PL001

Directed Assembly of Inclusions in Soft Matter

Kathleen Stebe

University of Pennsylvania, Philadelphia, PA, USA

We study interactions among microparticles placed in confined soft matter. Via confinement, the soft matter has within it fields related to its confining boundaries. Interfaces and tense lipid vesicles have curvature fields; nematic liquid crystals have director fields and topological defects. Particles placed in these materials distort them, and interact with such fields to form complex assemblies as if these fields were external fields, with exciting implications for directed assembly. Three examples are discussed. First particles trapped at fluid interfaces and particles adhered to tense lipid vesicles are discussed. In both settings, particles distort the interface (or bilayer), migrate and assemble at well-defined locations defined by the curvature field. Thereafter, particles placed in confined, oriented nematic liquid crystals are discussed. Particles, and their associated topological defects, interact to form assemblies guided by the nematic director field and bounding surface geometry. These examples reflect the tremendous opportunities for reconfigurable structure formation within such settings.

PL002

Some Applications of Surface Chemistry to Problems in Colloid Science

Gregory Warr

The University of Sydney, NSW, Australia

The title of this talk is lifted from the 1947 Tilden Lecture,[1] in which A.E. Alexander described how fundamental studies of macroscopic interfaces could yield insights into the intermolecular forces that govern the properties and behaviour of a diverse range of lyophilic and lyophobic colloidal systems "such as foams, emulsions, proteins, pastes, bacteria, etc." – and anticipates his landmark textbook with Johnson.[2]

The breadth of Alexander's work, from spread monolayers, adsorbed alcohols and micelles to organogels, polymer latices and electrokinetics, show his embrace of the zeitgeist of colloid science at the interface between applied and fundamental science. In this talk I will try to illustrate how Alexander's legacy persists in Australian research through some current problems in nanoscience, supramolecular chemistry, and soft matter.

[1] A.E. Alexander, *J. Chem. Soc.* **1947**, 1422-1425

[2] A.E. Alexander and P. Johnson *Colloid Science*, Oxford University Press, 1949

KN001

How Long and Short Range Forces Determine Wetting and Dewetting Morphologies

Ralf Seemann

Saarland University, Experimental Physics, D-66123 Saarbücken, Germany

Long range van der Waals forces determine the stability of very thin liquid films whereas liquid morphologies at larger scales are determined by short ranged interfacial tensions. Using the example of thin polymer films dewetting from silicon wafers of variable oxide layer thickness, we will give an overview, how the stability and the dewetting of thin liquid films and the equilibrium shapes of droplets in the nanometer range are determined by van der Waals forces. And vice versa how the effective interphase potential can be determined from dewetting patterns. The example of linearly grooved substrates will be used to exemplify how interfacial tensions and contact line pinning determine liquid morphologies in micron sized complex geometries. Depending on contact angle and cross sectional shape of the grooved substrates, stable and metastable morphologies can be found which can be switched by varying either geometry or wettability. We conclude with the dewetting of a liquid from another liquid substrate. Due to the penetration of the flow field into the liquid substrate and the low liquid-liquid interfacial tension, we find a strong dependence of the dewetting dynamics on the film thickness ratio. This applies both to the film breakup and dynamics and characteristic shapes of emerging rim profiles, which are remarkably different compared to solid substrates.

KN002

Assembling and de-assembling amphiphiles with cyclodextrins

Marcelo da Silva[1], Ángela García Peréz[1], Evelyne Weinzaepfel[1], Gustavo González-Gaitano[2], Margarita Valero[3], Cecile Dreiss[1]

[1]King's College London, London, UK, [2]University of Navarra, Pamplona, Spain, [3]University of Salamanca, Salamanca, Spain

Cyclodextrins (CDs), cyclic oligosaccharides of glucopyranose units, are widely used in pharmaceutical formulations to solubilise drugs, and are also attracting interest in the food industry as flavour carriers, protectants and emulsifiers. The attractiveness of cyclodextrins lies in their toroid shape with an apolar cavity, giving them the capacity to form host-guest complexes, either with small molecules or polymers; this process is driven by weak interactions and the release of water molecules from inside the CD cavity. These inclusion complexes – or polyrotaxanes, in the case of polymers - are the starting point of interesting supramolecular structures, which can be used to impart shielding, triggered release, multi-valency or responsiveness.

