet width for a Cd (100) wurzite surface that is periodic along the rod axis. (c) Potentials of mean force ( $\Phi_{\text{MF}}$ ) for two parallel nanorods as a function of the CdS-CdS surface separation ( $d_{\text{sep}}$ ) at several temperatures.

## Characterisation of Complex Nanoparticle Size Distributions Utilising Different Measurement Techniques

Åsa Jämting, Victoria Coleman, Heather Catchpole, Maitreyee Roy, Malcolm Lawn, Bakir Babic, Jan Herrmann

National Measurement Institute Australia, Lindfield, NSW, Australia

Comprehensive physical characterisation of nanoparticles has been identified as an essential prerequisite for studies on these materials. Size is a key physical characteristic, and here we present results from a comparison study of particle size distribution (PSD) measurements using six different characterisation techniques. The aim of the study was to compare PSD results from the different techniques and to highlight the strengths and weaknesses of commonly used particle characterisation instrumentation using well-characterised nanoparticle suspensions.

Measurement techniques included dynamic light scattering (DLS), atomic force microscopy (AFM), transmission electron microscopy (TEM), differential centrifugation sedimentation (DCS), particle tracking analysis (PTA) and flow-field flow fractionation (FFFF). Samples consisted of two suspensions of citrate stabilised gold colloids with mono-modal PSDs (NPS1: 20 nm and NPS2: 100 nm), and two suspensions with bi-modal PSDs that were produced by mixing NPS1 and NPS2 in ratios to generate equal peak heights in the intensity-weighted PSD in DLS measurements (NPS3) and in the number-weighted PSD in single-particle measurements (NPS4).

All techniques identified the PSD for NPS 1 and NPS 2. The DLS technique was able to distinguish the two peaks in the intensity-weighted PSD for NPS3 but not for NPS4, as shown in Figure 5a. In contrast, microscopy-based methods such as AFM and TEM were more suited to separate the PSD peaks in NPS4, but struggled to detect the comparatively few larger particles in the NPS3 sample (illustrated in Figure 5b). Methods that classify the particles by size before measurement, such as DCS and FFFF, were able to determine the PSD for all samples.

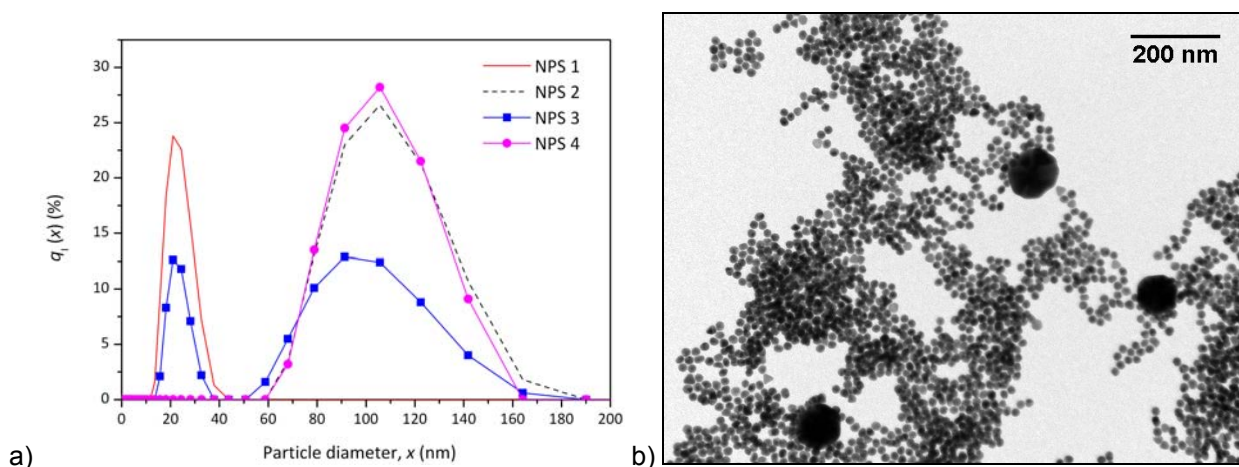


Figure 5. a) DLS results (intensity-weighted) of the four nanoparticle suspensions. b) TEM image of NPS 3, illustrating the sample composition producing equal peak heights in the intensity-weighted PSD in DLS measurements.

The results of this comparison demonstrate the strengths and weaknesses of different techniques used to characterise suspensions with both monomodal and more challenging bimodal PSDs.

## A combined experimental and simulation approach to design magnetic core-shell composite particles

Roberto Moreno-Atanasio, Frances Neville

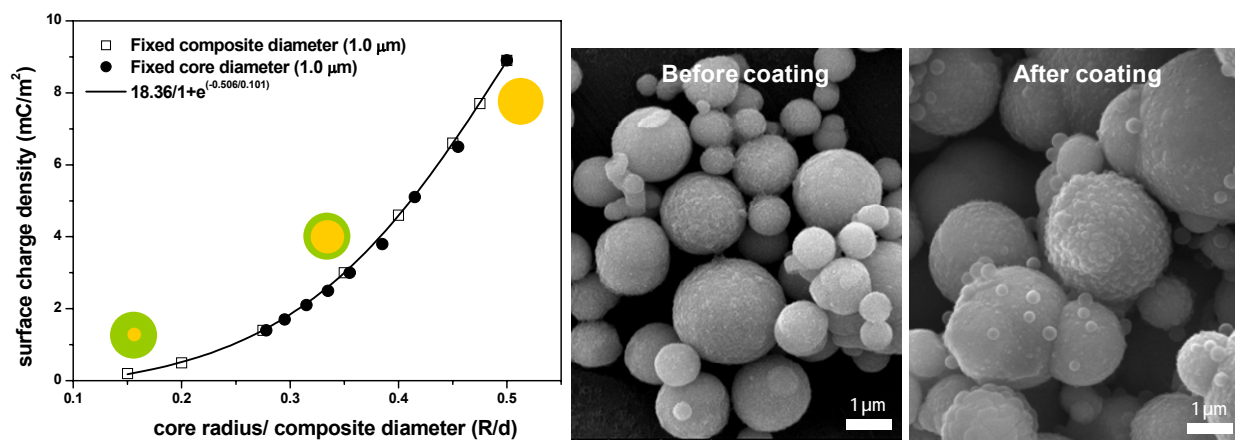
*The University of Newcastle,, Callaghan, NSW, Australia*

The aim of this research was to use a dual experimental and simulation approach to investigate the influence of the combined forces of magnetic cores and electrically charged shells of core-shell composite particles in order to control their aggregation behaviour and to enhance the experimental design of composite core-shell particles to minimise aggregation.

Experimental systems were designed with magnetic core particles surrounded by multifunctional polymer-silica shells. Computer simulations based on Discrete Element Method mimicked the experimental conditions by assigning physical properties to the cores and shells of the composites.

The results show that ferromagnetic iron particles can be coated in silica using a bio-inspired approach [1-3], to produce core-shell iron-polymer-silica composite particles which have a point of zero charge at around pH 12, compared to the value for uncoated iron particles of pH 4.5. The simulations showed that as the silica shell thickness increased, lower surface charge density was needed to avoid aggregation of the particles. For example, the simulations showed that for 1  $\mu\text{m}$  particles, a surface charge density of 3.0  $\text{mC}/\text{m}^2$  was needed to hinder flocculation for composites with a 150 nm silica shell thickness. A decrease of 48 % of the magnetic core radius was required to achieve a reduction in surface charge density of one order of magnitude.

A combined experimental and computer simulation approach has been applied in order to produce core-shell iron-silica particles whose interactions can be controlled. It is envisaged that the control of surface morphology, surface charge, particle density and magnetic properties will aid in the understanding of the behaviour of the magnetic composites.



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**OC408**

**Colloidal Processing meets Rocket Science: Ultra High Temperature Ceramic Components**

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<sup>1</sup>*Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, 3010 VIC, Australia,* <sup>2</sup>*Defence Materials Technology Centre (DMTC), 24 Wakefield St., Hawthorn VIC 3122, Australia*

Ultra high temperature ceramics (UHTC) have been excellent material candidates for different components of hypersonic vehicles, especially for the manufacture of leading edges. For aerodynamic reasons, these edges need a very sharp geometry and substantial machining is usually required to achieve the final shape, potentially introducing stresses or flaws into the component. The use of colloidal processing technique aids in reducing the number of defects in the green body and produces higher particle packing, which ultimately enable achieving fully densification at lower temperatures and pressures, even pressureless sintering. The combination of colloidal processing and pressureless sintering allow the preparation of near-net-shape components as leading edges with reasonable sintered densities and without the formation of secondary phases or significant oxidation. Leading edges have been prepared by slip casting and pressureless sintering from powder suspensions. The understanding of the interaction forces of the powder in suspension is the key to produce a low viscosity formulation that lead to a high density defect-free material. The promising results are the starting point in the development of other near-net-shape processes for the manufacture of UHTC components.

This work has been conducted in collaboration with the Institute of Materials Engineering at the Australian Nuclear Science and Technology Organization, ANSTO, (*NSW 2234, Australia*) and Defence Science and Technology Organization, DSTO (*Fishermans Bend, 3207, VIC, Australia*). These activities are being developed within the frame of the Defence Materials Technology Center, DMTC, with the previously mentioned institutions and with the University of Queensland, Swinburne University of Technology and BAE Systems.

## A Hyperelastic Description of Suspension Rheology

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Suspensions of particles in liquids are ubiquitous in industrial processes and consumer products. The flow and deformation of concentrated suspensions, determining their use and how they are processed, is very complex. Particulate suspension processing usually involves shear and compressional forces, often together and in multiple directions. Their bulk flow has shear and shear-rate dependent viscoelasticity, and the solid and liquid phases will separate unless the solid phase resists consolidation. The objective of this work is to develop a constitutive representation of suspension rheology that is capable of capturing the broad features of suspension behaviour such as yielding in generalised shear, self-limiting consolidation and the interaction between shear and compression. An accurate description along with methods of measuring material properties will enable design, control and modelling of suspension processing in many previously intangible areas. This impacts processes like pipe flow, drying and centrifugation in the ceramics, minerals, pharmaceuticals and wastewater industries.

Suspension constitutive behaviour, either in shear or compression, is often described plastically due to the sharp transition from solid-like to liquid-like behaviour. We propose to describe this behaviour not as critical state plastic yielding but in terms of non-linear viscoelasticity [1]. We start with general hyper-viscoelasticity where the stress and strain relations are governed by conservation and dissipation thermodynamic energy potentials. Simplifications thereafter are determined by phenomenological observations.

The shear behaviour can be described by strain softening and strain-rate thinning, with shear in multiple directions governed by von Mises' criterion.

The consolidation behaviour can be captured by volumetric strain hardening. Whilst the critical strains in shear are very small, large strains are encountered during consolidation such that the Hencky or 'natural' strain tensor is required.

Experimental evidence [2] indicates that the combined shear and compressive behaviour cannot be described by a critical state approach such as von Mises, with the important implication that shear and compressive yield are not collaborative. The results indicate that strain-rate softening of the modulus is appropriate.

This general hyper-elastic constitutive approach is capable of capturing many of the broad features of suspension deformation and phase separation. The approach enables the extension of suspension rheology into the multi-dimensional realm that is relevant to many important industrial applications.

[1] Wineman A, 'Nonlinear viscoelastic solids - A review', *Math. Mech. Solids*, 2009, 14(3): 300

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## Time-Dependent Shear Yield of Flocculated Colloidal Suspensions

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<sup>1</sup>*CSIRO Mathematics, Statistics and Informatics, Highett, Victoria, Australia,* <sup>2</sup>*The University of Melbourne, Parkville, Victoria, Australia,* <sup>3</sup>*MSACT Research and Consulting, Exeter, Devon, UK*

The ability of flocculated colloidal suspensions to form a cohesive particulate network with finite strength imparts solid-like properties to the bulk suspension. Typically this network is brittle in shear due to the small length scales of inter-particle colloidal forces characteristic of polymer flocculation or electrochemical coagulation. As such, the macroscopic shear rheology of such materials is typically modelled as a visco-plastic medium via e.g. Bingham or Hershel-Bulkley models.

Whilst such models which involve a shear stress yield criterion represent useful engineering approximations, experimental observations suggest the shear yield of flocculated colloidal suspensions is far more complex. Time-dependent yield, and yield over a range of applied shear stress has been observed across a number of detailed experimental studies, and it is difficult to reconcile this observed behaviour within visco-plastic models without appeal to more exotic phenomena such as thixotropy.

An alternate approach is to consider flocculated colloidal suspensions as brittle visco-elastic media which undergo rapid strain-softening toward purely viscous flow at a critical value of the shear strain energy. Whilst shear stress, shear strain, and shear energy yield criteria are equivalent for purely elastic materials, this is not so for visco-elastic materials due to the accumulation of energy via retarded elasticity. Hence such a failure criterion for visco-elastic materials qualitatively reproduces observed phenomena such as time-dependent yield and yield over a range of stress.

As the majority of flocculated colloidal suspensions exhibit significant non-linear visco-elasticity prior to yield, analysis of data from creep and stress relaxation experiments presents an ongoing challenge to quantitatively validate this theory. Current work involves development of novel data inversion techniques to deconvolute experimental data and development of materials which exhibit linear visco-elasticity for experimental testing.

Furthermore, flocculated colloidal suspensions also exhibit non-monotone flow curves and hysteresis in stress ramp experiments, which may only be explained by invoking both shear strain and strain-rate softening within the visco-elastic framework. These results suggest that flocculated colloidal suspensions can exhibit quite complex rheological behaviour under shear alone, and the development of complete constitutive model of such materials is an outstanding research challenge.

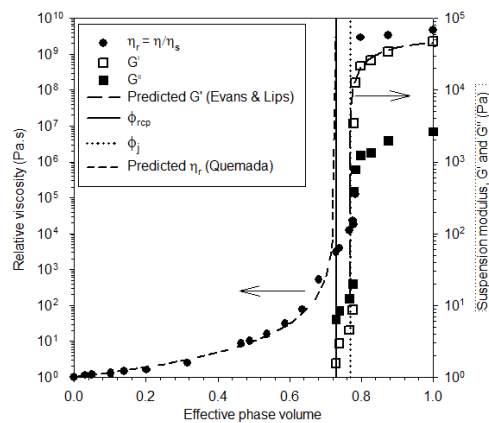


## Rheology of Soft Sphere Suspensions: Observation of an Unexpected Viscoelastic Fluid Regime at Phase Volumes above Random Close Packing.

Heather Shewan, Jason Stokes

*The University of Queensland, Brisbane, Australia*

Developing structure – property relationships for soft particle suspensions presents many challenges primarily due to an inability to precisely define phase volume, the apparent dependence of maximum packing fraction ( $\Phi_m$ ) on particle softness, and the difficulties in assessing surface forces between colloidal particles. In order to develop fundamental insights into such systems, and specifically to probe how particles suspensions are discretely controlled by the micromechanical properties of individual particles, we developed a model suspension of non-colloidal microgels as model soft particles, and show for the first time the presence of three different rheological responses with increasing phase volume. The microgels are comprised of agarose in water that do not osmotically deswell at high phase volumes so their specific volume is relatively constant with phase volume. The focus in this presentation is the observation of three distinct rheological regimes that occur for relatively firm spherical particles containing 5% agarose. At phase volumes below random close packing ( $\phi_{RCP}$ ), which is determined explicitly from the particle size distribution, purely viscous behaviour is observed and no ‘significant’ non-Newtonian behaviour occurs. In this region, the viscosity is precisely determined without fitting parameters using the Quemada model, i.e.  $\eta/\eta_s = (1-\Phi/\Phi_m)^{-2}$  and assuming  $\Phi_m = \Phi_{RCP}$ . At  $\Phi \geq \Phi_{RCP}$ , the suspension exhibits distinct shear-thinning and viscoelastic fluid behaviour such that the storage modulus ( $G'$ ) is less than the loss modulus ( $G''$ ). While the presence of this region has been previously speculated upon, this is the first experimental evidence for its existence that the authors are aware of. As the phase volume is increased further, a liquid-to-solid transition occurs so that the suspension behaves as viscoelastic solid that exhibits a yield stress. We consider this transition to be the jamming transition that occurs as the microstructures rearranges to accompany the soft particles. To show how the rheology is governed by Hertzian contact mechanics, we predict the viscoelastic response using the Evans & Lips model that utilises the particles modulus and Poisson ratio, the number of nearest neighbours ( $n=10$ ), and the phase volume corresponding to the liquid-solid transition ( $\Phi_j$ ). We discover that this model predicts the viscoelasticity of the suspension accurately. In this way we are able to predict both the viscous regime and viscoelastic solid regime without fitting parameters based on knowledge of the particle properties and size distribution. This should provide a foundation for studies into the structure-property relationships of colloidal and non-colloidal soft particle suspensions.



**Flocculated Particulate Suspension Rheology Measurement – Mind the Gap.**

Peter Scales<sup>1</sup>, Anthony Stickland<sup>1</sup>, Ashsih Kumar<sup>1</sup>, Nicky Eshtiaghi<sup>2</sup>

<sup>1</sup>University of Melbourne, Parkville, Victoria, Australia, <sup>2</sup>RMIT University, Melbourne, Victoria, Australia

Flocculated particulate suspensions are common to a wide range of industrial processes and the flow characteristics of these suspensions is critical to a range of end outcomes, whether the suspension be used as a product or as is often the case, becomes a waste or residual. Measurement of the response of these suspensions to an applied shear stress or range of shear stresses is a common way to characterise the flow properties. Constitutive relationships abound to quantify and parameterise the behaviour. Many of these invoke a yield criterion in which there is an elastic-plastic transition at a critical stress and then either shear thinning (Herschel Bulkley) or pseudo Newtonian (Bingham) behaviour thereafter, for example. It has long been debated as to whether the yield behaviour should be treated as a purely elastic-plastic transition and recent work would suggest this to be too simplistic a description for the majority of flocculated particulate suspensions. Characterisation of the transition has proven difficult none the less as slip and other phenomena make reproducibility across a range of measurement configurations difficult.

There are a range of techniques for measurement of the yield and flow behaviour of suspensions with vane in cup, parallel plate, cone and plate and vane in infinite media being the most familiar rotational geometry examples. Over the years, the non-homogeneous nature of flocculated suspensions has led to the development of the vane in infinite media to measure the yield stress and flow properties of mineral suspensions. The main reason has been to avoid the issue that the largest individual particle or aggregate in the suspension must be small relative to the gap between the rotational tools (i.e. the inner and outer surface in the case of a bob in cup configuration or top and bottom surface in the case of the parallel plate or cone and plate configuration). Despite all of the precautions and knowledge of what could go wrong, there is sparse data in the literature that reflects concordance of results between different measurement configurations.

