

UK Colloids 2011: An International Colloid and Surface Science Symposium

July 4th to July 6th 2011

De Vere Venue, Canary Wharf, London

www.ukcolloids2011.com



Abstract Booklet



Instructions

Final list of presentations is provided here. To access the abstract associated with a given speaker, please click on their name.

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Conference Programme

Day 1

Exhibition Opens: 9.00 am

Conference Opening: 10.00 am

Plenary 1: 10.15 – 11.15 <i>Microscale Patterning of Functional Materials via Direct-Write Assembly</i> Professor Jennifer Lewis			
Room	A	B	C
11:30	Nanoparticles Kekynote, NK1: <i>Colloidal molecules in the shape of multipod-like nanoparticles obtained from silica seeds by styrene emulsion polymerization</i> Etienne Duguet	Manufacturing keynote, MK1: <i>Fabrication methods for colloidal-scale particles</i> David Weitz	Characterisation keynote, CK1: <i>Surfactant adsorption and self-assembly: the insights from neutron reflectivity and small angle neutron scattering</i> Jeff Penfold
12:00	N1: <i>Synthesis of magnetic nanoparticles for biomedical applications</i> Nguyen Thanh*	M1: <i>Liposome preparation using a hollow fiber membrane contactor - Application to spirinolactone encapsulation</i> Abdallah Laouini	C1: <i>Dynamic forces between sterically stabilized oil droplets: How important is the polymer brush?</i> Raymond Dagastine
12:20	N2: <i>Synthesis of site specific cleavable, hydrophobic nanostructures</i> Matthias Maier	M2: <i>Preparation of controlled particle-stabilized emulsion droplets using Rotary Membrane Emulsification</i> Mohamed S. Manga	C2: <i>Self-assembly in solution of silica-based hybrid materials: contribution of in-situ SAXS studies</i> Marianne Imperor
LUNCH 12.40 – 14.00			
14:00	N3: <i>Nanoparticles bearing specific number of DNA probes for single nucleotide polymorphism detection</i> Lanry Yung Li Yue*	M3: <i>FACS Based High Throughput Screening Systems for Gene Libraries in Single and Double Emulsions</i> Radivoje Prodanovic*	C3: <i>Confined drying of polymer solutions</i> Laure Daubersies
14:20	N4: <i>Coordination chemistry on the surface of metal and metal oxide colloidal particles</i> Vladamir Kolesnichenko*	M4: <i>Microparticles with Bimodal Nanoporosity Derived by Emulsion Templating</i> Dimiter Petsev	C4: <i>Neutron Reflectivity Study of the Calcite-Water Interface</i> Isabella Stocker
14:40	N5: <i>Functionalized Titanate Nanotubes: a Potential Versatile Platform for Diagnostic and Therapeutics</i> Nadine Millot	M5: <i>Colloid flow control in sub-micrometer channels and detection by laser scattering</i> Stefano Pagliara	C5: <i>Structure of PEO in ethylammonium nitrate and adsorbed at the silica interface</i> Rob Atkin
15:00	N6: <i>Formation Mechanism of Anisotropic Nanoparticles Composed of Bismuth, Antimony and Tellurium</i> Shinya Maenosono*	M6: <i>Micromanipulation and release properties of biomineralised double-shell microcapsules</i> Rachael Allen	C6: <i>Interactions between oil droplets in concentrated surfactant phases</i> Rico Tabor

Tea Break 15.20 – 16.00

16:00	N7: <i>Chemical Imaging Through Tissue: X-Ray Excited Optical Luminescence Chemical Sensors</i> Jeffrey Anker*	M7: <i>Complex emulsions as a template of new hybrids particles for bionanotechnology applications</i> Abdelhamid Elaissari*	C7: <i>Discussing the measurement of surface zeta potential using laser Doppler electrophoresis</i> Jason Corbett
16:20	N8: <i>Fluorescent core-shell nanoparticles for Ca²⁺-sensing</i> Anja Schulz	M8: <i>Short-molecule stabilisation of indium tin oxide nanoparticles for highly stable colloidal dispersions</i> Claudia Grote	C8: <i>Profiling dispersion concentration & settling with an in situ acoustic backscatter system</i> Tim Hunter
16:40	N9: <i>Functionalised cellulose nanowhiskers</i> Wim Thielemans*	M9: <i>Fabrication of biodegradable poly(lactic acid) particles in flow focusing glass capillary devices</i> Goran Vladislavjevic	C9: <i>Passive microrheology : non intrusive measurement of the emulsions stability</i> Christelle Tisserand
17:00	N10: <i>In the search of 3-D bulk metamaterials</i> Yuri Barnakov*	M10: <i>Crystallization of binary colloidal monolayers with adjustable configurations at the air-water interface</i> Nicolas Vogel	C10: <i>NMR as an Analytical Tool to Characterize Dispersions</i> Stuart Prescott