In this contribution, I will present some of our work in this area over the past few years[1-9], in particular the ability of CDs to modulate the self-assembly of surfactants, from micelles to wormlike micelles and/or lamellar phases. I will discuss the interactions that drive these transitions, and how the macroscopic properties are sustained by morphological changes on the nanoscale, which are critically dependent on the nature of the substituents around the CD rim.

[1] González-Gaitano *et al.* (2015) *Langmuir, 31*, 4096-4105

[2] González-Gaitano *et al.* (2015) *Langmuir, 31*, 5645-5655

[3] Iza *et al.* (2015) *Langmuir, 31*, 2677-2688

[4] Peréz *et al.* (2014) *Langmuir, 30*, 11552–11562

[5] Da Silva *et al.* (2013) *Langmuir, 29*, 7697-7708

[6] Valero *et al.* (2012) *J. Phys. Chem. B, 116*, 1273-1281

[7] Castiglione *et al.* (2011) *J. Phys. Chem. B, 115* 9005-9013

[8] Valero *et al.* (2010) *Langmuir*, *26,* 10561-10571

[9] Dreiss *et al.* (2009) *Soft Matter, 5* 1888-1896

KN003

Janus Particle Assembly in Solution and at the Interface – What have we learned?

Ilona Kretzschmar

City College of New York, New York, NY, USA

Janus particles, i.e., particles with two distinct halves, have been heralded as new materials for assembly, drug deliver, autonomous motion, and emulsion stabilization since deGennes' 1991 Nobel lecture. Our laboratory has spent the past 12 years developing methods to make a versatile set of Janus particles with magnetic, photonic, and catalytic properties and studying the behaviour of such Janus particles in electric and magnetic fields and at fluid/fluid interfaces. In this talk, two specific parts of our work will be highlighted; (i) assembly behaviour of magnetic Janus particles in an external magnetic field and (ii) the behaviour of Janus particles at fluid/fluid interfaces. In the presence of an external magnetic field, for example, two chain types are formed by iron oxide capped Janus particles as a consequence of their shifted magnetic dipoles resulting from their cap compositions. These particle chains can be used to either measure the viscosity of a fluid or give the fluid they are immersed in interesting new rheological properties. In contrast, the behaviour of Janus particles confined to fluid/fluid interfaces strongly depends on their surface wettability and amphiphilicity and is of importance for various colloidal applications. Langmuir trough experiments show that the mechanical properties of air/liquid interfaces decorated with Janus particles of various chemical anisotropies are strongly impact by their wettability and amphiphilicity.

KN004

X-ray Studies of Electrostatic Processes at Soft Interfaces

Mark L. Schlossman

University of Illinois at Chicago, Chicago, IL, USA

Electrostatic interactions at interfaces underlie many scientific and industrial processes, including macromolecular interactions, bio-sensing, and energy storage and generation. We have used liquid-liquid interfaces as an experimental model to probe interfacial ion distributions and voltage-tunable electrostatic processes. X-ray scattering from electrochemically controlled liquid-liquid interfaces reveals the role of ion-solvent interactions and ion-ion correlations on the distribution of ions near the interface. Under appropriate experimental conditions, these effects alter the conventional diffuse electrical double layer, thereby changing the effective electrostatic interactions between interfaces and charged particles or molecules in solution. These experiments test our understanding of ion interactions with soft interfaces, as well as provide measurements of ion potentials of mean force. The extension of these techniques to probe the voltage-tunable interfacial ordering of phospholipids, peripheral membrane proteins, and charged nanoparticles will be discussed.

KN005

Current Developments in the Colloidal Delivery of Nutrients

Brent Murray

University of Leeds, Leeds, W. Yorks, UK

The ingenuity of colloids scientists knows no bounds. 'New' colloidal structures continue to be invented, for example: microgels, nanogels, bijels, coacervates, Pickering emulsions, Mickering emulsions, multilayer emulsions, water-in-water emulsions, multiple emulsions, microemulsions, nanoemulsions, dry water emulsions, air-filled emulsions, Pickering foams, colloidosomes, etc., continue to be invented or re-invented, to name (or re-name) but a few.