A series of experiments examining the elastic-plastic transition for model, flocculated suspensions has been conducted to explore the role of gap size on the reproducibility of rheological measurement using a vane in cup configuration. The usual explanation as to why one would move to this measurement configuration is to avoid slip, as was the case for flow measurement [1]. Data will be presented that is supportive of the need to measure the rheology of flocculated suspensions in an 'infinite' gap configuration but not solely because of slip. Indeed, issues such as shear banding appear to be just as important. Whilst an easy enough recommendation to make, a difficulty that arises in moving to a wide gap configuration is that many research programs are not blessed with large quantities of material for testing. Calculations show that at a vane to cup diameter ratio of greater than 1:3, the behaviour should be as though in an infinite medium.

[1] DT Fisher, SA Clayton, DV Boger and PJ Scales, "The bucket rheometer for shear stress - shear rate measurement of industrial suspensions," *Journal of Rheology*, 51: 821-831 (2007)

**High Speed Video Observations of the Stability and Coalescence Dynamics of Two Particle-Stabilized Bubbles**Sin-Ying Tan<sup>1</sup>, Seher Ata<sup>1,2</sup>, Erica Wanless<sup>1</sup><sup>1</sup>Priority Research Centre for Advanced Particle Processing and Transport, University of Newcastle, Callaghan, NSW, Australia, <sup>2</sup>University of New South Wales, Sydney, NSW, Australia

The stabilization mechanisms of particle-stabilized bubbles have received considerable amount of attention in recent years due to their widespread applications in everyday products such as food, cosmetics and medicine. It was found that solid particles enhanced bubble stability and it is well-accepted that the stability of these bubbles depends on factors such as particle size, concentration and wettability, interparticle interactions and solution conditions. Majority of these studies, however, were conducted in the presence of surfactants<sup>1</sup> or at high solution ionic strength<sup>2</sup>. In addition, these studies were also generally undertaken in a column which is difficult to interpret at the level of developing a detailed stabilization mechanism<sup>3</sup>. Here, we investigated the stability of two individual particle-stabilized bubbles at low solution ionic strength ( $\leq 100$  mM) in the absence of surfactant with the aid of a coalescence rig<sup>4</sup> and the experiments were carried out in two modes: asymmetric (a coated and an uncoated bubble) and symmetric (both coated bubbles). In this technique, air bubble was produced at the tip of a capillary and then coated with particles of known size and hydrophobicity to the desired surface coverage. They were then moved towards each other to provoke coalescence; the coalescence process was recorded using a high speed camera. From the captured images, it was then possible to probe the stability of the bubbles and also their coalescence dynamics. In the asymmetric system, the stability of the bubble decreases with increasing solution ionic strength and decreasing bubble surface coverage. These observations can be explained by the decrease in electrostatic repulsion and increase in steric repulsion, respectively. Interestingly, a different trend was observed with the symmetric system; bubbles stability increases with increasing solution ionic strength. This is consistent with the observation where bubbles coalescence was inhibited at a transition concentration<sup>5</sup>. In addition, it suggested that electrostatic interaction does not play an important role in those cases but probably a specific interaction between the salt and the particles<sup>2</sup>. Until now, there is no simple explanation for these increases. Following the rupture of the liquid film separating the two bubbles, the change in surface area of the resultant bubble revealed that these bubbles system exhibit a simple damped harmonic motion. The damping coefficient is much larger in the symmetric case and a slight change was observed with increasing solution ionic strength. It is hoped that the outcome of this study will provide a new insights into the stabilization mechanisms of particle-stabilized bubbles and thus improve multiphase processes which involve these combinations.

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5. Craig, V.; Ninham, B.; Pashley, R. The effect of electrolytes on bubble coalescence in water. *J. Phys. Chem.* 1993, 97, 10192-10197.

## Pulsed Laser Modulated AFM Cantilevers

Hongjie AN<sup>1</sup>, Drew Evans<sup>2</sup>, Ponlawat Tayati<sup>1</sup>, Vincent Craig<sup>1</sup>, Tim J. Senden<sup>1</sup>

<sup>1</sup>*Australian National University, Canberra, ACT, Australia*, <sup>2</sup>*University of South Australia, Mawson Lakes, SA, Australia*

**Introduction:** The current study aims to develop photon modified dynamic AFM method for studying nano-mechanical properties of solvents and polymers. The photon modulated cantilever sensor offers high sensitivity of very small amplitude and phase, making the stiffness and viscosity measurable quantitatively at pico-meter scale. Good signal to noise is achieved by the use of a lock-in-amplifier.

**Methods:** A modulated laser with 405 nm wavelength was coupled into an Asylum Research AFM (MFP-3D) system through an inverted optical microscope, and aligned onto the lower surface of a rectangular cantilever. The analysis of the dynamic interaction of photons with the cantilever, including thermal dynamics and photon pressure, was conducted. The sensor movement in air and also in water was determined by a lock-in amplifier (SR830 DSP) using the modulated laser signal as reference. The deflection of the cantilever with time was also analysed using power spectral density.

**Results:** The present work shows that an extremely small amplitude vibration of cantilever derives from a modulated pulse laser of 1 microwatt. When pulse time is significantly less than the thermal response time, the effect of laser on cantilever heating was dramatically reduced, by at least two orders of magnitude, particularly in water. Decreasing the laser power also induces even lower amplitude oscillations of the cantilever. An amplitude of 10 pm was determined with a commercial available cantilever (CSC 38 C, spring constant = 0.06 N/m, resonance = 11.36 kHz) at pulse frequency of 6 kHz with laser power of 200 nW.

**Discussion:** The photothermal effect of the laser beam on cantilever deflection arises from adsorbed and can be reduced by shortening pulse time and laser power. At the same time, the conservation of momentum can also cause the oscillation of cantilever, when photons were reflected and adsorbed by the cantilever. The total movement of cantilever due to photon irradiation is resulted from cantilever heating and cooling plus photon pressure. The high resolution and extremely small oscillation of cantilever allows for a wide range of interactions from hydrodynamics to chemical forces, and molecular structural changes during energy transfer.

## OC415

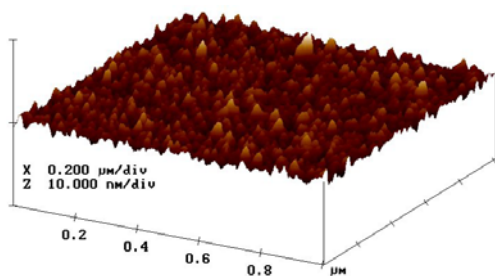
### Surface force measurements between titania surfaces prepared by Atomic Layer Deposition in aqueous electrolyte solutions.

Rick Walsh, Vincent Craig

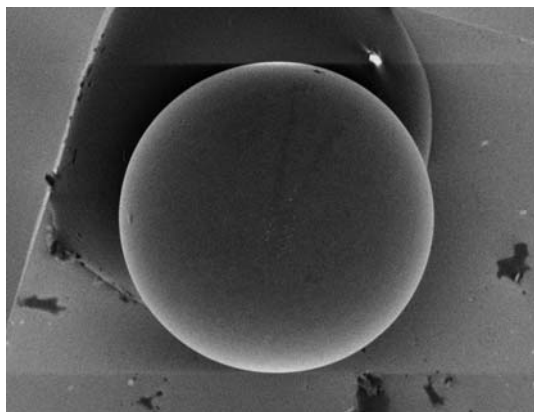
ANU, ACT, Australia

The investigation of surface forces between titania surfaces is of fundamental interest as, like silica, the surface potential is determined by acidic hydroxyl groups, but titania has a much higher iep and significantly larger dispersion forces. As such the balance between hydration forces and van der Waals attraction should differ considerably between silica and titania. However it is challenging to find titania surfaces that are sufficiently smooth for force studies. Using Atomic Layer Deposition (ALD), we have produced suitably smooth titania surfaces (RMS roughness 0.4nm) by coating smooth borosilicate spheres and silicon wafers.

Examining the surface forces under a range of salt and pH conditions has allowed us to examine the measured short and long-range forces in the context of DLVO theory and hydration forces<sup>1</sup>.



AFM Image of Si wafer coated with titania using ALD



FESEM image of a borosilicate sphere (20μm diameter) coated with titania using ALD

1. Walsh, R. B.; Nelson, A.; Skinner, W. M.; Parsons, D.; Craig, V. S. J., Direct Measurement of van der Waals and Diffuse Double-Layer Forces between Titanium Dioxide Surfaces Produced by Atomic Layer Deposition. *Journal of Physical Chemistry C* **2012**, *116* (14), 7838-7847.

## Destabilisation of Concentrated Pickering Emulsions

Catherine Whitby, Lisa Lotte, Melinda Krebsz, Chloe Lang

Ian Wark Research Institute, University of South Australia, Mawson Lakes, S.A., Australia

Packing spherical particles so closely together that they touch all their neighbours and resist flow produces many useful materials including mayonnaise, emulsion explosives and moisturizer creams.

Studies of the coalescence dynamics between pairs of particle-coated drops indicate that coalescence can be inhibited at an intermediate stage.<sup>1</sup> We used microscopy techniques to investigate the structural changes in particle-stabilised (Pickering) emulsions as the drops were compressed together under gravitational and shear forces.

Particle-coated drops deform into hexagonal polyhedral shapes as they pack closely together under gravity. The length of their polyhedral sides increase with compression until no more area can be encapsulated by the particle layer profile in the available space (Figure 1). At the drop volume fraction where the emulsions start to break down there is a jump in drop elongation and thus in the number of drops in contact with each other. A key finding is that the rigidity of the droplet surfaces controls emulsion destabilisation.<sup>2</sup>

Shearing emulsions of densely packed drops that are weakly coated by particles destabilises the emulsions above a critical applied stress. Non-spherical structures are formed by partially merged clusters of drops. Further compression causes the surfaces of merging drops to crumple. The periodicity of the buckling is consistent with predictions<sup>3</sup> made by treating interfacial particle layers as two dimensional solids.

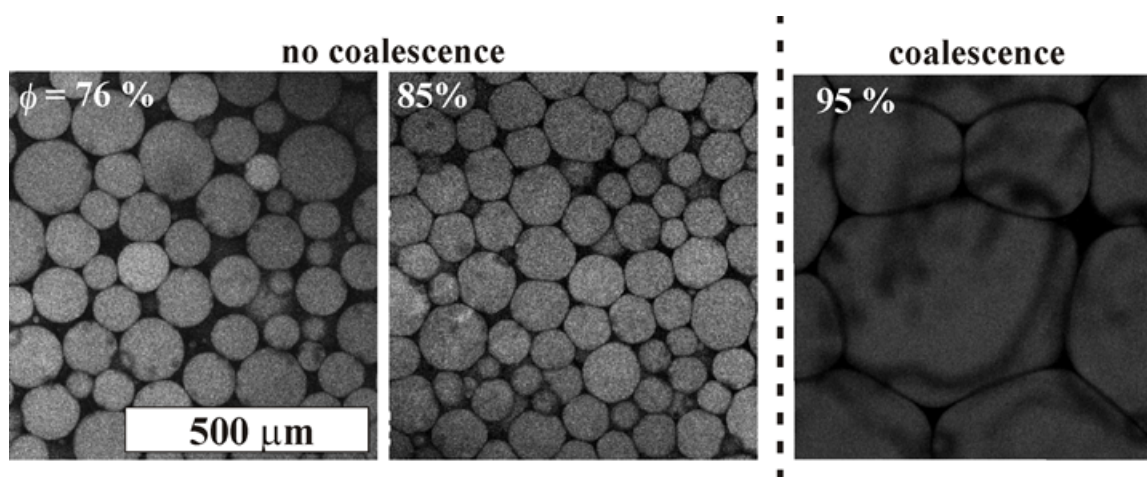


Figure 1. Droplet packing in compressed layers of Pickering emulsions.

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OC417

## Colloidal Separation Driven By Ionic Dispersion Forces

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The asymmetric interaction between model oil and rock surfaces across a moderately strong divalent solution is considered. Theoretical modelling is performed with a modified Poisson-Boltzmann description that includes nonelectrostatic ion dispersion interactions [1]. The oil surface is modelled as tetradecane with a regulated (pH dependent) surface charge taken from crude oil measurements [2]. The rock surface was modelled as mica, also with a charge regulated surface.

In 0.1M MgCl<sub>2</sub> at pH 4, a repulsive barrier can be found in the oil-rock interaction. This is in stark contrast to classic DLVO theory (with only electrostatic ionic interactions), which predicts an attractive oil-rock interaction at all surface separations. The repulsive barrier found in our model occurs as a consequence of “charge reversal” (more correctly, electric field reversal), which is caused by the ionic dispersion interaction of the counterion Mg<sup>2+</sup> at the mica surface.

The cosmotropic Mg<sup>2+</sup> ion is strongly hydrated and therefore experiences a strong dispersion attraction to the mica surface due to polarisability contributions from water in the hydration shell of the cation. This enhances the physisorption of the cation to the negatively charged mica surface, resulting in a reversal of the surface potential of mica from negative to positive (“charge reversal” or “overcharging”). Consequently strong adsorption of the coion Cl<sup>-</sup> can occur at the mica surface. The combination of the change in ion concentration profiles compared to classic DLVO theory together with the direction contribution of ionic dispersion energies to the overall surface force results in the repulsive barrier.

The dispersion-induced repulsive barrier is observed in a charge regulated model assuming an ideal charge regulation equilibrium [3]. It is also observed under constant surface charge conditions using surface charges determined from a charge regulated calculation at large surface separation.

The mechanism offers new insight into questions of phase separation and heterocoagulation.

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**Stability and Rheological Properties of Particle Suspensions in Protic Ionic Liquids**

Jacob Smith<sup>1</sup>, Grant Webber<sup>1</sup>, Gregory Warr<sup>2</sup>, Rob Atkin<sup>1</sup>

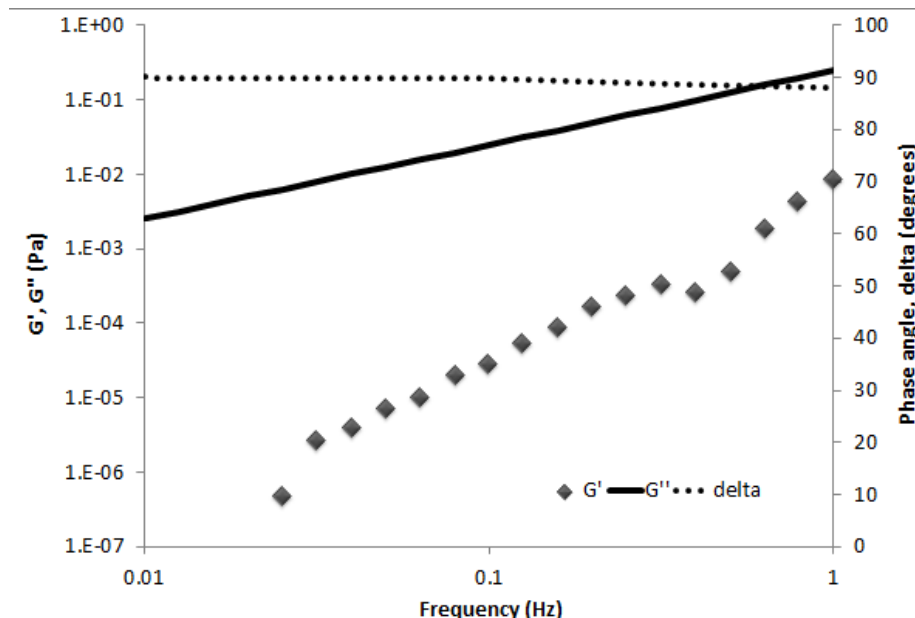
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The protic ionic liquids (ILs) ethylammonium nitrate (EAN), ethylammonium formate (EAF), ethanolammonium nitrate (EtAN), propylammonium formate (PAN) and dimethylethylammonium formate (DMEAF) have been investigated as media for silica particle dispersions. Depending on the ionic liquid and the temperature, the particles can exist as single particles, aggregated networks or a coexistence between these two states. Table 1 shows how the stability of 10 wt% dispersions of 1µm silica spheres varies with liquid species and temperature, as well as their settling behaviour, normalised by the Stokes equation for settling velocity. Only EAF behaves as may be expected for a stable suspension in a Newtonian liquid.

Table 1: Stability and normalised settling velocity for 10 wt% 1µm silica particles dispersed in ionic liquids as a function of temperature. Stable dispersions are indicated by black text on white, unstable suspensions by white text on black and coexistence between states by black text on grey. The numbers are the ratio of the observed settling velocity rate ( $\omega_{obs}$ ) and the velocity predicted by the Stokes equation ( $\omega_{calc}$ ).

T (°C)	<u>EAN</u>	<u>EtAN</u>	<u>PAN</u>	<u>EAF</u>	<u>DMEAF</u>
	$\omega_{obs}:\omega_{calc}$	$\omega_{obs}:\omega_{calc}$	$\omega_{obs}:\omega_{calc}$	$\omega_{obs}:\omega_{calc}$	$\omega_{obs}:\omega_{calc}$
20	6.73	1.52	0.57	1.15	0.49
30	18.44	1.46	22.85	1.17	9.38
50	7.76	55.36	3.23	1.12	0.51

In order to probe faster (EAN, EtAN) and slower (DMEAF, PAN) than expected settling rates for stable dispersions,



oscillatory rheological studies of the systems have been completed to determine whether the suspension is Newtonian, gel-like, or a viscoelastic solid or liquid.

Rheology data for EAN is presented in Figure 1. The constant phase angle,  $\delta$ , is consistent with a gel. If the gel is weak, this could mean that aggregates of silica particles could settle as a group, with a velocity greater than that predicted by Stokes. Slower than Stokes settling could occur if the gel network is stronger, such that particle settling is impeded.