Poster/Drinks 17.30 – 20.00

Day 2

Plenary 2: 08.45 – 09.45

Aqueous Dispersion Polymerisation: A New Paradigm for the Facile Synthesis of Bespoke Organic Nanoparticles in Concentrated Solution

Professor Steven Armes

Room	A	B	C
10:00	Nanoparticles Keynote, NK 2: <i>How can we commercialize nanotechnology and where are the unique applications?</i> Peter Dobson	Manufacturing Keynote, MK2: <i>Continuous Miniemulsification Using Static Mixers</i> Tim McKenna	Applications Keynote, AK1: <i>Polymersome nanoreactors as artificial organelles</i> Jan van Hest
10:30	N11: <i>Continuous and Controlled Green Syntheses of Inorganic Nanoparticle Libraries</i> Jawwad Darr*	M11: <i>Hydroxyapatite nanoparticle-amored biodegradable polymer microspheres fabricated via Pickering emulsion route</i> Syuji Fujii	A1: <i>Surface force measurements between titania surfaces prepared by atomic layer deposition in aqueous electrolyte and CTAB solutions</i> Vince Craig
10:50	N12: <i>Network analysis on the applications of magnetic nanoparticles for healthcare</i> Daniel Ortega*	M12: <i>Novel method of producing highly uniform silica particles using inexpensive silica sources</i> Marijana Dragosavac	A2: <i>Phases in Coexistence in a Mixture of Neutral Hard Colloidal Spheres and a Depletion Agent</i> S. K. Lai

Coffee Break 11.10 – 11.40			
11:40	N13: <i>Superparamagnetic Nanoparticles for Drug Delivery</i> Nick Darton	M13: <i>Multilayer microcapsules based on supramolecular structures produced from bovine serum albumin and high methoxy pectin</i> Yul Arsianti	A3: <i>Janus Composite Colloids</i> Zhenzhong Yang*
12:00	N14: <i>Selection of nanocrystalline oxides cores for magnetic fluid hyperthermia</i> Emil Pollert*	M14: <i>Nanoemulsification via Ultrasound</i> Elijah Nazarzadeh	A4: <i>Suspension processing and suspension engineering rheology</i> Richard Buscall
12:20	N15: <i>Functionalisation of iron oxide nanoparticles for biomedical applications and dendritic and phosphonate approaches to develop T2 contrast agent for MRI</i> Sylvie Begin*	M15: <i>Uniform Drops by Microchannel Emulsification</i> Shabnam Elahi	A5: <i>Interaction and Attachment of Particles and Bubbles in an Aqueous Environment</i> David Verrelli
LUNCH 12.40 – 14.00			
14:00	Nanoparticles Keynote, N13: <i>Colloidal suspensions for stimuli responsive drug release</i> Dihendra Bahadur	Polymer Colloids Keynote, PCK1: <i>Compositional ripening of particle- or surfactant-stabilised emulsion</i> Bernie Binks	Applications Keynote AK2: <i>Optical manipulation of aqueous droplets in air and in oil</i> David McGloin
14:30	N16: <i>Magnetically responsive (nano)biocomposites and their applications</i> Ivo Safarik*	PC1: <i>New interactions between aqueous droplets dispersed in oil</i> Michael O'Sullivan	A6: <i>Phase separation in mixtures of silica particles of two sizes, dispersed in dimethylformamide, on the addition of polystyrene</i> Brian Vincent
14:50	N17: <i>Targeted Delivery of Encapsulated Therapeutics using Nanoengineered Capsules</i> Angus Johnston	PC2: <i>New Route to highly concentrated polymer dispersions and structure-property relationship of their films</i> Riaz Choudhery	A7: <i>Stimuli-responsive capsules for instantaneous delivery</i> Sam Fincham
15:10	M16: <i>Gold Nanoparticles-Based Point-of-Care Diagnostics</i> Robert Tshikhudo*	PC3: <i>Synthesis and characterization of PNIPAM/SiO₂/Fe₃O₄ microparticles for controlled delivery</i> Viola Tokarova	A8: <i>Physico-chemical networks: enzymatically cross-linked chitosan/gelatin hydrogels</i> Marcelo da Silva
Tea Break 15.30 – 15.50			
15:50	M17: <i>Manipulating fluids for fabricating functional materials</i> Anderson Shum*	PC4: <i>One-step Preparation of Functional Colloidosome Microcapsules</i> Olivier Cayre	A9: <i>Recent Advances in Oleic Acid-Based Gemini Surfactants</i> Kenichi Sakai