These systems have been usually been developed not only to impart improved colloidal stability under specific conditions, but also to effect more controlled or 'intelligent' delivery of various ingredients. In many industrial sectors the choice of ingredients required to assemble these structures is not of primary concern (beyond cost), but in foods this is a vital issue, since any ingredients must approved and recognized as safe for consumption. Similar restrictions apply for pharmaceutical and agrochemical formulations, although these are generally not as Draconian.

When such new colloidal structures are developed in non-food areas there is therefore usually a big challenge in mimicking this behaviour using food-grade materials alone. On the other hand, all food is derived from natural, living material and Nature has been infinitely more inventive in developing diverse colloidal structures at all length scales and in all possible environments imaginable. Furthermore, many of these diverse structures are of direct relevance to the *in vivo* digestion of many food stuffs, whether they are present either on ingestion or when they arise as part of the natural digestive processes.

Thus, if the basic underlying principles of formation and stability of these structures can be understood, there are many opportunities for using natural food materials in all sorts of news ways to give better or more controlled delivery of macro and micro-nutrients. This could be for improvement of foods in terms of their organoleptic properties and health aspects, as well as potential gains in costs of production and efficiency.

The above aspects will be illustrated by various recent examples from the literature as well as from the Author's own research. Although the focus here will be on food applications, the considerations could equally well apply to non-food use of various food materials in chemical, agrochemical and pharmaceutical industries.

KN006

Surface Nanobubbles on Defined Self-Assembled Monolayers on Gold Studied by Combined AFM-Fluorescence Microscopy Approaches

Holger Schönherr, Nicole Hain, Sergey I. Druzhinin, Daniel Wesner, Wiktoria Walczyk, Stephan Handschuh-Wang

University of Siegen, Department of Chemistry & Biology, Physical Chemistry I, Siegen, Germany

In the past decades surface nanobubbles, which have been recently confirmed to be indeed gas-filled nanoscale features, were shown to reside e.g. at the solid-water, but also at the solid-liquid interface of some protic solvents. Even though key properties of surface nanobubbles have been widely investigated and plausible theories and explanations for the universal highly deviating (compared to macroscopic wettability data) contact angles as well as the surprisingly long lifetimes have been put forward, a certain controversy remains in the discussion of surface nanobubbles.

While the presence of surface nanobubbles has been confirmed by many groups in recent years, concerns regarding surface contaminations on the one hand and the accuracy of the nanobubble dimensions estimated predominantly from AFM data mandate a closer look at new characterization approaches in systematic structure-property relationship studies. This is in particular necessary, since the details of nanobubble nucleation / formation, their properties and stability have not been exhaustively explained yet for certain experimental conditions. In addition, the unequivocal differentiation among gas-filled surface nanobubbles and droplets of contaminants was not realized in all key experiments published in the literature, which adds to some uncertainty.

In this presentation the properties of surface nanobubbles on highly defined self-assembled monolayers (SAMs) of end-functionalized alkane thiols on ultra-smooth template stripped gold substrates will be discussed. In these experiments the macroscopic wettability was systematically altered and the identical macroscopic wettability was realized by widely different surface chemistries. The application of various AFM imaging modes will be compared to highlight the limitations of these AFM approaches, if not adequately employed, to non-invasively determine the shape of surface nanobubbles. In addition, the recently introduced Fluorescence Lifetime Imaging Microscopy (FLIM) and combined AFM-FLIM approach will be applied to nanobubbles on these and related surfaces to determine how the effect of different surface chemistries affects the nanobubbles. In particular, different cleaning protocols and their impact on nanobubble formation will be compared.