**Figure 1:** Oscillatory frequency sweep for 10wt% 1 µm silica spheres in EAN at a controlled 100mm/mm strain.



OC419

## **An acoustic Backscatter System for the *In Situ* Characterization of Settling Dispersions and Suspensions**

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The measurement of suspended particle concentration changes within settling multiphase systems is important to many engineering and environmental applications; in particular in minerals processing and water treatment. Many industrial separation operations rely on gravitational free-settling of particles (such as clarifiers or thickeners) where potentially complex flow interactions make it difficult to predict particle behaviour. Hence, the ability to monitor concentration changes and particulate stratification within these environments can greatly aid in developing efficient separators and allow more accurate modelling of behaviour. Ultrasonic transducer instruments are potentially a practical and relatively cheap characterization technique, which give the ability to gain information on dispersion changes from backscattered pulse echoes with minimal intrusion<sup>[1,2]</sup>.

In this study, we have investigated the use of an acoustic backscatter system (ABS) as a novel *in situ* technique to profile segregation in particle separation systems. Such instruments are currently used in dilute environmental sedimentology applications to track near-bed particle changes in rivers and estuaries. However, their use in higher concentration industrial suspensions is more complicated and unstudied. Firstly, the limitations of backscatter analysis were studied by comparing the theoretical response to experimental measurements in homogenous glass particle dispersions. It was found that above concentrations of  $\sim 2.5$  g/L (or  $\sim 0.25$  wt.%) the influence of interparticle scattering on signal attenuation invalidated the theoretical approach. Despite this, a novel qualitative technique was adopted, by comparing the measured depth-wise attenuation in different particle concentrations. Importantly, it was found that a linear correlation exists between attenuation and particle concentration, which was independent of depth. Such analysis was then applied to the study of segregating and settling dispersions in both small and large scale environments.

Both settling colloidal TiO<sub>2</sub> and larger flocculated glass particle dispersions were studied in batch scale columns. The ABS was able to measure both the settling cloud-front interface as well as the build-up and compaction of the sediment bed; although, due to increased inter-particle scattering effects in the smaller TiO<sub>2</sub> particles, system attenuation was increased in this case (reducing acoustic penetration). Significantly however in both cases, changes in depth-wise particle concentrations with time were also able to be profiled, by correlating the segmental attenuation within the sludge zone, giving information critical to analyzing the separation mechanism in large scale systems. Additionally, ABS was also utilized as an *in situ* profiler in full scale trials on a water treatment thickener and sludge ballast mixing tank. Again, analysis of the depth-wise attenuation allowed quantification of the density profile of these sludge systems, and indicate the potential of acoustic techniques for monitoring and characterisation in a range of industrial separation operations.

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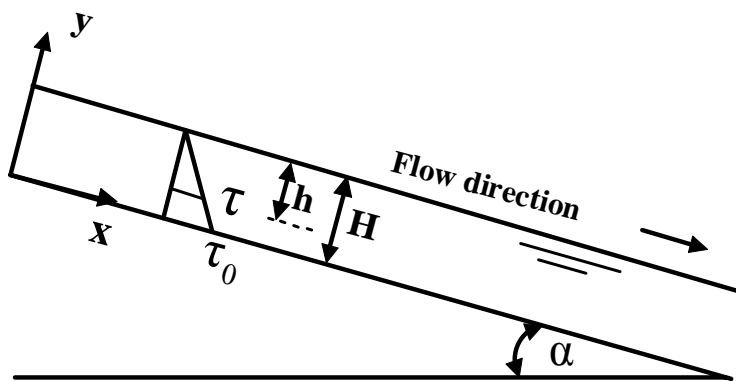
[2] Hunter, T.N., Peakall, J., Biggs, S. *Miner Eng*, **2012**, 27-28, 20-27.

## Scale-Up and Flow Characterisation of Visco-Plastic Free Surface Sheet Flows

Paul Slatter

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The sheet flow of viscous material is of critical importance in many industrial settings. Our previous studies have shown that a sheet flow diagram can be constructed using, and that these flows could be scaled for engineering design purposes in a manner similar to the approach of Metzner and Reed for tube flow. However, many unresolved issues remain for the rheometrical measurement and flow behaviour analyses of sheet flow. Arguably, the most acute of these are the application to viscoplastic material and the concomitant location of the Laminar/Turbulent transition. The objective of this present investigation is to develop and evaluate this approach for the flow behaviour analyses, rheological characterisation, and prediction of the Laminar/Turbulent transition for viscoplastic sheet flows. Using experimental data, it is shown that this approach works well for the analysis of viscoplastic materials.



**Figure 6 Shear stress distribution for sheet flow**

The previously developed approach (Slatter et al. 2010), which was shown to be successful for power law fluids (Slatter et al. 2011), has now been extended to viscoplastic fluids. The approach has been validated against experimental viscoplastic data, and found to have significant merit in this case. Issues requiring further work are identified and discussed.

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OC421

## Compression and Elastic Rebound of Particulate Suspensions in Centrifugation

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The properties that quantify the rate and extent of particulate suspension dewatering through sedimentation and consolidation are critical to the prediction of dewatering performance for industrial processes such as gravity settling, centrifugation and filtration. The strength of a network of particles in compression is quantified as a compressive yield stress or modulus,  $P_y$  (greek phi). This property can be characterised over a broad range of solids concentrations in equilibrium sedimentation, centrifugation and filtration tests for a diverse array of materials including coagulated mineral slurries, flocculated mineral slurries, paper pulp, potable water sludges, wastewater sludges, algal sludges and red blood cells. However, when the compressive stress is released, the solids network structure undergoes re-expansion. This elastic rebound is poorly understood, difficult to quantify and the subject of current research. The extent of this elastic rebound varies from material to material, being relatively minor for mineral slurries but more significant for some biotic materials such as wastewater sludges.

Centrifugation data has been generated for the equilibrium centrifugation of a range of particulate suspensions. The tests include equilibrium compression data at a range of rotation speeds, first ramping up and then ramping back down. Models have been proposed to predict this elastic rebound phenomenon and characterisation methods are being developed to quantify the elastic rebound phenomena from the experimental data. Analysis results will be presented to quantify the variation in the extent of elastic rebound for a range of materials.

**OC422**

**Rheology of Flocculated Thickener Underflow: Comparison of Temperature Responsive Flocculants with Conventional Flocculants**

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The shear and compressive rheology of the underflow of silica suspensions from a small pilot scale continuous thickener has been investigated. Comparison is made between newly developed temperature responsive flocculants based on poly (N-isopropyl acrylamide) (PNIPAM) and conventional commercial poly acrylamide (PAM) flocculants. The temperature responsive flocculant switches between a flocculant at temperature above the Lower Critical Solution Temperature (LCST) (32°C for PNIPAM) and a dispersant at temperature below the LCST. Underflow viscosity and solids concentration as well as overflow clarity have been examined. Comparison of the temperature responsive flocculant to conventional poly acrylamide (PAM) based flocculants is favourable. In continuous operation, the enhanced consolidation of the underflow is limited by the relatively short residence times of the sediment bed within the thickener compared to earlier batch sedimentation tests. The amount of time required for the liquid to permeate through the relatively deep sediment bed is greater than the residence time in the thickener. It appears the most significant benefit of the flocculants may be in the significantly reduced underflow rheology of the cooled thickened sediment. This would result in reduced pumping energy and cost.

# Monday Posters

**PP001**

**The effect of small polar molecules on skin membrane hydration and electrical properties**

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The mammalian skin owes its remarkable barrier function to its relatively thin (20  $\mu\text{m}$ ) and dead outermost layer, the *stratum corneum* (SC). This complex colloidal biomembrane consists of anucleated keratin filled cells (corneocytes) embedded in a continuous multilamellar lipid matrix, which helps to uphold the body homeostasis. At normal condition, there exist a large gradient in water activity across the membrane as it separates a water-rich interior from a dry exterior. Changes in this water gradient affect the membrane permeability, which might be explained by hydration-induced structural transformation of the extracellular SC lipids. Furthermore, the SC contains so call Natural Moisturizing Factor (NMF) which is a group of low-molecular weight polar compounds that are suggested to retain fractions of lipids in the liquid crystalline state at low relative humidities. NMF compounds are also commonly used in many commercial skin care products for treatment of dry skin. In this study we are interested in how these small polar molecules of NMF, e.g. urea and glycerol, affect the skin barrier properties. With confocal Raman spectroscopy we have investigated the change in SC hydration when varying the external water activity and followed the diffusion of urea and glycerol in excised porcine skin membranes. With two-dimensional spectral maps we have been able to create novel spatial high-resolution Raman images of the skin SC and we show that it is possible to distinguish between water-rich and lipid-rich domains within the membrane. In addition, we utilized electrical impedance spectroscopy to evaluate the skin membrane resistance and effective capacitance in presence of urea and glycerol. The outcomes of the impedance measurements indicate that topically applied urea and glycerol have different effects on the skin membrane electrical properties. This present data provide valuable information to understand the effect of urea and glycerol when used in skin care products.

PP002

## **Aqueous Biopolymer Lubrication and the Influence of Fluid Components on Adsorbed Film Properties**

Nichola Selway, Jason Stokes

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Biopolymers contribute to the functionality of many biological systems and are also used extensively in biomedical applications, foods, cosmetics and other industries, primarily as water-soluble thickeners and gelling agents for stabilisation and modification of fluid properties. The lubricating capacity of biopolymers in aqueous solution is potentially an important parameter in industrial applications and at biointerfaces within natural and biomimetic systems. We investigate the lubrication properties of xanthan and pectin in aqueous solution, as well as salivary proteins in human whole saliva (HWS), a powerful natural and readily available lubricant, using tribological measurement. We use a ball-on-disc tribometer, with soft PDMS contacts to mimic the low pressure conditions typical of bio-lubrication, and the friction coefficient is measured as a function of entrainment speed. Both xanthan and pectin are shown to enhance the lubrication of aqueous solutions across the boundary and mixed lubrication regimes. This is attributed to the formation of an adsorbed polymer layer on the hydrophobic PDMS tribo-surfaces<sup>1</sup>. Addition of 10 wt% sucrose exacerbates the lubricating effects of both polysaccharide solutions, with a greater reduction in boundary friction being evident for xanthan. Since sucrose alone in solution (up to 20 wt%) is shown to have no effect on lubrication, it is hypothesised that, in polymer solutions, sucrose may slow the local dynamics of polymer chains, thus facilitating a more wear resistant, hydrated polymer film. High-shear viscosity measurements reveal that changes in viscosity upon polymer and/or sucrose addition only partially account for differences in tribological behaviour, indicating that adsorbed-film properties dominate the frictional response. It is observed that HWS generates extremely low friction, attributed to the formation of a multi-layer adsorbed film consisting of a dense inner anchoring layer and a highly lubricious, hydrated outer layer<sup>2</sup>. Surface plasmon resonance (SPR) and quartz crystal microbalance with dissipation monitoring (QCM-D) are used to investigate the effect of fluid components (e.g. sweeteners) on the structure, hydration and viscoelasticity of adsorbed polysaccharide and salivary films. These techniques, combined with isothermal titration calorimetry (ITC), are used to explain the observed tribological behaviour by elucidating potential interaction mechanisms between species and their effect on adsorbed film properties.

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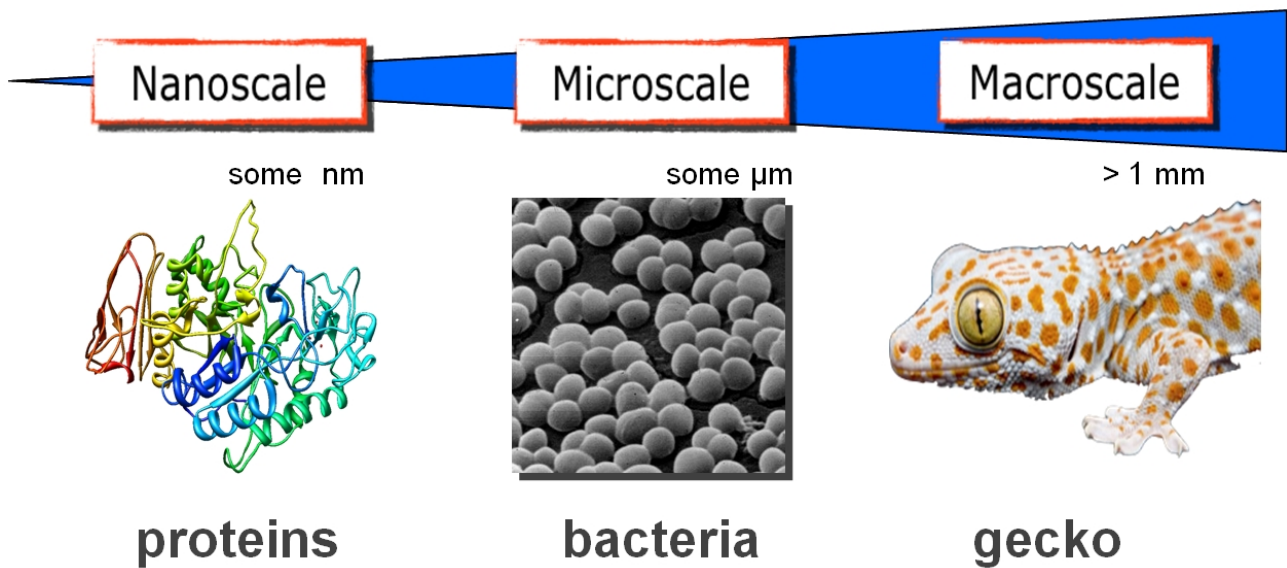
PP003

## Is Adhesion Superficial? Experiments with Proteins, Bacteria and Geckos Adhering to Tailored Si Wafers Reveal Subsurface Material Force Contributions

Karin Jacobs, Peter Loskill, Hendrik Hähl, Frank Müller, Samuel Grandthyll, Thomas Faidt

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Adhesion is a key issue for researchers of various fields, it is therefore of uppermost importance to understand the parameters that are involved. Commonly, only surface parameters are employed to determine the adhesive forces between materials. Yet, van der Waals forces act not only between atoms in the vicinity of the surface, but also between atoms in the bulk material. In this contribution, we describe the principles of van der Waals interactions and outline experimental and theoretical studies investigating the influence of the subsurface material on adhesion. In addition, we present a collection of data indicating that silicon wafers with native oxide layers are a good model substrate to study van der Waals interactions with coated materials (1).



With tailored Si wafers, adhesion can be probed on all length scales.

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## The Role of Nanostructure in Controlling Lipase-Mediated Digestion

Paul Joyce, Angel Tan, Catherine Whitby, Clive Prestidge

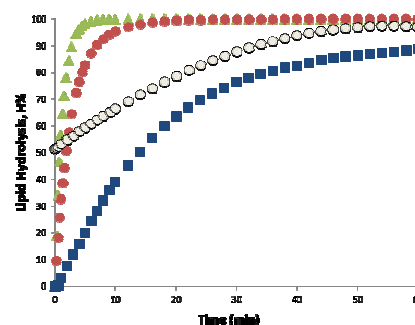
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Lipid-based colloidal systems increase the oral bioavailability of encapsulated therapeutics by mimicking the positive food effect, i.e. poorly-water soluble drug absorption increases significantly when co-administered with high-fat meals. The oral delivery of poorly-water soluble drugs is improved in hybrid lipid-based nanomaterials due to an increase in drug dissolution. A novel system that has demonstrated this is that of silica-lipid hybrid (SLH) microparticles, which have shown an increase in the oral absorption of several model poorly soluble drugs [1]. The ability to precisely control enzymatic digestion in these hybrid nanomaterials would enable an improved selectivity in the retention, release and absorption of encapsulated materials [2]. By forming new lipid-hybrid structures with various mesoporous silica particles, it may be possible to further enhance and control lipid digestion in these systems for optimal oral absorption.

The aim of this study was to determine the role of nanostructure on lipase mediated digestion in porous nanoparticles. This was investigated by loading lipid in three mesoporous silica species with distinctly different porous structures, i.e. Syloid 244P, Aerosil 380 and silica nanospheres KCC-1 with surface areas of 311 m<sup>2</sup>/g, 380 m<sup>2</sup>/g and 641 m<sup>2</sup>/g, respectively. Lipid loading was confirmed via confocal microscopy and quantified using thermogravimetric analysis (TGA). Lipid digestion was determined over a 60-minute period by measuring the release of free fatty acids using a pH-stat titrator.

Lipase mediated digestion of lipid loaded into the porous nanoparticles was significantly faster than from stabilised and non-stabilised sub-micron oil-in-water emulsions. It was hypothesised that this is due to the higher specific surface area and nanostructure of lipid in these materials, resulting in a higher degree of interfacial lipase binding. This was confirmed by the increase in digestion rates with the specific surface area of the porous silica nanoparticles. Stabilised sub-micron emulsions inhibit lipase binding due to the presence of an emulsifier at the interface, causing a slower release of free fatty acids when compared with a non-stabilised emulsion.

The kinetic mechanisms for each system were explored and identified, providing further understanding of the influence of nanostructure on enzyme action in lipid based systems.



**Figure 1.** Time dependence of lipase mediated digestion for triglyceride in (▲) Aerosil 380 particles, (●) Syloid 244P particles, (○) a non-stabilised sub-micron oil-in-water emulsion and (■) a stabilised sub-micron emulsion using lecithin as an emulsifier.

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**PP005**

**Biological synthesis of metal nanoparticles using plant leaf extracts**

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Five plant leaf extracts (Pine, Persimmon, Ginkgo, Magnolia and Platanus) were used and compared for their extracellular synthesis of metal nanoparticles. Stable gold, silver, copper, and platinum nanoparticles were formed by treating aqueous solution of  $\text{HAuCl}_4$ ,  $\text{AgNO}_3$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , respectively, with the plant leaf extracts as reducing agent. Magnolia leaf broth was the best reducing agent in terms of synthesis rate and conversion to nanoparticles. Only 11 and 3 min were required for more than 90% conversion to silver and gold nanoparticles, respectively, at the reaction temperature of 95 °C using Magnolia leaf broth. The silver nanoparticles were relatively spherical and uniform, while mixture of triangles, pentagons, hexagons, and spheres were obtained with gold nanoparticles. The average particle size ranged from 15 to 500 nm. Particle size could be controlled by changing the plant type, temperature and composition of the reaction mixture. As possible ecofriendly alternatives to chemical and physical methods, biologically synthesized nanoparticles using plant extracts may have applications in various human body-contacting areas. These biologically synthesized silver nanoparticles were coated on the surface of latex foam products by dip coating (exposure to nanoparticle solution) or ultrasonic treatment. Foams coated with silver nanoparticles showed higher antibacterial activities compared with foams untreated. Smaller silver nanoparticles synthesized at higher temperature showed higher antibacterial activity due to the higher content of silver nanoparticles and larger specific surface area.

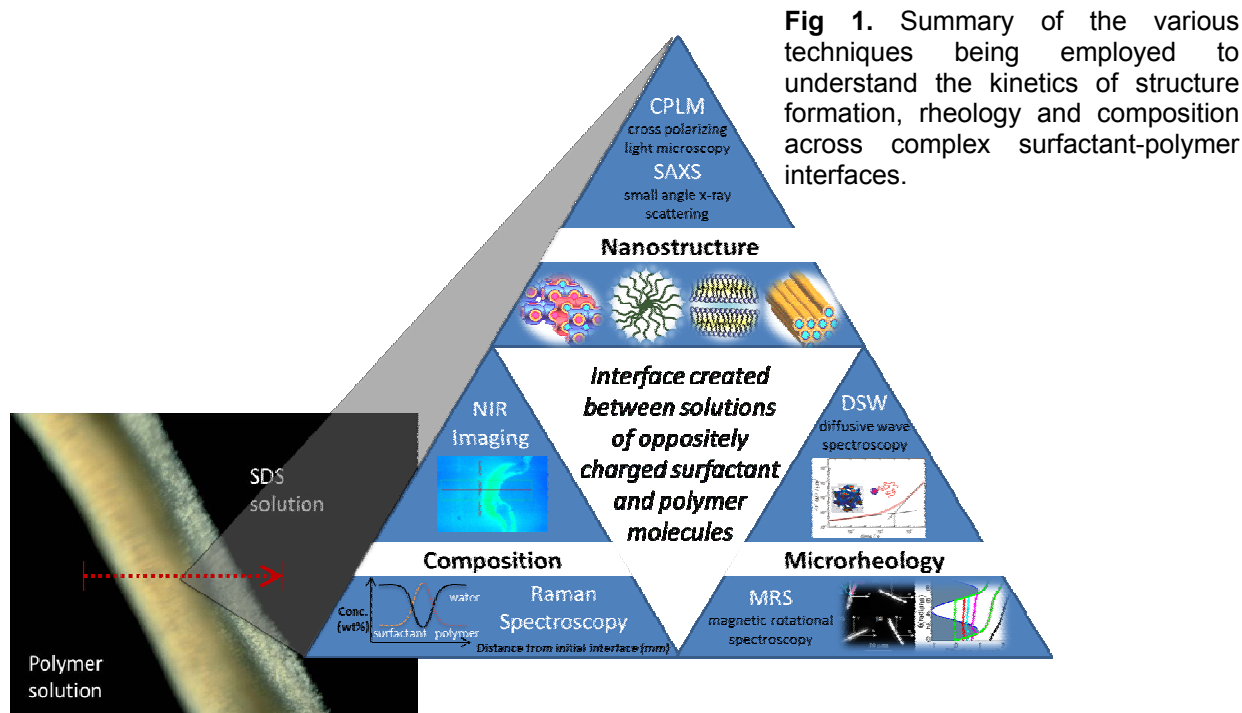
## Linking nanostructure, composition and microrheology of mesophases formed between oppositely charged solutions of surfactant and polymer molecules at non-equilibrium

Kristian Tangso<sup>1</sup>, Patrick Hartley<sup>3</sup>, Seth Lindberg<sup>2</sup>, Patrick Spicer<sup>4</sup>, Ben Boyd<sup>1</sup>

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It has been known for three decades that liquid crystalline structures can arise within mixtures of oppositely charged surfactant-polymer solutions<sup>1</sup>. However, the dynamics of formation of the complex nanostructure at the interface between these two components have yet to be investigated. This project seeks to understand the relationship between the micromechanical properties and microstructure of these systems at equilibrium and non-equilibrium by utilising techniques such as magnetic rotational spectroscopy (MRS) or diffusive wave spectroscopy (DSW) to probe microrheology, cross polarising light microscopy (CPLM) and small angle x-ray scattering (SAXS) for nanostructure characterisation and Raman microscopy/NIR imaging for determining the composition through the interface.

The outcomes will be significant in understanding how such systems may be manipulated to produce new controlled release materials. We know that liquid crystalline structure is an important determinant in controlling drug release<sup>2</sup>, hence controlling the interfacial structural attributes in particles prepared using such combinations of materials may provide a novel and interesting route to tailored release nanomaterials.



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**PP007**

**The Interesting is Not Always Inside: Microfluidic Platform to study Membrane Properties**

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Droplet based microfluidics is typically used to conduct (bio-) chemical reactions within individual droplets using minute amounts of reactants. A concept that is only rarely referred to is to use the surfactant stabilized water-oil interface of emulsion droplets to explore properties of artificial membranes (droplet interface bilayer). We explore microfluidic techniques to generate symmetric and asymmetric (phospho-) lipid membranes of controlled composition and to probe their properties. This microfluidic technique shall be suitable to study e.g. transport properties across membranes or SNARE protein mediated fusion processes. We also discuss why the membrane stabilization in microfluidic settings is orders of magnitude faster compared to conventional bulk settings.

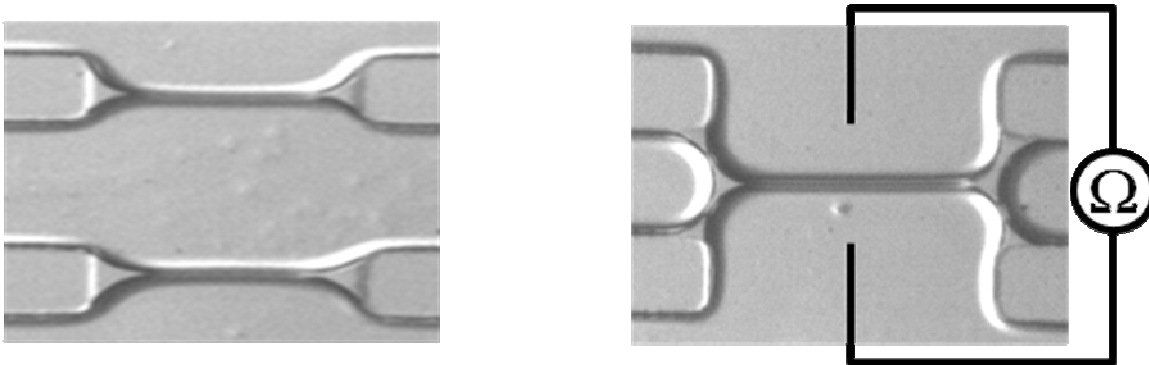


Figure 7: *left*: lipid membranes formed in a microfluidic device; *right*: lipid membranes as shown in left tile could be approached in a controlled way to study e.g. fusion processes.

PP008

**Self-assembled protein particles by templating on decomposable carbonate cores. Mechanical properties, stability, and cellular uptake**

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Formulation of therapeutic proteins into particulate forms is a main strategy for site-specific and prolonged protein delivery as well as for protection against degradation. Precise control over protein particle size, dispersity, and shape is extremely challenging to achieve this strategy. Mild preparation conditions, purity, and minimal processing steps are also highly desirable. It is, however, hard to fit all these criteria with conventional techniques to produce microparticulate protein formulations. Here we report new approach - hard-templating synthesis at soft conditions to fabricate monodisperse pure protein microbeads with adjusted size. A number of different proteins such as insulin, catalase, hemoglobin have been tested. The method is based on pH-mediated removal of porous CaCO<sub>3</sub> microparticles filled with isoelectrically precipitated protein. pH is a single trigger with a double function: formulation of protein insoluble matrix and template decomposition. The main requirement is an overlap of the solid template stability and protein insolubility as well as solubility for a certain parameter (here pH or EDTA) and a remaining protein insolubility upon template decomposition. Additional protein crosslinking upon protein infiltration into the carbonate templates is considered to improve particle stability in terms of mechanical properties and release characteristics. The mechanism of the microbeads formation, internal structure, mechanical properties, protein release, cellular uptake as well as some aspects of pulmonary delivery are addressed. The approach provides a simple way to assemble protein microparticles with tuned size, release profile, and mechanical properties.

## Influence of the Hydrophobic Force model on the Capture of Particles by Bubbles using Discrete Element Method

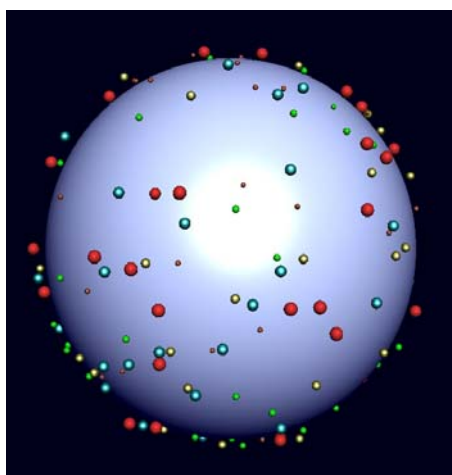
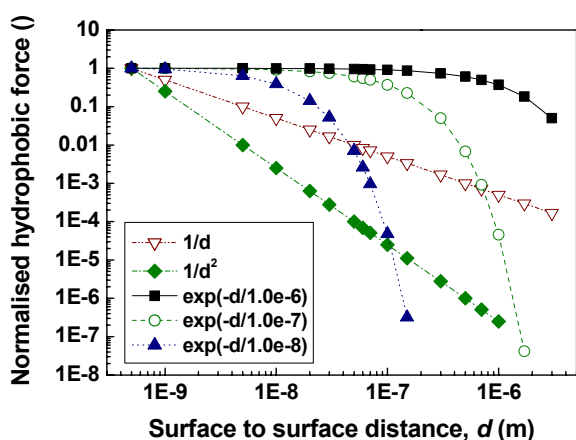
Roberto Moreno-Atanasio, Erica Wanless

University of Newcastle, Callaghan, NSW, Australia

Discrete Element Method computer simulations have been carried out to analyse the kinetics of collision of multiple particles against a central bubble whilst immersed in water. The model included hydrophobic, lubrication and drag forces as previously described in the literature [1-2].

Systems of three hundred particles, with diameters ranging between 20  $\mu\text{m}$  and 60  $\mu\text{m}$  with an average value of 30  $\mu\text{m}$ , were randomly positioned within a maximum distance from the surface of a bubble of 1000  $\mu\text{m}$  in diameter. Initial particle velocities were random in direction and value and followed Gaussian distributions with standard deviations of 1.0, 0.1 and 0.0. Three possible cases corresponding to relationships of the hydrophobic force with the distance between the particles and bubble have been analysed. In the first case the relationship had the form  $1/d$ ; in the second case a relationship in the form  $1/d^2$  was considered; and in the third case an exponential decay in the form  $\exp(-d/\lambda)$  where  $\lambda$  is the characteristic length of decay of the exponential function was used.

The differences in the capture efficiency of the particles predicted by the three models were drastic. All particles were captured by the bubble in the first case ( $1/d$ ). However, only 60 % of the particles were captured in the second case ( $1/d^2$ ) even for distances smaller than 100  $\mu\text{m}$ . In the case of the use of an exponential decay, only particles that were very close to the bubbles were captured. This work shows that the capture of particles from a fluid flow is drastically influenced by the hydrophobic force model and therefore there is a strong necessity to provide not only AFM data for the strength of the interaction forces but also experimental measurements of particles approaching to bubbles in order to determine the suitable hydrophobic force model with the highest capture efficiency.



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Process Parameter Identification in Thin Film Flows Driven by a Stretching Surface

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The flow of a thin liquid film over a heated stretching surface is considered in this study. Due to a potential non-uniform temperature distribution on the stretching sheet, a temperature gradient occurs in the fluid which produces surface tension gradient at the free surface of the thin film. As a result a result, the free surface deforms and these deformations are advected by the flow in the stretching direction. This work focuses on the inverse problem of reconstructing the sheet temperature distribution and the sheet stretch rate from observed free surface variations. This work builds on the analysis of Santra et al. [International Journal of Heat and Mass Transfer 52(2009) 1965-1970] who, based on the long-wave expansion of the Navier-Stokes equations, formulate a partial differential equation which describes the evolution of the thickness of a film thickness over a non-isothermal stretched surface. In this work, we show that, after algebraic manipulation of a discrete form of the governing equations, it is possible to reconstruct either the unknown temperature field on the sheet and hence the resulting heat transfer or the stretching rate of the underlying surface. We illustrate the proposed methodology and test its applicability on a range of test problems.

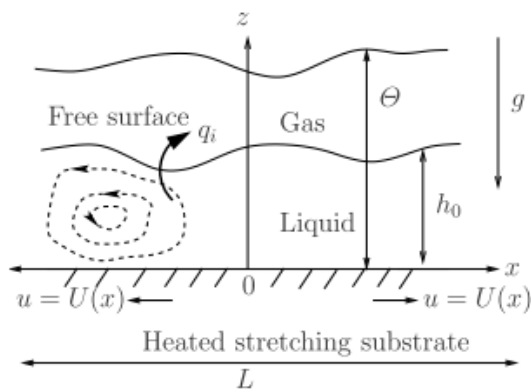


Figure 8: Sketch of the flow geometry

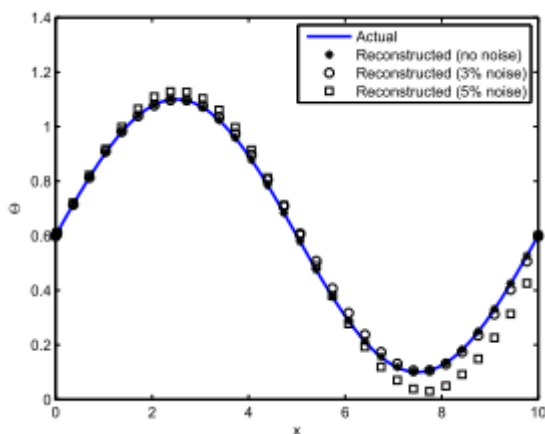


Figure 9: Actual and reconstructed temperature profiles at the substrate with and without noise in the input signal.

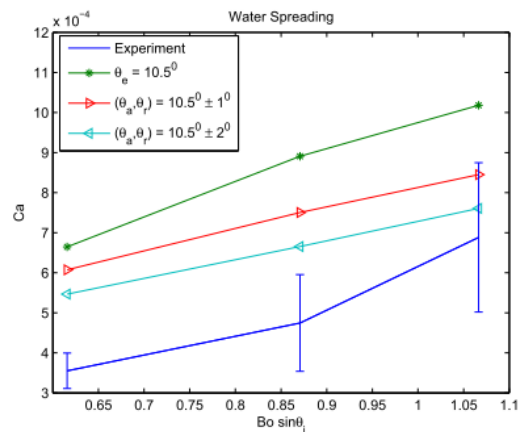
## Modelling Droplets Sliding Down an Inclined Plane: the Importance of Contact Angle Hysteresis

Gulraiz Ahmed<sup>1</sup>, Michael Taylor<sup>2</sup>, Mathieu Sellier<sup>1</sup>

<sup>1</sup>University of Canterbury, Christchurch, New Zealand, <sup>2</sup>ESR, Christchurch, New Zealand

Droplets sliding down an inclined planes are ubiquitous in natural and industrial processes. A good illustration of this process, familiar to most, is a droplet sliding down a car windscreen on a rainy day. It is, of course, also relevant to many other applications such as the application of pesticides, the coating of surfaces, or falling film evaporators to name a few. Such widespread applications have motivated numerous studies, see [1-3] and references therein for example. Forensic science provided the impetus for us to revisit this problem. Forensic scientists are able to extract a lot of information from the shape and distribution of bloodstains at crime scenes. This discipline, known as Bloodstain Pattern Analysis, is extensively based on the experience of practitioners accumulated over a long time and empirical correlations, the validity of which is not always well understood. There has therefore been a recent drive to understand from a more fundamental angle the processes involved in bloodstain formation. The work presented here is an early step in that direction. It focuses on an apparently simple configuration (a droplet sliding down an inclined plane) and fluids with a simple behaviour relative to blood (water, silicon oil, or glycerine). In spite of its apparent simplicity, this problem already poses significant challenges when it comes to trying to model it.

In this work, we present a comparison of the sliding velocity of droplets on an inclined surfaces measured experimentally and obtained numerically from the solution of a mathematical model based on the long-wave approximation. We have tested a range of substrate inclination angles and fluids. One of the challenges associated with the mathematical model is the singularity which arises at the dynamic wetting front. We have adopted in this work a contact line model introduced by Schwartz and Eley in [4] and tested repeatedly since. This model is based on the introduction of a thin precursor film maintained in equilibrium under the action of the disjoining pressure. A new contribution of this work is the implementation of an algorithm which automatically locates the part of the contact line which is advancing and the part which is receding. This enables us to impose different contact angles for the advancing and receding fronts and therefore take into account contact angle hysteresis. With the inclusion of the contact angle hysteresis, simulation results were brought in much better agreement with the experimental ones as illustrated in the Figure above.



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PP012

## Hydrodynamic boundary conditions at imidiazolium-based ionic liquid-air interface: effect of confinement

Pasindu Sellapperumage, Marta Krasowska, John Ralston, Mihail N. Popescu

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Ionic liquids (ILs) are salt-like materials composed of an ion pair of one positively charged molecule (cation) and one negatively charged molecule (anion). The possibility of altering the chemical and physical properties of an IL by changing the cation-anion combination allows them to be tuned to fit specific tasks or applications. Consequently, ILs are rapidly developing into a popular class of alternative solvents for numerous applications in chemistry and materials science [1].

For many of the applications, it is crucial to know how IL flows over the surface (i.e. liquid slip or no-slip). The knowledge of these so-called hydrodynamic boundary conditions (BC) is rather limited at present, and this hinders the development of ILs for new applications.

We have studied motion of small bubbles ( $Re \ll 1$ ) in imidiazolium-based ionic liquids of different alkyl chain lengths ( $C_4$ ,  $C_6$  and  $C_8$ ). The study focused on two particular cases: (i) in non-confined geometry, i.e. when bubble reached its terminal velocity but was far away from the interface and (ii) under confinement, i.e. bubble approaching free interface.

In order to determine the hydrodynamic BC at the IL-air interface the experimental terminal velocities of the bubbles rising far away from the interface were compared to those described by Stokes' law [2] or by the Hadamard-Rybczynski equation [3,4]. The amount of slip was correlated with the structure of IL and the size of the rising bubble.

In order to determine the hydrodynamic BC at the IL-air interface under confinement the hydrodynamic drainage force,  $F_{h(B)}$ , exerted on the bubble in close proximity of the interface was compared to Brenner's equation [5] as well as as equations given by Vinogradova [6,7].