KN007

Imaging SIMS of Cells and Tissues: Advancing our Understanding of Biology

Lara Gamble

University of Washington, Seattle, WA, USA

Imaging mass spectrometry can provide images of cells and tissues with chemical and molecular specificity. These chemically specific images could revolutionize our understanding of biological processes such as increasing our understanding of chemical changes in cells and tissues as a function of an applied stress or as a result of disease, and enable tracking the spatial distribution of metabolites and lipids. The mass spectral imaging capability of ToF-SIMS holds potential to achieve this goal with sub-cellular resolution. Chemistry of tumor microenvironments, lipid metabolomics relationship to cancer, delivery of nanoparticles to cells, and tissue repair could be visualized on a cellular and sub-cellular level. In this presentation, ToF-SIMS analysis of biological samples from 2D images of tissues to 3D images of nanoparticles in cells will be presented. Multivariate analysis techniques such as principal component analysis (PCA) of the images are use to compare the chemistry of different types of tissue areas within cancer tumor samples. To add specificity to the tissue biopsy comparisons, PCA is initially used to define regions of interest (ROIs) that are then used to compare the same 'type' of region (e.g. stromal) between different tissue samples. Results indicate a trend in lipid composition between tissue biopsies taken pre and post chemotherapeutic treatment for the same patient. [1]

[1] B. Bluestein, D. J. Graham, F. Morrish, J. Guenthoer, D. Hockenbery, and P. Porter, L. J. Gamble, *Analyst*. 2016 Mar 7;141(6):1947-57. doi: 10.1039/c5an02406d.

KN008

Cracking during Drying of Colloidal Dispersions

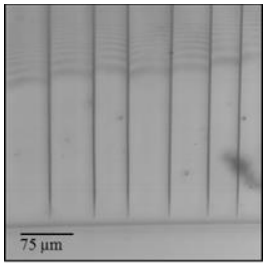
Alexander Routh

University of Cambridge, Cambridge, UK

When a colloidal dispersion of rigid particles is spread as a film and dried, a number of transitions occur: The particles consolidate at an edge and a solidification front is seen to traverse laterally across the film. This is closely followed by an array of cracks, with well-defined crack spacing.

This talk will concentrate on why the cracks develop and how they propagate. The driving force for cracking is the capillary pressure, generated during the drying process. The resistance to cracking is the material fracture toughness, which transitions from a low value in the fluid to a final value in the fully developed solid. We show a method of measuring the film fracture toughness using confocal microscopy. It is found to scale with the particle size to the power of minus one half. In addition films created with low evaporation rates display higher fracture toughness.

The image below shows an array of cracks propagating through a drying dispersion of 7 nm silica particles



KN009

Hierarchical layered double hydroxide nanocomposites for drug and siRNA delivery

Li Li, Zhi Ping Xu

University of Queensland, Brisbane, Australia

Hierarchical nanocomposites have great potentials in bioapplications such as drug delivery, biomedical imaging, biochemical sensing and biocatalysts owing to their structure features and unique properties.[1] In our group, we have developed hierarchical SiO_2@MgAl-layered double hydroxide nanocomposites (SiO_2@MgAl-LDH) with various functional groups (-NH_2, -SH, -PEG) via nanodot-coating strategy. These nanocomposites have showed enhanced siRNA and drug delivery to cancer cells. The functional SiO_2@MgAl-LDH nanocomposites retained the layered structure and plate-like morphology as MgAl-LDH NPs. Moreover, functional SiO_2@MgAl-LDH showed good dispersion in aqueous solution and cell culture medium. The in vitro tests have demonstrated anticancer drugs or siRNA delivered by functional SiO_2@MgAl-LDH apparently inhibited the cancer cell growth.[2, 3]

References:

1. Gu, Z.; Atherton, J.J.; Xu, Z. P. Hierarchical layered double hydroxide nanocomposites: structure, synthesis and applications. *Chem. Commun*. (Camb) **2015**, *51*, 3024–3036.

2. Li, L.; Gu, Z.; Gu, W.Y.; Liu, J.; Xu, Z. P. Efficient drug delivery using SiO_2-layered double hydroxide nanocomposites, *J. Colloid Inter. Sci.,* **2016**, *470*, 47-55.

3. Li, L.; Gu. W.Y.; Liu, J.; Yan S. Y; Xu, Z. P. Amine-functionalized SiO_2 nanodot-coated layered double hydroxide nanocomposites for enhanced gene delivery, *Nano Res.*, **2015**, *8*, 682-694.