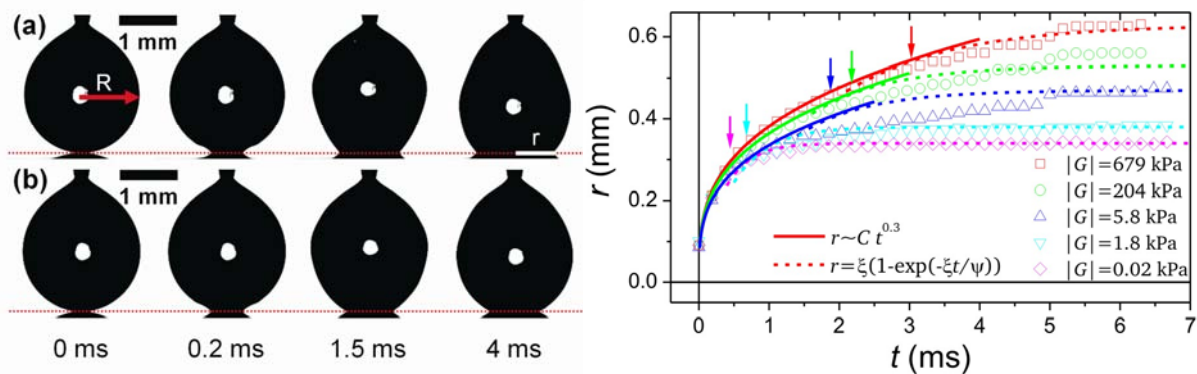
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## Time scales of Spontaneous Spreading of Drops on Soft Viscoelastic Surfaces

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It is known that liquid droplets spreading on a soft, viscoelastic surface can be slowed down considerably by the formation of a *wetting ridge*, or protrusion of the substrate near the triple phase contact line (TPCL) due to capillary forces. Viscoelastic dissipation in the solid surface can prevail over viscous dissipation in the liquid and dominate the spreading process. In this contribution we show that a short, rapid spreading stage does exist after the contact of a drop and a viscoelastic surface. The requisite balance determining speed of motion of the TPCL is initially between capillary forces and inertial effects. As spreading proceeds, inertia lessens while the lower spreading speed allows for viscoelastic effects to emerge. We study the transition between inertial and viscoelastic regime by high-speed video microscopy and explain it by a simple theory.



**Figure:** (L) High speed video images of a water droplet spreading on PDMS surfaces with different elasticity; (R) Plots of the spreading radii  $r$  as a function of surface elasticity versus spreading time  $t$ .

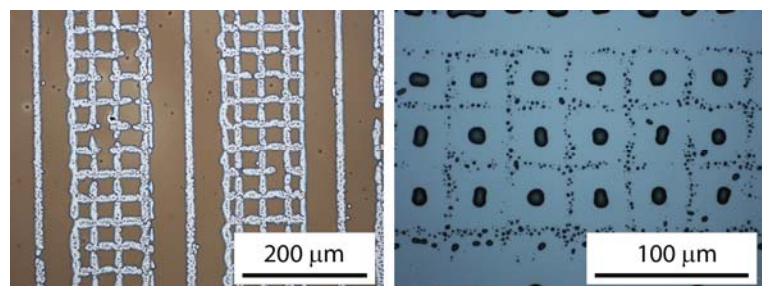
**Micropatterned Polymer Thin Films for Biological Applications**Manuel Ghezzi<sup>1</sup>, Stuart Thickett<sup>2</sup>, Andrew M Telford<sup>1</sup>, Chiara Neto<sup>1</sup>

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Polymer films on top of rigid substrates have received significant attention in the development of bio-related and medical-related devices. Polymer films on non-wettable substrates are unstable and dewet from the solid surface upon annealing above the glass transition temperature. Polymer dewetting is an easy, versatile and robust process to form surface patterns. The present work involves two main applications of polymer dewetting: the development of patterned polymer surfaces with spatially controlled features and the development of patterned polymer surfaces for controlled adhesion of protein and cells.

Ordered patterns produced by polymer dewetting could be useful in applications that require spatially localized features of controlled surface chemistry, such as proteomics, single cell studies, and biosensors. In the present work we investigated the early and intermediate stages of guided dewetting of polystyrene (PS) thin films on chemically patterned silicon, achieved by micro-contact printing of non-wettable self-assembling monolayers of an alkylsilane.<sup>1</sup> Different types of ordered patterns could be achieved depending on the annealing temperature and time (Figure 1). The study of the dynamics of hole growth revealed a deviation of the growth profile from the trend on homogeneous substrates, attributed to the pinning of the PS rims on the borders of the hydrophobic regions.

Patterned polymer bilayers have been successfully employed in literature for selective adsorption of proteins and cells.<sup>2,3</sup> The aim of the present work is to design and develop a patterned polymer bilayer for controlled cell adhesion with a biodegradable and protein repellent top layer. Biodegradability and protein repellency are achieved by employing a poly(lactic-co-glycolic) acid (PLGA) film grafted with poly(ethylene glycol) (PEG) chains.



**Figure 1.** Ordered patterned obtained by dewetting of PS thin films on micro-contact printed silicon.

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**PP015**

**Adsorption of dextrans on talc: Dewetting, AFM imaging, and flotation studies**

Mohammad Kor, Agnieszka Mierczynska-Vasilev, Jonas Addai-Mensah, David Beattie

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Talc is an unwanted waste mineral that appears in most complex sulphide ores. Due to natural hydrophobicity, talc can easily be collected in flotation, which causes a reduction of the recovery of valuable minerals, in addition to causing problems with downstream operations. Polymers are usually used to prevent talc flotation, presumably by rendering surface of talc hydrophilic. A range of studies have been employed to relate measured static contact angles to the effect of polymers on talc flotation [1, 2]. Although measurements of static contact angles can give an indication of what will happen when bubbles collide with hydrophobic particles, they do not allow one to describe the dynamics of the bubble–particle attachment process (thin liquid films, dewetting, etc.). We report on the effect of three polysaccharide-based polymers (normal dextrin as well as hydrophobically modified dextrans Capsul and Capsul TA) on bubble-surface interactions for talc, studied using high speed video capture of the bubble-surface collisions. The bubble-surface collision data reveal that the polymers affected thin film rupture times and dewetting rates differently. These measurements are compared with measurements of equilibrium adsorbed layer properties, as determined by adsorption isotherms for the polymers on talc, tapping mode atomic force microscopy (TMAFM) imaging of polymer-treated talc, and batch flotation testing of talc.

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**PP016**

**Dynamic response in electric field induced wetting**

Michael von Domaros<sup>1,2</sup>, Davide Vanzo<sup>1</sup>, Dusan Bratko<sup>1</sup>, Alenka Luzar<sup>1</sup>

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Electric field applied across a hydrophobic nanopore can control wetting/dewetting transitions. This switching effect is of potential importance in applications like fluid flow control in nanofluidic devices and imbibition of nanoporous materials. Dynamic response to the imposition or (cessation) of the field occurs at two stages characterized by different timescales. The fast response involves the change in effective surface tension, which takes place along with water polarization. Wetting transitions, involving liquid infiltration or expulsion, are essentially slower. We characterize the kinetics of both processes by using molecular dynamics simulations. We uncover a new and significant polarity dependence of polarization dynamics in the solvation layer, which takes place within 0.1-10 ps regime. Field controlled wetting and dewetting events in a nanopore open to exchange with bulk liquid occur at several orders of magnitude longer timescales and show pronounced hysteresis reflecting considerable activation barriers to the transition (Supported by U.S. NSF and DOE).

**PP017**

**Thermodynamic of Polymer-Surfactant Interaction in Catanionic Mixtures**

Behnoosh Tajik Ahmadabad, Beheshteh Sohrabi

*Science and Technology University, Tehran, Iran*

The behavior of aggregation in the mixture of cetyltrimethylammonium bromide (CTAB) and polyethyleneglycole (PEG), sodiumdodecylsulfate (SDS) and polyethyleneglycole (PEG) and the mixture of SDS/CTAB and polymer in anionic- and cationic-rich regions was investigated by surface tension and conductometry. The data based on plotting of surface tension( $\gamma$ ) as a function of solution composition and total surfactant concentration enabled us to determine three critical concentrations, the formation of mixed surfactant aggregations on the polymer ( $T_1$ ), the saturation of polymer from mixed surfactant aggregations ( $T'_1$ ) and the formation of free mixed aggregates (CAC or  $T_2$ ).

The thermodynamic parameters of micellization ( , and ) for these mixtures were also calculated. Temperature and polymer effects on adsorption and effectiveness of surface reduction were discussed in term of these parameters.

PP018

### The Interaction of Functionalised Cubosomes with siDNA using QCM-D

Behnoosh Tajik Ahmadabad<sup>1,2</sup>, Ben Muir<sup>1</sup>, Keith McLean<sup>1</sup>, Tracey Hinton<sup>1</sup>, Anastasios Polyzos<sup>1</sup>, Frances Separovic<sup>1,2</sup>

<sup>1</sup>CSIRO, Melbourne/VIC, Australia, <sup>2</sup>University of Melbourne, Melbourne/VIC, Australia

Lyotropic liquid crystalline nanoparticles (cubosomes™) have the potential to act as amphiphilic carriers of biologically active materials in therapeutic delivery applications. Previous studies have shown that cubosome systems comprised of the non-ionic amphiphile 1, 2, 3-trihydroxy-3, 7, 11, 15-tetramethylhexadecane (phytantriol) and the cationic lipid (DOTAP) effectively deliver small interfering deoxyribonucleic acid (siDNA) to cells [1]. However the mechanism of uptake and release of (siDNA) from the cubosome nanocarrier is poorly understood. In order to monitor the association and release kinetics of the cubosome-siDNA interaction under various biologically relevant conditions, time-resolved quartz crystal microbalance with dissipation monitoring (QCM-D) was used. The QCM-D studies required surface immobilization of the cubosomes to the gold surface of the QCM sensor chip. To achieve the specific cubosomes binding, a secondary biotinylated lipid, 1, 2-distearoyl-sn-glycero-3-phosphoethanolamine- N-[biotinyl(polyethyleneglycol)-2000] was added to cubosomes, which enabled attachment of the particles to a neutravidin (NAv)alkanethiol monolayer functionalized QCM sensor chip [2]. This poster reports on our initial studies of the surface immobilization of DOTAP / Phytantriol cubosomes to a modified QCM-D gold chip and the binding interaction of siDNA with the bound cubosomes.

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## Enhancing the Biocompatibility of Antimicrobial Nano-Silver Coated Surfaces through Appropriate Functionalized Silver Nanoparticles

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Bacterial colonization of biomedical devices is a major health issue which can cause death or financial burden on patients as a result of repeated surgery for repair or replacement [1, 2]. An important strategy to overcome such healthcare associated infections (HAIs) is surface modification of biomedical devices by alteration of their mechanical and chemical properties which will directly affect cell attachment, bacterial adhesion and colonization and subsequent biofilm development [3]. Development of nano-structured multilayers as coatings on implantable biomaterial devices [4] is one approach. Presence of small amounts of silver nanoparticles, as a broad-spectrum antibacterial agent, on the surface can kill bacterial cells [5].

We have applied a plasma polymerization technique, to attach nano-silvers onto the surface in such a way that their functionalities are preserved and the resulting film remains stable over time on the surface. The resulting thin layer polymer coating is highly branched and highly cross-linked, and so adheres well to any solid substrate surface [6]. In addition, we can create surfaces containing functional groups common in the human body such as N-H, C-N, C-O and O-H, and this can boost their biocompatible superficial properties [7].

Chemically altering the surface properties of nano-silvers with different capping agents is being studied: (a) electrostatically stabilized (Citrate and PVS); and (b) covalently stabilized (MSA). These capping agents affect the pH, particle size, color and stability of the colloidal solution. They also have direct effects on the rate of deposition and final concentration of nano particles on the surface and can determine the antibacterial activity and biocompatibility of the resulting surfaces. Deposition of nanoparticles is performed through wet chemistry by the mean of simple and time-dependant immersion of amine-rich plasma polymerized coated surfaces in the solution of colloidal silver using a dip-coater. The interactions between three different bacteria as well as human cells with AgNPs coated surfaces were studied. We found that among the solutions we prepared, functionalizing covalently AgNPs with MSA enhances the chance for silver to be attached in larger amounts to the surface thus boosting the bactericidal efficacy of coated surfaces. This surface modification makes the surfaces non-toxic to mammalian cells so the approach is appropriate for therapeutic applications.

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**PP020**

**Ultrasonic Studies on Micellar Behaviour of Surfactants in Non- Aqueous Solvents.**

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*University of Bahrain, Sakheer, Bahrain*

Ultrasonic measurements were performed on of sodium soaps such as sodium caprylate, sodium laurate, sodium in N- methyl acetamide, N,N- dimethyl acetamide and in formamide, to determine the critical micelle concentration (cmc), soap- solvent interaction and various acoustic and thermodynamic parameters. The values of the cmc decrease with increasing chain length of fatty acid constituent of the soap molecule. The ultrasonic velocity, specific acoustic impedance, apparent molar compressibility and relative association increase while the adiabatic compressibility, intermolecular free length, apparent molar volume, solvation number and available volume decrease with increasing soap concentration. The dissociation constant and thermodynamic parameters for dissociation and micellization processes of sodium soaps were evaluated from conductivity measurements. The results showed that these soaps behave as weak electrolytes in dilute solutions and the micellization process is dominant over the dissociation process.

## Strategies for linking composition and colloidal structure in digesting lipid-based drug formulations

Stephanie Phan<sup>1</sup>, Xavier Mulet<sup>1,2</sup>, Adrian Hawley<sup>3</sup>, Lynne Waddington<sup>2</sup>, Ben Boyd<sup>1</sup>

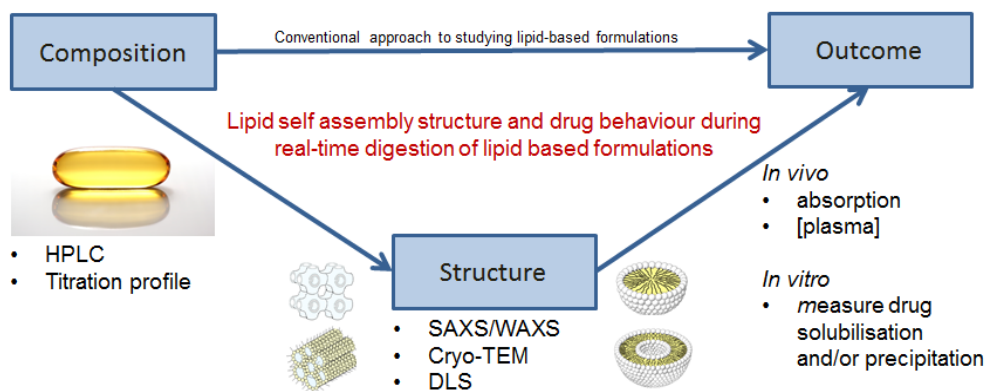
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Digestion of lipids is a dynamic process with continuous changes in composition and conditions. When lipids are exposed to gastrointestinal fluids during digestion, they self-assemble into colloidal phases and liquid crystalline structures, which are important in digestion and are of relevance to the drug delivery field. Currently there is little structural information about the colloidal species formed under dynamic lipolysis conditions. We seek greater understanding of the nanostructure of these systems using small angle x-ray scattering (SAXS) and cryo-TEM.

Systems were studied in equilibrium and dynamically. In equilibrium studies, monoglycerides and fatty acids in fasted simulated intestinal fluid (FSIF) pH 6.5 representative of the endpoint of triglyceride digestion were studied by SAXS. It was found that lipid structure, lipid loading and digestive conditions influenced the structures formed. For dynamic structure studies, an *in vitro* digestion model was used. The digestion medium was pumped through a quartz capillary which was fixed in the X-ray beam, enabling SAXS measurements to monitor changes in nanostructure in real-time during digestion. Lipids were added to FSIF pH 6.5 in the thermostatted digestion vessel at 37 °C. Pancreatin was added to initiate digestion and the liberation of FA was titrated with NaOH to maintain the system at pH 6.5. The volume of NaOH used indicates extent of digestion, assuming stoichiometric reaction between FA and NaOH. Structural changes were correlated with the titration curve, enabling digestion and composition to be linked with structure.

Cryo-TEM was used as a complementary technique to study the structure-composition link. Digesting lipid samples were observed in their native environment and it was possible to distinguish between the different colloidal species present. Oil droplets, protein aggregates, micelles and unilamellar and multilamellar vesicles were evident.

These findings are consistent with dynamic SAXS studies reported recently using long-chain and medium-chain commercial triglycerides<sup>1</sup>. The results provide our first insights into likely structure formation for ultimate correlation to nanostructure during dynamic lipolysis studies *in vitro* and *in vivo*.



<sup>1</sup> Warren, D. B.; Anby, M. U.; Hawley, A.; Boyd, B. J., Real Time Evolution of Liquid Crystalline Nanostructure during the Digestion of Formulation Lipids Using Synchrotron Small-Angle X-ray Scattering. *Langmuir* **2011**, 27 (15), 9528-9534.

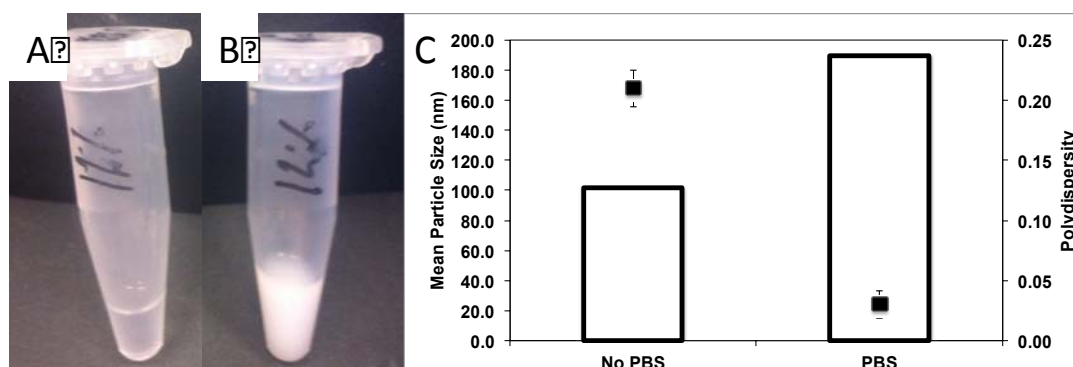
## Charge Shielding of Anionic Lipid Containing Dispersions Regulates Phase-Behaviour

Terence Hartnett<sup>1,2</sup>, Katharina Ladewig<sup>1</sup>, Patrick Hartley<sup>1</sup>, Keith McLean<sup>1</sup>, Andrea O'Connor<sup>1</sup>

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The efficient delivery of bioactive therapeutics within the body is important for the treatment of a variety of diseases. Lyotropic liquid crystalline nanoparticles (cubosomes) that are formed by the self-organization of amphiphiles such as phytantriol and monoolein may be suitable delivery vehicles. The amphiphiles self-organize into a highly complex network of bilayers that enables the encapsulation of hydrophilic and hydrophobic therapeutics that may then be released over an extended period of time. However, a limitation to the use of cubosomes as drug delivery vehicles for bioactive therapeutics is their energy intensive production methods.<sup>1,2</sup> Further, cubosomes produced via these energy intensive methods have also been suggested to be less stable, which - in a commercial sense - is not desirable.<sup>3</sup> Recently two new methods were reported that require minimal energy input to form cubosomes with a size range similar to that obtainable using energy intensive methods.<sup>4,5</sup> One of these methods, developed at CSIRO, utilizes phosphate buffered saline (PBS) as a charge shield for the conversion of a lamellar phytantriol/didodecyl-dimethyl-ammonium bromide (DDAB) phase to its cubic counterpart.

We have built on this earlier work by replacing the cationic lipid with the anionic lipid, dipalmitoyl phosphatidyl-serine (DPPS). Here, we show that the charge shielding method is amenable and can be used to regulate the phase behaviour of DPPS/phytantriol dispersions producing nanoparticles in the range of 150-250nm with a low polydispersity (Fig. 1 C). The addition of the PBS induces a visual transformation of the solution to a milky colour that is commonly observed when the cubic phase is present (Fig 1 A and B).



**Figure 1** – (A) Phytantriol dispersion containing 12% (w/w) dipalmitoyl phosphatidylserine (DPPS) without phosphate buffered saline (PBS). The DPPS prevents the cubic phase from forming resulting in a clear solution. (B) Phytantriol dispersion containing 12% (w/w) DPPS with PBS. PBS induces a phase change that transforms the dispersion into a milky colour commonly observed when the cubic phase is present. (C) Size (columns) and polydispersity (squares) of the nanoparticles without and with PBS. The size increases and polydispersity decreases due to charge shielding of the anionic lipid DPPS by PBS causing a phase transition.

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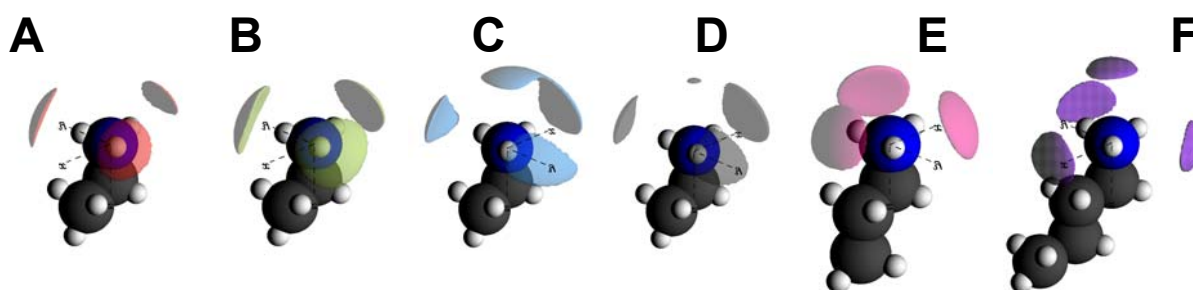
(5) Muir, B.; Zhen, G.; Gunatillake, P.; Hartley, P. G. *J. Phys. Chem. B* **2012**, *116*, 3551–3556.

## Hydrogen bonding in Protic Ionic Liquids

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Hydrogen bonds are the most important directional intermolecular interaction in chemistry.[1,2] The structure and properties of many chemical systems (eg. water, DNA, macromolecules, crystalline or glassy phases) are characteristically determined by the number and strength of hydrogen bonds. Protic ionic liquids (PILs) are a new class of solvents composed entirely of ions.[3] Despite their pure ionic composition, PIL are solvents distinguished by their ability to hydrogen bond; ions are formed because proton transfer is induced from a Brønsted acid to a Brønsted base. Notably, the hydrogen bonding capacity of PILs is tuneable, and is linked to revelations of bulk nanostructure in these solvents.[4-6] In this presentation, model fits to neutron diffraction data for a series of PILs will be presented. This enables us to systematically explore how PILs hydrogen bond in the bulk, with the aim to link concepts such as liquid nanostructure, solvent properties, and  $\Delta pK_a$ .



**Figure 1-** Spatial density plots which show the distribution of the H-bond acceptor-atom as a function of angular position and distance relative to a central ammonium-based cation for PILs (A) ethylammonium thiocyanate (B) ethylammonium hydrogen sulphate (C) ethylammonium formate (D) ethylammonium nitrate (E) propylammonium nitrate (F) butylammonium thiocyanate.

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**Physicochemical Investigation of Biocompatible Mixed Surfactant Reverse Micelles: Temperature-Induced Percolation, Energetics of Percolation, Effect of Additives and Dynamic Light Scattering Studies**

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Temperature-induced percolation behaviour in mixed biocompatible reverse micellar systems (RMs) comprising sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and polyoxyethylene(20) sorbitan trioleate (Tween-85) in polar lipophilic oils e.g., ethyl oleate (EO), isopropyl myristate (IPM) and isopropyl palmitate (IPP) have been studied at a total surfactant concentration ( $S_T$ ) of  $0.25 \text{ mol dm}^{-3}$ . Droplet dimensions of some selected systems have been measured by dynamic light scattering (DLS) studies at different physicochemical environments (viz., water content ( $\omega$ ), content of non-ionic ( $X_{\text{Tween-85}}$ ),  $S_T$ , [NaCl] and temperature). Our study focuses primarily on coupling the conductance study with DLS technique to gain better insight on the percolation mechanism and size aspects of mixed surfactant RMs. And, also our objective is to provide a rationale for the impact of oil architecture on the conducting properties and droplet size distribution in RMs. This will serve as a basis for further investigations of these systems useful in drug delivery. The threshold percolation temperature ( $T_p$ ) of these systems has been found to be decreased with increasing  $\omega$ ,  $X_{\text{Tween-85}}$ ,  $S_T$ ; whereas  $T_p$  has been increased with increasing [NaCl] and molar ratio of oil to surfactant (S). Not only molar volume or fatty acid chain length but also the chemical structure of the oil plays an important role in determining  $T_p$  of these systems. Scaling laws for the temperature-induced percolation have been found to be obeyed and demonstrates the dynamic nature of the percolation process.  $T_p$  has also been determined for these systems in presence of acetyl modified amino acids (MAA) as additives [viz., N-acetyl-L-glycine (NAG), N-acetyl-L-cysteine (NAC), N-Acetyl-L-leucine (NAL) and N-acetyl-L-glutamic acid (NAGA)] of different molecular structures. At constant composition, MAA have been found to delay the percolation process in all systems. The value of  $T_p$  follows the order: NAG > NAGA > NAC > NAL > without at comparable concentrations. The activation energy,  $E_p$  of these systems has been estimated both in absence and presence of additives.  $E_p$  values have been found to be followed the order; without > NAL > NAC > NAGA > NAG and decrease with the increase in concentration of MAA for AOT/Tween-85/oil(s)/water RMs. The standard free energy change ( $\Delta G_{cl}^0$ ), enthalpy change ( $\Delta H_{cl}^0$ ) and entropy change ( $\Delta S_{cl}^0$ ) of cluster formation have been evaluated at different physicochemical environments.  $\Delta G_{cl}^0$  has been obtained as negative for all of the formulations, indicating the spontaneous formation of the droplet cluster. The values of  $\Delta H_{cl}^0$  and  $\Delta S_{cl}^0$  have been found to be positive (i.e., an enthalpically disfavored endothermic process). The endothermicity of the clustering process accounts for a strong heat absorbing step in it. The clustering process has been found to be highly entropically driven. At constant composition,  $\Delta G_{cl}^0$  has been found to be dependent on oil type and follows the order; IPM > EO > IPP, whereas  $\Delta H_{cl}^0$  and  $\Delta S_{cl}^0$  values follow the order; IPP > EO > IPM. The near equivalence in the magnitude of  $\Delta G_{cl}^0$  results in the linear compensation between  $\Delta H_{cl}^0$  and  $\Delta S_{cl}^0$ . Hydrodynamic diameter ( $d_h$ ) mixed RMs has been found to be increased with increasing  $\omega$ ,  $X_{\text{Tween-85}}$ ; whereas it is decreased with increasing  $S_T$  and [NaCl] with other factors kept constant. It has also been observed that with increasing temperature,  $d_h$  increases for single AOT/EO/water RMs, whereas it decreases for mixed AOT/Tween-85/EO/water (at  $X_{\text{Tween-85}} = 0.1$  and  $0.2$ ) RMs at comparable conditions. The droplet radius depends on oil type and follows the order; IPM < EO < IPP at comparable composition. An attempt has been made to underline the microstructures of these systems in the light of percolation of conductance vis-à-vis thermodynamics of droplet clustering and droplet dimensions.

# **Tuesday Posters**

PP050

## The Effect of Trace Amounts of Water in AFM Adhesion Measurement

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Atomic Force Microscopy (AFM) has been used to study the effects of water on solvation and adhesion forces in the liquids n-hexadecane and n-dodecanol confined between an AFM tip and a graphite surface. We find that trace amounts of water dissolved in these liquids (up to ~500 ppm water by volume) do not destroy the solvation layering. However, adding water does cause a decrease both in the number of observed solvation layers and the magnitude of the measured oscillatory forces, as previously reported using the Surface Force Apparatus.

Our new observation is that added trace water may result in a repulsive pull-off force when the tip is in apparent mechanical contact with the substrate. This effect is most pronounced for dodecanol, which can readily solvate water, but is also observed when water is added to hexadecane. We hypothesize this effect arises because a repulsive hydration force arises as water hydrates onto oxide covered AFM tips due to the presence of surface hydroxyl groups. Strong support for this hypothesis comes from the slow increase in pull-off force from negative to positive values as Aluminium coated tips oxidize over time.

A possible application is to generate repulsive forces on oxide surfaces in the presence of trace water to lower friction or adhesion in microelectromechanical (MEMS) structures; almost all materials used in MEMS fabrication have a surface oxide. Perhaps a more important outcome of the observations is that adhesion measurements (i.e. as used in Chemical Force Microscopy) in non-aqueous solutions may be misleading or uncertain because the contribution from the hydration force cannot be ascertained independently for a given tip. Thus, for adhesion measurements, it may be preferable to use Au or Pt tips in place of commonly used AFM tips (e.g. Si<sub>3</sub>N<sub>4</sub>, Silicon, most metal coatings) which can all oxidize.

PP051

## Particle sizing via CCD image analysis of TIRM resonant scattering hotspots

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In colloidal force measurement, accurate determination of particle size is often an important aspect of experimental design and data analysis. Total internal reflection microscopy (TIRM) is a direct force method for probing sub-kT interaction potentials of colloiddally levitated, micron-scale particles undergoing Brownian motion in close proximity to a flat plate. Data analysis is highly sensitive to particle size, but extant TIRM methods for determining this parameter are not always viable. Since Lorentz-Mie theory was extended and refined (1,2) to provide 3-D analytic expressions for the scattering of light by spherical particles immersed in an evanescent field, substantial attention has been given to the characterisation of morphology-dependent resonance (MDR) hotspots (3). A seemingly uninteresting corollary of this theory is that these MDR scattering hotspots should occur at, or near, the periphery of a particle frustrating an evanescent field. One aspect of TIRM that has yet to be explored is the potential to use these hotspots for particle sizing. We propose a simple new CCD technique to exploit this phenomenon, estimating radius by comparing the location of centroids computed for a particle and its associated hotspot.

Implementing Hough transform edge-finding routines to identify regions enclosing unique scattering particles and dynamically trainable centroid-finding routines to compute individual radii, we developed an algorithm to perform bulk analysis of TIRM images. This was employed to automate construction of particle size distributions (PSDs) for 1,000 polystyrene and silica spheres in each of six monodisperse species ranging in reported size from 2–10 $\mu$ m. Transmission electron microscopy was used to generate comparative PSDs, which were congruent within the bounds of experimental error and also showed good agreement with accompanying NIST certifications. For ten particles from each species, the CCD technique was compared directly against a well-established TIRM method for determining particle size from potential energy profiles by varying the applied optical body force. In each case the deviation between measured radii obtained from each method fell within  $\pm 5\%$ , and was found to have a minor correlation with particle size as expected (3).

This combination of ensemble and case-by-case methods establishes predictable size- and material-dependent upper bounds on the uncertainty associated with estimating particle size using this new technique, and explicitly verifies the location of MDR hotspots described by evanescent Lorentz-Mie theory. Additionally, the relative simplicity of the technique coupled with its capacity for high-throughput particle sizing intimates strong potential for an industrial application.

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**PP052**

**Interaction between bubbles in aqueous non-absorbing polymer systems**

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The interactions between bubbles are important in the stability of food products containing foams, separation processes such as flotation and personal care products. As the forces between bubbles are not fully understood further understanding of these interactions could lead to improvements in many industrial applications.

The aim of this work was to investigate the forces between bubbles in aqueous solutions containing non-absorbing polymers. As the name suggests, non-absorbing polymers do not absorb to the air/water interface of a bubble. The technique of Atomic Force Microscopy (AFM) was used to measure the forces between bubbles. A combination of bubble-bubble, bubble-plate and particle-plate measurements were taken to explore the interactions present within the aqueous system. This allowed the differences in forces between deformable and rigid surfaces to be determined. This study also focused on the effects of bubble velocity, solution viscosity, polymer concentration and molecular weight of the polymer on the forces.

## PP053

### Ideal vs. Nonideal Chemisorption and the Role of Ionic Dispersion Potentials for Charge Regulated Surface Forces

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Colloidal interaction forces are deduced from the interaction free energy of the system, which in turn is dictated by how the chemical potential ( $\Delta\mu$ ) is defined. The chemical potential comprises of two parts: physisorption and chemisorption, where the latter is omitted for surfaces modeled with constant charge. When chemisorption of potential determining ions occurs at the interface, the chemisorption part of the chemical potential may be charge density independent and the chemisorption process is ideal such that  $\Delta\mu$  does not change with amount of ions already adsorbed or desorbed. Traditional constant potential is the special case of such conditions where the surface electrostatic potential is also independent of intersurface separation. For charge regulated surfaces the chemisorption chemical potential has typically been modelled as charge density dependent or nonideal, and under the assumption that adsorption isotherms derived to describe equilibrium states can also be used to describe nonequilibrium states. By modeling charge regulation under ideal conditions this assumption can be avoided.

Furthermore, when ion-surface nonelectrostatic interactions, such as dispersion, are included, an additional term due to those interactions contributes to the physisorption process, with a corresponding contribution to the interaction force from the physisorption part of the chemical potential. This term is present for all boundary conditions commonly invoked and the only dispersion term under constant charge conditions.

However, under constant potential or charge regulated conditions, previously ignored dispersion contributions from the chemisorption chemical potential arise due to a shift in the equilibrium condition balancing the chemical potentials of physisorbed and chemisorbed ions at the surface,

$$\Delta\mu_{\text{chemisorption}} + \Delta\mu_{\text{physisorption}} = 0 ,$$

where now the dispersion potential contributes to the physisorption process

$$\Delta\mu_{\text{physisorption}} = e\Phi_0 + U_0^{\text{disp}} .$$

We explore the effects of these points and their implications on the interaction force and the prediction of surface parameters such as the potential and acid equilibrium constants.

**PP054**

**Droplet collisions in high concentration surfactant and worm-like complex fluids**

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Highly concentrated surfactant systems are commonly used in colloidal dispersions and emulsions in the formulation of complex fluids for a range of applications including personal care products, foods, lubricants, and in pharmaceuticals. At higher surfactant concentrations, surfactant aggregates often transition from smaller aggregate structures (e.g. spheres, ellipsoids, etc) to larger structures including worm like micelles, sponge phases and lamella phases. Worm like micelles are useful for increasing viscosity, commonly through a shear thickening behaviour, with the advantage of their ability to dynamically reform.

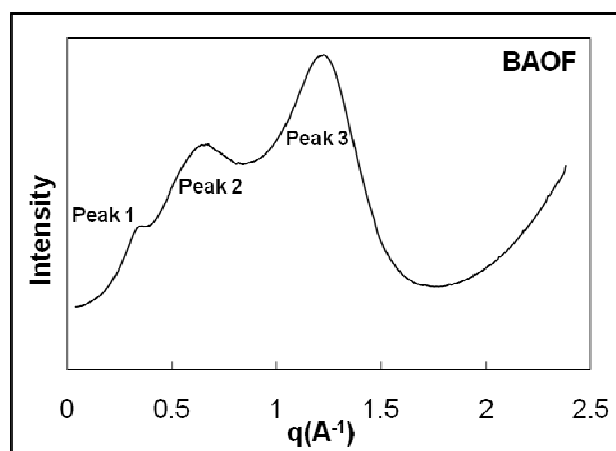
This study examines the effects of worm like micelles on droplet collisions. Measurements were taken using atomic force microscopy (AFM) to investigate the interactions between drop-drop, drop-plate and particle-plate systems. Solutions containing Sodium Dodecyl Sulphate (SDS) and Sodium Bromide (NaBr) were used to generate micelles of varying profile. The influence of the micelle shape on both static and dynamic interactions with a particular focus on structural forces was investigated. A comparison between the contrasts of rigid and deformable interfaces in the case of differing micelle geometry was examined. In addition the relationship between the structural force profile and potential packing structures as well as the possibility of variations in viscosity arising from the exclusion of larger micelles within the thin film were studied.