KN010

Unlocking Intracellular Therapeutic Targets through Novel Nanostructured Biomaterials

Millicent O. Sullivan

Centennial Associate Professor of Chemical & Biomolecular Engineering, University of Delaware, USA

Nucleic acid cargoes offer unmatched diversity in gene regulatory potential and therapeutics, and understanding of nucleic acid functionality continues to expand rapidly and dramatically through seminal discoveries including RNA interference approaches and gene editing technologies. In nature, the basis for gene regulation is ultimately encoded by the exquisite specificity with which cells are able to control both the location and accessibility of nucleic acid constructs to govern their activation states. My research program seeks to mimic these activities through the design of stimuli-responsive synthetic materials whose interactions with nucleic acids and cells can be controlled dynamically by specific intracellular or external triggers. We exploit our ability to regulate binding/release and cellular processing to gain new mechanistic insights over nucleic acid delivery mechanisms.

This presentation will outline recent work in my laboratory to develop peptide and polymer constructs that respond to specific intracellular signals (e.g. enzymes) or exogenous stimuli (e.g. light) to control the release of plasmid DNAs and siRNAs, respectively, and thereby enhance nucleic acid activity while enabling spatiotemporal control over gene suppression/activation. Specifically, in one case, we capitalized on newly recognized and highly pivotal roles for histone tails in native gene regulatory control to develop a gene transfer method that utilizes native, histone-based processing pathways *via* incorporation of post-translationally modified (PTM) histone tails within controllably-assembled DNA vehicles (polyplexes). Our efforts proved that polyplexes displaying PTM-modified histone tails promote nuclear accumulation, DNA release, transcription, and enhanced transfection. Moreover, our group has combined detailed nanostructure engineering with sophisticated cellular imaging to identify novel aspects in the cell biology framework regulating polyplex transport to the nucleus. In another example, we have developed versatile and highly tunable light-based strategies to release siRNAs with control at cellular length scales. Light-triggered delivery materials exhibit innate advantages in spatiotemporal control as compared with chemically responsive delivery materials or strategies to control nucleic acid exposure based upon “stamping” or liquid-liquid patterning, yet existing light-triggered nucleic acid delivery materials have minimal dynamic range in gene modulation. We demonstrated a new class of light-sensitive polymers that provide biocompatibility and rapid application with proven on/off initiation of gene silencing and the ability to locally “dial-in” the level of siRNA deployment and gene regulation. The ability to control the spatial placement and induction of biomolecular signaling programs through this on/off switch will be essential in developing and modeling complex tissues such as cardiovascular and neural networks.

IN001

Drops on superhydrophobic and lubricant infused surfaces: Similarities and differences

Frank Schellenberger, Hans-Jürgen Butt, Doris Vollmer

Max Planck Institute for Polymer Research, Mainz, Germany

Liquid droplets are omnipresent. This has inspired numerous studies on the wetting behavior of liquid droplets under static and dynamic conditions.A great deal of research has gone into developing novel surfaces. In particular, super-liquid-repellent surfaces have been investigated extensively. Superhydrophobic surfaces were expected to show high receding contact angles and low roll-off angles. Water droplets partially rest on an air cushion between the protrusions greatly reducing the solid-liquid contact areas. This results in low adhesion. An alternative strategy to achieve surfaces with low roll-off or sliding angles is to infuse textured or porous surfaces with lubricant. However, liquid drops resting on lubricant-infused surfaces are surrounded by an annular wetting ridge. In some cases the drops are even cloaked by a thin layer of lubricant.

Here, I discuss the differences and similarities between superhydrophobic and liquid infused surfaces. We use laser scanning confocal microscopy to image the shape of the three phase contact line, to visualize the thickness of the air cushions, or to monitor the height and shape of the wetting ridge. Surprisingly, both, drops on superhydrophobic and lubricant infused surfaces show a high receding contact angle. Typically, the receding process proceeds through depinning of the contact line leading to a well-defined apparent receding contact angle. On the advancing side the drop–air or drop–lubricant interface gradually bends downwards until it touches the top face of the foremost protrusion. The effective advancing contact angle is 180°. Our data suggest that slippery surfaces resemble superhydrophobic surfaces, with the main differences being that drops on a slippery surface are surrounded by a wetting ridge of adjustable height and that the air underneath the drop in the case of a superhydrophobic surface is replaced by lubricant.