**Fluorous Protic Ionic Liquids Containing Hydrocarbon, Fluorocarbon and Polar Domains in their Nanostructure**Tam Greaves<sup>1</sup>, Danielle Kennedy<sup>1</sup>, Yan Shen<sup>1,2</sup>, Gonghua Song<sup>1,2</sup>, Calum Drummond<sup>1</sup><sup>1</sup>CSIRO, VIC, Australia, <sup>2</sup>East China University of Science and Technology, Shanghai, China

Fluorinated Protic ionic liquids (FPILs) were prepared which contained a hydrocarbon amine cation paired with a perfluorinated anion.[1] In the liquid state these FPILs contained intermediate range order due to segregation of the hydrocarbon and fluorocarbon moieties into separate domains leading to polar, hydrocarbon and fluorocarbon domains. While many ionic liquids contain polar and non-polar domains, we believe these are the first ionic liquids reported which contain three domains, or which contain a fluorocarbon domain.

A series of 11 FPILs were prepared which contained alkyl or heterocyclic ammonium cations with the perfluorinated anions of heptafluorobutyrate or pentadecafluorooctanoate. The nanostructure of the FPILs was established by using small- and wide-angle X-ray scattering (SAXS and WAXS) at the Australian Synchrotron. The SAXS/WAXS pattern for butylammonium pentadecafluorooctanoate is shown below. The physicochemical properties and thermal phase transitions were also characterised. The FPILs were mostly solids at room temperature, however two examples 2-pyrrolidinonium heptafluorobutyrate (PyrroBF) and pyrrolidinium heptafluorobutyrate (PyrBF) were liquids at room temperature and all of the FPILs melted below 80 °C.

The nanostructure of ionic liquids has a significant influence on their interactions with other solutes. We investigated the interactions of FPILs with water and with the primary alcohols of ethanol and butanol, and generally found they were miscible. SAXS/WAXS was used to characterise the changes to the nanostructure on addition of the solvents. Typically there was a phase progression from sponge to lamellar on addition of water. The addition of alcohols led to the presence of new nano-sized species which we propose are islands of alcohols within the polar domain.



Peak 1: fluorocarbon domain (19.04 Å)

Peak 2: hydrocarbon domain (9.97 Å)

Peak 3: distance between alkyl chains (5.15 Å)

[1] Y. Shen, D. F. Kennedy, T. L. Greaves, A. Weerawardena, R. J. Mulder, N. Kirby, G. Song and C. J. Drummond, *Phys. Chem. Chem. Phys.*, 2012, **14**, 7981-7992.

**PP056**

**Thermodynamic Casimir Forces Beyond the Critical Point in CO<sub>2</sub>**

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Supercritical CO<sub>2</sub> is an interesting solvent of the future because it is non-flammable, chemically inert and non-toxic. It exhibits liquid-like density, gas-like diffusivity and its surface tension is very small. It is already found in a range of applications such as environmentally friendly solvent in polymer syntheses, in materials processing, for extractions, tissue engineering, or microelectronic processing.

We present the first direct measurement of surface forces across supercritical carbon dioxide. An important finding is that long-range attractive surface forces are detected not just near the critical point, but along the supercritical extension of the coexistence line, which is commonly discussed as the supercritical ridge.

Using a precisely adjustable model slit pore, our experiment can measure the change of thermodynamic potential together with changes in refractive index (mass density) in the confined CO<sub>2</sub>. The model slit pore is realized between two atomically smooth mica surfaces in a specially designed high-pressure surface forces apparatus. Our data suggest that thermal fluctuations of higher density are selectively depleted, which results in observation of a time- and space- averaged density reduction in the confined film. Direct observation of this confinement effect has consequences for theoretical understanding as well as technological applications of CO<sub>2</sub> in porous materials.

In the presence of small amounts of an acrylate solute (polyethyleneglycol-dimethacrylate), we found that multiple stable menisci of solute can be created between the surfaces and stretched out several micrometers. These liquid bridges are observed as an apparent birefringence effect and are interrelated with the (super)critical Casimir effect.

**PP057**

**Formation and Properties of Polyelectrolyte Multilayers of Fucoidan and Chitosan**

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A drive towards creating biologically relevant functional surface coatings has led to the emergence of polysaccharide-based polyelectrolyte multilayers (PEMs) for applications in biomaterials. These polysaccharide-based PEMs are biocompatible and lubricious, and are easily formed through the Layer-by-Layer (LbL) assembly technique, which involves sequential adsorption of alternating layers of polycations and polyanions through electrostatic interactions between their functional groups. In this study, we focus on the formation and properties of polysaccharide-based PEMs consisting of alternating layers of polyanionic fucoidan and polycationic chitosan. Whereas chitosan is a well-studied component of polysaccharide PEMs, fucoidan, a sulfated polysaccharide extracted from seaweed, is relatively little studied in PEM formation. The formation of the fucoidan/chitosan PEMs were investigated by quartz crystal microbalance with dissipation monitoring (QCM-D) and spectroscopic ellipsometry. We found that the fucoidan/chitosan PEMs experience an exponential-like growth during layer formation, similar to other polysaccharide-based PEMs (e.g. hyaluronic acid/chitosan). The changes in the multilayer structure upon changes in pH and ionic strength post assembly were also measured. In addition, normal and lateral force measurements using colloidal probe atomic force microscopy were performed to determine the effect of the fucoidan/chitosan PEMs on the surface interaction forces for two opposing surfaces coated with the PEMs.

### From Foams to Phonons: Dynamic Reorganizations of Droplet Arrangements

Jean-Baptiste Fleury<sup>1</sup>, Shashi Thutupalli<sup>2</sup>, Martin Brinkmann<sup>1,2</sup>, Ohle Claussen<sup>2</sup>, Ulf Schiller<sup>3</sup>, Gerhard Gompper<sup>3</sup>, Ralf Seemann<sup>1,2</sup>

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Variations in droplet packing flowing in microfluidic channels are explored as function of volume fraction and flow velocity. If the volume fraction of a monodisperse emulsion is very large, the droplets assemble into well-defined foam like arrangements and the shape and the position of every droplet is fully determined by geometry. Lowering the droplet volume fraction below a critical value the droplets are mechanically stabilized by virtue of the Laplace pressure. For a certain regime of volume fraction and droplet size the droplet packing have negative compressibility and separate into areas of different droplet arrangements. Depending on flow velocity this might lead to oscillations or even to avalanches in packing density. When lowering the packing fraction even further, so that the droplets do not touch each other, the droplets experience each other by hydrodynamic interactions and can develop a collective behaviour similar to travelling sine-waves which can be explained by a phonon-type behaviour.

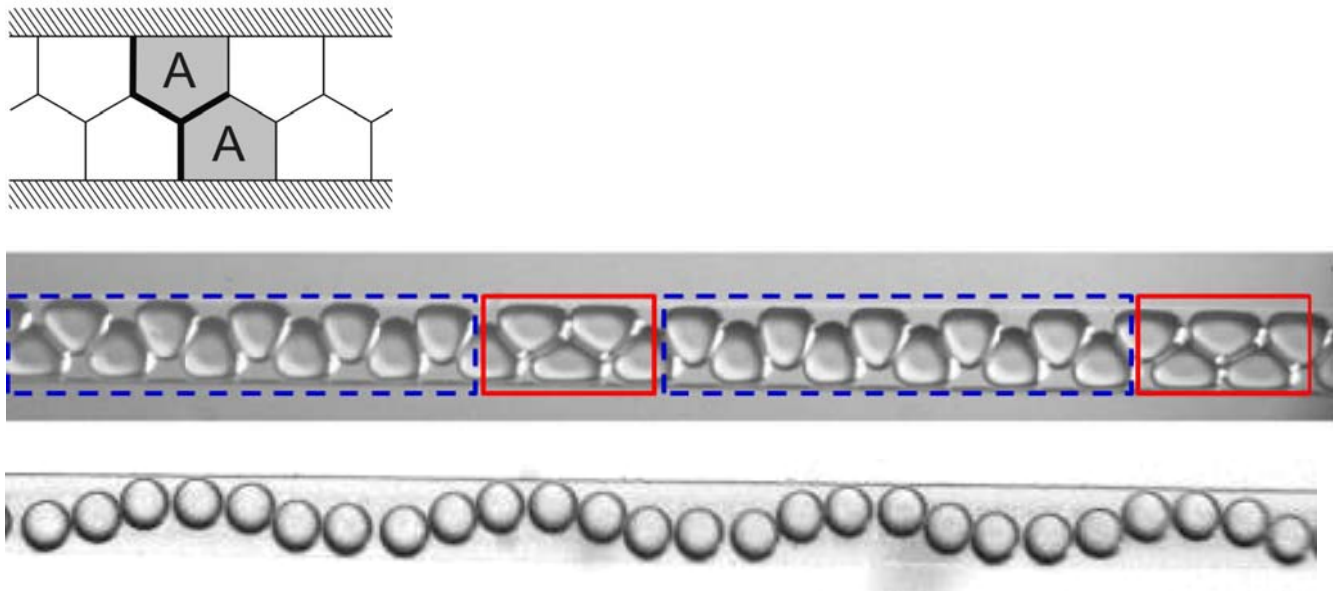


Figure 10: *top*: foam like droplet arrangement; *middle*: unstable droplet arrangement which separated into regions of larger and smaller packing fraction; *bottom*: periodic oscillations of a train of droplets.

**PP059**

## **Toward Broad Colloidal Stability of pH-Responsive Hybrid Particles**

Joshua Willott, Benjamin Cheesman, Grant Webber, Erica Wanless

*University of Newcastle, NSW, Australia*

The behaviour of colloidal silica particles can be drastically affected by modifying the surface of the particles with, for example, polymer brushes creating a brush-coated silica hybrid. With suitable monomer selection, the brush layer can be tailored to respond reversibly to an environmental stimulus such as pH.

We have recently shown that activators regenerated by electron transfer atom transfer radical polymerisation (ARGET ATRP) can be employed to prepare pH-responsive poly(2-(diethylamino)ethyl methacrylate) (poly(DEA)) brushes from macroinitiator-modified silica particles.<sup>1</sup> The ARGET variant of ATRP allows for low copper catalyst concentrations, while its living nature permits the synthesis of diblock copolymer brushes. An area of specific interest is the design of brushes containing blocks of different responsive behaviour.

Poly(DEA) is a weak polybasic polymer and thus displays pH-dependent solubility. In our case, as the pH is decreased below the  $pK_a$  of poly(DEA) at pH  $\sim 7.5$ ,<sup>2</sup> the hydrodynamic volume of the brush-coated silica hybrid particles increases due to protonation and swelling of the polyelectrolyte brush. Considerable volume increases of up to 200 % have been observed. Furthermore, the swelling was reversible when the pH was cycled between pH 4 and 7.

A noteworthy disadvantage of these hybrid particles is that they are only colloidally stable at pH values below the  $pK_a$  of poly(DEA), due to the hydrophobic nature of the unprotonated poly(DEA) brushes. Therefore, an area of continuing research is focussed on fine-tuning the colloidal stability of such pH-responsive hybrids to be stable over a broader pH range.

Poly(2-(dimethylamino)ethyl methacrylate) (poly(DMA)), a more hydrophilic analogue of poly(DEA) with a similar  $pK_a$  at  $\sim$ pH 7.5,<sup>2</sup> was investigated. These poly(DMA) hybrid particles exhibited similar pH-responsive volume swelling and importantly were stable up to  $\sim$ pH 8.5, notably above the  $pK_a$  of the brushes owing to their increased hydrophilicity providing greater steric stability.

An alternative approach to improve the colloidal stability of the poly(DEA) hybrids, the addition of an outer hydrophilic block, has also been investigated. By polymerising (2-hydroxyethyl) methacrylate (HEMA), onto the end of the existing poly(DEA) block, a diblock copolymer brush with a hydrophilic second block has been prepared. Preliminary work has shown that this approach may provide the increased colloidal stability desired.

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**PP060**

**Bulk behaviour of colloidal particles in ionic liquids: a combined DEM-AFM approach**

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The behaviour of colloidal particles dispersed in an ionic liquid (IL) was studied using a combination of Discrete Element Method (DEM) computer simulations and Atomic Force Microscopy (AFM) experiments. The colloidal system under investigation was made of silica particles in ethylammonium nitrate (EAN). Force-distance data recorded normal to the surface show the typical stepwise shape observed in EAN at low approach velocities. This structure is understood to be caused by a succession of alternating non-polar and polar solvent layers. AFM experiments have also been conducted at various approach velocities, supplementing previous research regarding IL-solid interfaces. This allows velocity-dependent interaction forces to be implemented into the DEM simulation. Adhesion and frictional forces were quantified using the AFM technique, further enhancing the DEM code.

DEM simulations were conducted using AFM data to simulate the approach between particles. The AFM experimental curve was simulated as a sequence of five solvation layers, with only one of them having an attractive nature, between 1.0 and 1.5 nm particle-particle separation. The value of the attractive force within this layer was 21 nN. Two single particles of 100 nm in diameter were launched against each other with velocities up to  $10 \text{ ms}^{-1}$ . Despite the high velocity of the particles, the repulsion originated by the solvation layers prevented the particle collision. Bulk particle behaviour indicated that Brownian forces had little influence on the probability of particle surface-to-surface collisions and, hence, on the possibility of aggregation in the system.

During the second stage of the simulations a system made of 100 particles in EAN was considered. The interaction between particles during approach was simulated using EAN force curves by simplifying its shape to a step function. In this case the strength of the structural forces on aggregation was probed by considering that during retraction the particles no longer feel the structural forces of the liquid. The simulations showed that under these conditions it is possible to observe the aggregation of particles in an EAN suspension.

These results highlight the importance of distinguishing between forces measured quasistatically and dynamically in order to clearly elucidate the conditions under which particles aggregate in ionic liquids. Furthermore, it is necessary to extrapolate these results to the case of other ILs, such as EAF, though the use of AFM data of particle – particle interactions.

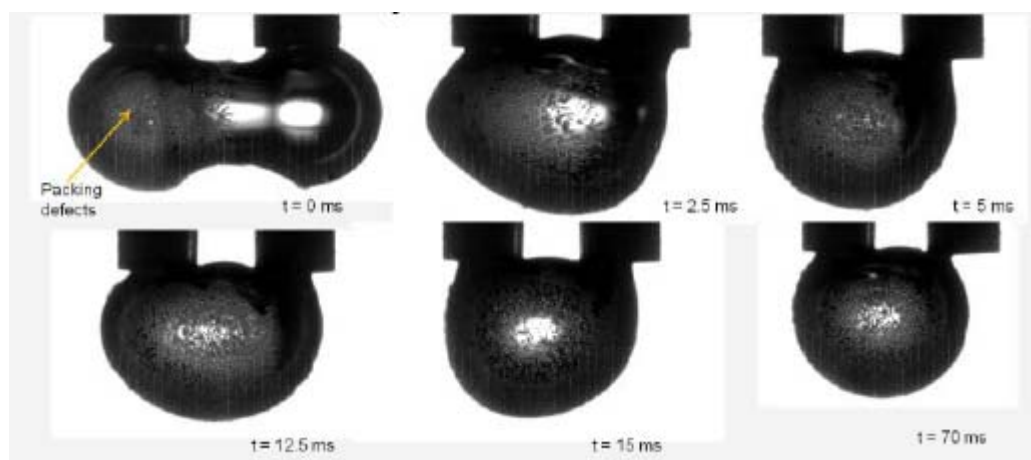
## Relationship Between Particle Armoured Air Bubble Stability and Interfacial Elasticity

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Previously, the stability and coalescence dynamics of particle-stabilized bubbles have been investigated using a coalescence rig<sup>1</sup>. In this technique, two particle-coated air bubbles were moved together on adjacent capillaries until they were just touching. The bubbles were left in this position until the thin liquid film which formed between them drained out and ruptured. The coalescence process was recorded using a high speed camera. From the captured images, it is possible to determine the stability and post-rupture oscillatory behaviour of these bubbles.

The interfacial elasticity is believed to play an important role in the stability of particle-stabilized bubbles; with increasing stability at high elasticity interfaces. Previous investigations have shown that bubbles or drops with high interfacial elasticity exhibit superior stability and vigorous post-rupture oscillations<sup>2,3</sup>. All these studies, however, were conducted using polydisperse particles or sub-visible particles. In this work, monodisperse cross-linked polymethylmethacrylate particles (PMMA) of 40  $\mu\text{m}$  diameter were used to correlate the interfacial elasticity of individual particle-coated bubbles to the coalescence dynamics of bubbles pair. To the authors' knowledge, this is the first study of this type conducted using monodisperse visible particles. Interfacial elasticity measurements were conducted on a pendant drop tensiometer while the coalescence dynamics studies were performed using the bespoke coalescence rig. Despite the presence of visible packing defects on the bubble surfaces, a lower damping of the post rupture oscillations was observed upon coalescence of these monodisperse PMMA particle-stabilized bubbles which suggests that these bubbles are very stable and therefore exhibit high interfacial elasticity.



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**PP062**

**Fabrication of Carbon Microcapsules Containing Silicon Nanoparticles for Anode in Lithium Ion Battery**

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Carbon microcapsules containing silicon (Si) nanoparticles (NPs) were prepared from silicon embedded polymer microspheres. The precursors, polymeric microspheres containing silicon nanoparticles were fabricated by a facile emulsion polymerization with surfactants, sodium dodecyl sulfate and dodecyltrimethylammonium bromide. The effects of monomer, surfactant concentration, and ionic character of surfactant on the formation of microspheres were demonstrated. The successful fabrication of polystyrene/polydivinylbenzene microspheres with Si NPs was confirmed by scanning electron microscopy. Subsequent thermal treatment produced carbon microcapsules having Si NPs. Volume shrinkage of polymer spheres during carbonization step resulting in the formation of internal free spaces in carbon microcapsules is the critical process in this experiment, which can accommodate volume changes of Si NPs during Li ion charge/discharge processes. The successful encapsulation of Si NPs with exterior carbon shell was clearly shown by transmission electron microscopy and X-ray diffraction. The change in size distribution and structure of polymer and carbon microspheres was also revealed. The cyclic performances of these Si@C microcapsules were measured with lithium battery half-cell tests.

PP063

## Spontaneous Particle Coating of Droplets on Packed Porous Beds

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Particle wetting at liquid surfaces is important in powder technologies, such as dispersion and granulation, where droplets are in contact with granular or powdery surfaces. Rolling water drops over hydrophobic powder forms liquid core-particle shell structures (liquid marbles) that have large contact angles on any substrate.<sup>1</sup> Recent observations that organic solvents can form marbles raised questions about the role of the liquid surface tension in marble formation.<sup>2</sup> We investigated particle coating of liquid drops gently placed (without rolling or shaking) onto beds of hydrophobic powders.

Drops are trapped on the surfaces of coarse particle beds. They become coated in particles within seconds of liquid contact with the bed (Figure 1). Particles attach to the fresh liquid surface created during the droplet oscillations immediately after contact. Minimising the kinetic energy of the drop impact revealed that maximum particle coating occurs at liquid surface tensions just above the critical wetting tension of the beads.<sup>3</sup>

In contrast, drops freely roll and bounce along the surfaces of beds of fine powders. The drops collect an irregular, unevenly distributed coating of particles as they move. The distance that the drops travel, and hence the area of the droplet surface coated with particles, depends on the liquid surface tension. Spontaneous coating is a precursor to liquid marble formation.

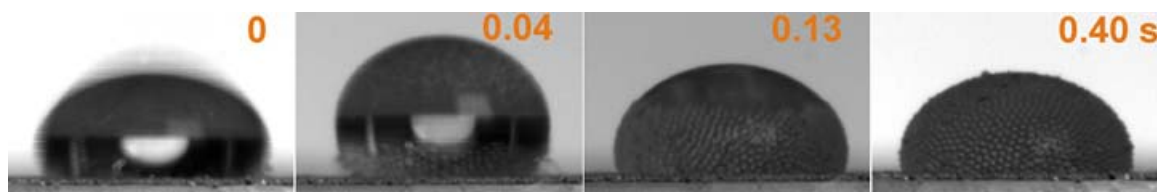


Figure 1. Hydrophobic glass spheres (98  $\mu\text{m}$  in diameter) coat ethanol-water droplets (10  $\mu\text{L}$  volume) of intermediate ethanol concentrations within seconds of droplet deposition.

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**PP064**

**Synthesis of ZrB<sub>2</sub>-Based Powders by Sol-Gel Method**

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Zirconium diboride (ZrB<sub>2</sub>) ceramic material has many excellent properties; however, it has not been utilized widely due to its poor sinterability and poor oxidation resistance at high temperatures. In the present study, ZrB<sub>2</sub> and ZrB<sub>2</sub>-20v% SiC composite powders were synthesized by sol-gel method from zirconium *n*-propoxide (Zr(OPr)<sub>4</sub>), tetraethoxysilane (TEOS), boric acid (H<sub>3</sub>BO<sub>3</sub>), and sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>). A single phase ZrB<sub>2</sub> and ZrB<sub>2</sub>-SiC composite were obtained at 1550 °C for 2 h, respectively. Furthermore, we investigated the influence of the temperature of sol-gel formation on morphology of ZrB<sub>2</sub> particles. Varying the temperature of sol-gel formation, the particle shapes changed from sphere-like at 65 °C, kabob-like at 75 °C to rod-like at 85 °C. Moreover, the average grain size of sphere-like ZrB<sub>2</sub> and ZrB<sub>2</sub>-SiC composite particles were ca. 50 nm and 500 nm, respectively. The photomicrograph revealed a spherical morphology of ZrB<sub>2</sub>-SiC composite particles with a uniform size distribution.

**PP065**

**Wood swelling with humidity: the Equation of State of Wood and the mechanism of wood-protectants**

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Wood consists of parallel, hollow, cylindrical cells. The so-called “wood material”, i.e. the materials the cell walls are made of, is a complex, highly anisotropic and hierarchically organized nanocomposite. It is characterized by stiff cellulose nanofibers parallel to each others embedded in a matrix of a much softer, less anisotropic, macromolecules (hemicelluloses and lignin). The matrix is hygroscopic and swells with increasing relative humidity providing a source of internal stress while the cellulose fibrils, winding with a spiral angle (the microfibril angle, MFA) around the central lumen, passively extend and reorient following the stress applied to them. This behaviour of wood fibres upon swelling is a major technological problem, but it is essential to plants to actuate movements and to react to external forces.

The swelling of the wood polymers is traditionally described as arising from the H-bond interactions of water molecules with the hydrophilic polysaccharides and the sorption isotherms interpreted with modified BET, Dent, HH or GAB models. Although those expressions fit the sorption data excellently, they do not take into account neither the structure of the composite at the nanometric scale nor its hierarchical arrangement.

In this work we demonstrate that, at the molecular level, the force driving water sorption in wood is mainly the hydration force, as introduced by Marcelja and Radic theoretically and by V A Parsegian experimentally in the case of gels made from lipid bilayers in the seventies. Considering a hexagonal arrangement of the wood material’s building blocks at the two molecular levels (cellulose nanocrystals and single matrix polysaccharide chains) and taking into account the current wood structural models, we attempt an energy balance between hydration, Van der Waals and H-bond energies between the wood constituents. From the energy balance, the osmotic pressure is computed and the theoretical sorption isotherm calculated. The resulting EOS predicts with one single parameter wood swelling in large range of temperature as well as the effect of “protectant”s.

**PP066**

**Efficient Recycling of Rare Earths : optimized extraction by reverse micelles**

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There is actually no economic way of recycling rare earths from technological waste, i.e. batteries, magnets from small size to motors used in windmills: recycling these devices is crucial for the sustainability of electricity production by windmills. All known processes rely on w/o swollen reverse micelles. Prediction of separation factors currently come from extensive testing of liquid-liquid extraction formulation, since no predictive quantitative model of selectivity and stability is available.

In this context, we first show that equilibrium of electrolytes between a solvent phase containing amphiphilic extractants and salts are not only dependent on complexation of the metal towards nearest neighbours but also on all other long range colloidal interactions (LRI). Taking into account bulk, polarization and chain reorganization terms, we show that the net free energy difference associated to one ion pair transfer from water can depend by more than 50% on long range interactions dominating complexation.

Most efficient processes moreover involve more than two surface-active extractant molecules in synergy. We demonstrate also that synergy in selectivity emerges when for a defined formulation of the solvent phase, there is enhancement and exaltation of distribution coefficients for some cations in a mixture. To characterize the synergistic mechanisms, we determine for the first time to our knowledge the free energy of mixed co-assembly in aggregates. Aggregation in any point of a phase diagram can be followed not only structurally by SANS, SAXS and SLS, but also thermodynamically by determining the concentration of monomers coexisting with reverse aggregates.

As a conclusion, development of environmental-friendly extraction processes, including mining, rely heavily on new knowledge-based formulation of reverse micelles that are stable in the presence of trivalent ions, at as mild pH than possible. A factor of hundred in volume of acidic secondary waste, i.e. two units of pH in settling tanks, seems possible from knowledge of micellisation in solvents..

**PP067**

**The soft glassy viscoelastic behaviour of raw and digested sludge**

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Renewable energy is one of the cornerstones of sustainable energy. Biogas from the anaerobic digestion of organic waste materials can provide a clean, easily controlled source of renewable energy, replacing firewood and/or fossil fuels. In order to maintain the requisite constant homogeneous conditions within digesters, operating conditions must be regulated according to the rheological characteristics of the sludge.

Sludge was obtained from the Mount Martha wastewater treatment plant (Melbourne, Australia) at the inlet (raw sludge) and the digester outlet (digested sludge). Time, stress and frequency sweep measurements were carried out with a stress-controlled rheometer. Temperature was varied from 10 to 80°C for this experimental work.

This paper shows that the viscoelastic behaviour of sludge presents strong similarities with soft-glassy materials, and also that significant differences can be observed between raw and digested sludge. Furthermore, colloidal glasses and emulsions may be used to model the rheological behaviour of raw and anaerobically digested sludge.

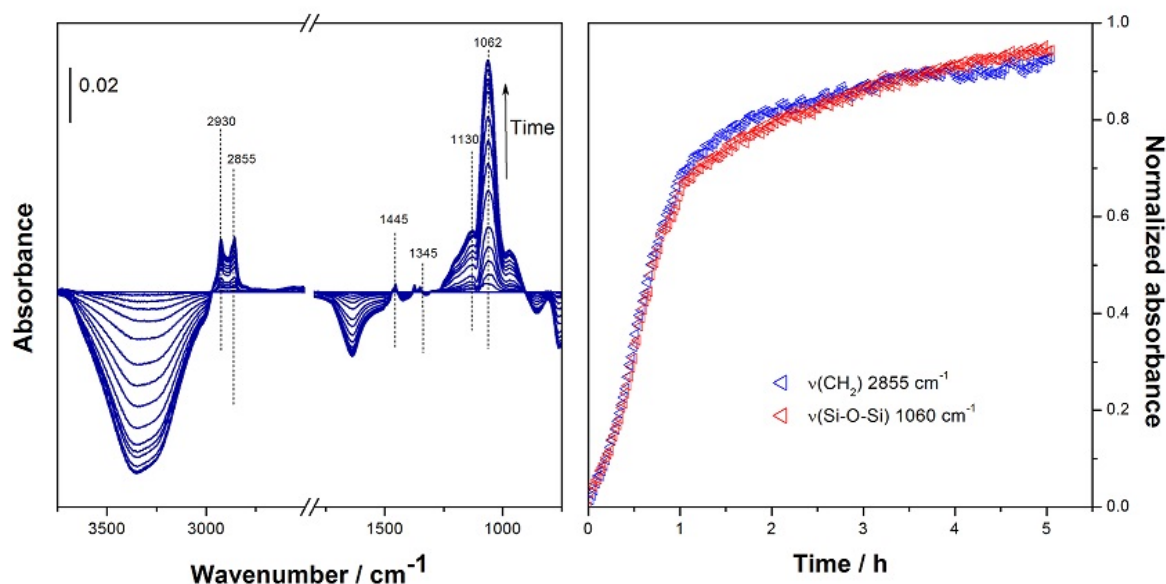


## Adsorption of alkyl-phenol non-ionic surfactants on silica and aggregation effects

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PEO functionalized molecules have been found to exert aggregation effects on silica suspensions, with a multitude of techniques used to probe these processes such as calorimetry, HPLC, UV-vis, SEM and small angle neutron scattering [1]. The limitations of most of the aforementioned techniques are their inability to monitor the adsorption to and consequent aggregation of silica particles as it occurs, making it difficult to gain insight into the molecular details of the processes. The use of ATR-IR spectroscopy, however, allows an *in situ* analysis of both the adsorption events and aggregation of silica particles in an aqueous environment to evaluate the efficacy of different PEO based surfactants. This can be achieved by monitoring the increase in the TO  $\nu(\text{Si-O-Si})$  band at  $\sim 1040$ – $1160\text{ cm}^{-1}$  of silica and the alkyl stretching modes of the surfactant at  $\sim 2855\text{ cm}^{-1}$ . This study utilises ATR-IR spectroscopy to monitor spectroscopic changes of a thin silica particle film during adsorption of three different alkyl-phenol non-ionic surfactants. Other techniques such as batch adsorption, zeta-potential measurements and SEM have been used to complement the IR data.



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## Incorporating Graphene in Carbon Based Foams for Water Treatment Processes

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The use of microporous carbon based materials such as activated carbons, is widespread in municipal water treatment processes. This is due primarily to the high chemical adsorption capacity of these materials, which is also associated in part, with surface area<sup>1</sup>. Recently, Graphene, a carbon allotrope consisting of single layer macroscopic carbon sheets, has attracted considerable interest in a range of research fields due to its unique 2D structure. As a consequence of this unique structure, graphene possesses a high specific surface area, which makes it an ideal material for pollutant removal<sup>2</sup>.

When used in water treatment processes, ordered macrostructures such as foams should act to maximize the surface area in contact with non-potable water and therefore adsorption capacity of contaminants. One possible approach to develop these types of macrostructures could involve the deposition of graphene layers onto a flat substrate, followed by templating the graphene onto sacrificial substrate cores which are subsequently removed by dissolution. The current study is concerned with the first stage of this process, and focuses on the integration of graphene into polyelectrolyte multilayers. Graphene dispersions were created using a method of surfactant-assisted exfoliation from synthetic graphite. A Quartz Crystal Microbalance (QCM) technique was then used to investigate the effect of pH, ionic salt and concentration of polyelectrolyte on the formation of graphene-polyethyleneimine multilayers. It was demonstrated that when a low concentration of polyethyleneimine was coupled with graphene exfoliated using non-ionic surfactant, acidic conditions were more favourable for the formation of graphene multilayers. Conversely, when a high concentration of polyethyleneimine was coupled with graphene exfoliated using non-ionic surfactant, basic conditions assisted the formation of graphene multilayers. The stability and surface charge of the graphene dispersions in relation to pH, ionic salt and salt concentration were also investigated using zeta potential measurements. The measurements indicated that using non-ionic surfactants during the surfactant-assisted exfoliation process resulted in graphene particles yielded only a slight negative charge, independent of pH. Using anionic surfactant however, resulted in a significant negative surface charge. These results give an indication as to the surface charge behavior of graphene particles, in addition to the optimal conditions for graphene multilayer formation, which may guide further studies regarding graphene-based foams.

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**PP070**

**Particle - Surface Interactions in Agarose Microgel Pastes**

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Suspensions of soft particles are found both at the forefront of nano and biotechnology and in products we are all familiar with, such as paint or tomato puree. Emulsions, micelles, micro and nano-gels and plant and animal cells are just a few examples of soft particles incorporated into foods, pharmaceuticals, personal care products, lubricants and biological fluids. Improved understanding of the rheological behaviour of these highly complex suspensions is critical to engineering of novel products with health and environmental benefits. To further understand these complex suspensions it is necessary to go beyond bulk rheology and investigate suspension microstructure, particle - particle and particle - surface interactions.

Flow of concentrated soft particle suspensions is influenced by particle phase volume, particle morphology and particle interactions. We have used a model system of spherical agarose microgels with varying particle softness (as measured by their shear modulus) to understand the influence of phase volume and particle modulus on bulk suspension rheology (Shewan and Stokes, in preparation). With this as a foundation for understanding the influence of particle phase volume and morphology we now investigate particle interactions.

The significance of slip between particles and plate surface has been recognised in high phase volume colloidal microgel pastes and has been measured using advanced particle tracking velocimetry to determine the magnitude and influence of the slip layer for this type of microgel system of unknown particle modulus (Seth et al., 2012). We hypothesise that at high phase volume the particle softness will have a direct influence on both the suspension rheology and degree of slip. We utilise the particle tracing velocimetry method to determine the influence of particle modulus on slip and for experimental verification of the simulation data (Seth et al. 2011).

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**PP071**

**An integrated surface charge and rheological analysis of phyllosilicate minerals**

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The phyllosilicate (clay) group of minerals is closely associated with several processing issues, including reduced flotation performance and complex tailings treatment. However, the understanding of the specific effects of these minerals remains poor, with the fundamental analysis of phyllosilicates still relatively new in its application to the minerals processing industry. The colloidal behaviour of these minerals is complicated by their non-spherical morphology and anisotropic charge properties. Conventional surface charge analyses have often relied solely on electrokinetic zeta potential measurements, which are based on an assumption of sphericity and isotropic charge. This study uses an integrated approach, incorporating potentiometric titrations which are based on the principle of ion exchange and are not subject to particle morphology. These techniques are used in tandem to provide a comprehensive surface charge analysis of select phyllosilicate minerals. Using the deviation between the point of zero charge (as determined by the potentiometric titration) and the iso-electric point (as determined by zeta potential measurements), it was possible to estimate the degree of charge anisotropy of illite, kaolinite and talc. This was correlated to variations in rheological behaviour, taking into account aspect ratio, effective volume and particle crystallinity effects. Such an analysis is foundational towards future advances to better understand the colloidal interactions and flow behaviour of phyllosilicates within the minerals processing context.

**PP072**

**Macroscopic inspections of sub-yield suspension behaviour**

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Success in the colloidal processing of concentrated particulate suspensions hinges upon the accurate determination and sensible application of their rheological properties. To a major extent, these properties are influenced by inter-particle forces between suspended particles within the fluid. At concentrations above the gel point, the inter-particle force balance becomes attractive and particulates gel together to form a network that can resist external force and behave elastically as a solid or yield and express fluid when that yield strength is overcome. Externally applied forces are classified as either shear, compression, or a combination of both. The current understanding has been successfully employed in suspension rheology to processes that are predominantly one-dimensional, such as the pipe line flow of non-settling suspensions and pressure leaf filtration, but is restricted in application when processes involve multi-dimensional loads. Such combined loading operations, like roll compression, raked thickening and belt press filtration, occur in many industrial processing techniques.

In order to further the insight of yield mechanics and hence the constitutive behaviour of particulate suspensions, a general hyper-viscoelastic constitutive approach has been proposed where the total stress is the sum of the stored and dissipated energy potentials. Yielding can be described in this way through sharp strain softening rather than a plastic transition, which accounts for phenomena such as time-dependent yield.

To partially validate the hypothesis, the strain and strain-rate dependencies of a model coagulated inorganic suspension were explored rheometrically using a vane geometry. Strain dependence was tested by varying angular displacement (at a constant rotational rate to reach the displacement), allowing a family of stress relaxation curves to be realised. Subsequently, strain-rate dependence was investigated through variation of shear strain-rates at constant final angular displacement under sub-yield conditions. These constant strain / stress relaxation and constant shear strain-rate data enable the yield stress, steady-state viscosity and shear modulus to be determined. In addition, experimentation of the effect of compressive loads on the shear properties of the model system is underway. Results will be further discussed at the conference.

**PP073**

**Functional thin film nanocomposite coatings on plastic substrates**

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Thin Film coatings are used in many everyday devices such as smart windows, solar cells and flat panel displays. The majority of these coatings are deposited on hard substrates (i.e. glass or metals) which yield mechanically robust devices, however they are typically heavy and are limited with the substrate shapes. With the increasing interest in light weight and flexible devices there is high demand for the development of coatings on plastic substrates. Plastic materials with all their benefits also impart many limitations – i.e. low thermal dimensional stability and low hardness. This requires new approaches in order to produce hard and environmentally stable coatings.

The presented research focuses on the development of decorative thin nanocomposite coatings for real world applications, such as plastic automotive mirrors. Chromium based nanocomposites were prepared by magnetron sputtering as a hard reflective mirror surface. This combination of material and method enables the formation of metastable phases, such as the hexagonal omega phase present in selected Cr based nanocomposites. Coatings developed by our group exhibit abrasion and corrosion resistance equal to, or exceeding, the current commercial coatings on glass substrates without any post processing (i.e. high temperature annealing). Moreover, the Cr based nanocomposite coatings exhibit anomalous resistivity – temperature relationship (constant resistivity with temperature). Such properties enable the use of these coatings as electrical conductors in a wide range of temperatures and reflective layers in light weight automotive plastic mirrors.

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