16:10	M18: <i>Remotely Controlled Hydrogel Sponges</i> Ales Zadrazil	PC5: <i>Competition at the nanoparticle surface: one polymer, two surfactants, many possibilities</i> Beatrice Cattoz	A10: <i>Colloidal particle stability in inkjet inks</i> Huai (Grace) Yow
16:30	M19: <i>Fabrication of Colloidal Grid-Pattern Network by Two-Step Convective Self-Assembly</i> Satoshi Watanabe	PC6: <i>Covalently Cross-linked Colloidosomes</i> Kate Thompson	A11: <i>Novel hydrogel composites containing pH-responsive microgels</i> Sarah Lally
16:50	M20: <i>Liquid Marbles Stabilized by Particle Assemblies with Liquid-Repellent Character</i> Ryo Murakami	PC7: <i>Double crosslinked pH-responsive microgels for intervertebral disc repair: Design and properties</i> Brian Saunders	A12: <i>Many-body effects on depletion interactions</i> Jan Forsman
Break			
Thomas Graham Lecture: 17.30 – 18.30 <i>Micelle Processes at Surfaces and in Solution</i> Professor Colin Bain			

Day 3

Plenary 3: 08.45 – 09.45 <i>Physics and Chemistry of Nanoparticle Self Assembly</i> Professor Robert Prud'homme			
Session	A	B	C
10:00	Characterisation keynote, CK2: <i>Optical-trapping-based microrheology to study non-equilibrium colloids and polymer networks</i> Christoph Schmidt	Polymer Colloids keynote, PCK2: No Abstract Stuart Clarke	Applications keynote, AK3: <i>How do interfacial interactions influence the phase behavior and molecular ordering of molecularly thin films at solid surfaces?</i> Hans Riegler
10:30	C11: <i>Wettability and Behaviour of Solid Particles in Thin Liquid Films, Foams and Emulsions</i> Tommy Horozov	PC8: <i>All-acrylic film-forming colloidal polymer/silica nanocomposite particles prepared by aqueous emulsion polymerisation</i> Lee Fielding	A13: <i>Toward Soft-Brain Materials with Toporogical Colloidal Array in Discreet Wrinkle Space</i> Hiroshi Endo
10:50	C12: <i>Interactions between Hollow Silica Shells using Total Internal Reflection Microscopy (TIRM)</i> Stefanie Sham	PC9: <i>Biodegradable pH-responsive hollow polymer particles: triggered particle swelling, gel-formation and disassembly</i> Robert Bird	A14: <i>DNA-loaded calcium alginate nanoparticles</i> Alexandra Machado
Coffee Break: 11.10 – 11.40			

11:40	C13: <i>From Wenzel to Cassie: what are the wetting properties of anodized alumina?</i> Hannah Leese	PC10: <i>Preparation of durable biomembrane-mimetic hydrogels by water channel confined photocrosslinking of complex fluids</i> Millicent Firestone	A15: <i>Amphiphilicity Determines Nanostructure in Protic Ionic Liquids</i> Robert Hayes
12:00	C14: <i>Determination of Pore Space of a Highly Monodisperse O/W Emulsion Using NMR Diffusometry</i> Panithi Wiroonpochit	PC11: <i>Auto-stratification in latex coatings</i> Richard Trueman	A16: <i>Studies on the Deposit Microstructure formed from Drying Sessile Drops containing Dispersed Phases through Changes in Marangoni Flows and Rheology and the Consequences for Bodelivery Enhancement</i> Malcolm Faers
12:20	C15: <i>Spreading of surfactant solutions over hydrophobic substrates</i> Victor Starov	PC12: <i>Ultrafine Translucent Nano-latexes via Semicontinuous Microemulsion Polymerisation</i> Yan Chen	A17: <i>Microfluidic evaporation for nanoparticles assembly</i> Julie Angly

LUNCH: 12.40 – 14.00

14:00	C16: <i>Real-time monitoring of complex moduli from micro-rheology</i> Taiki Yanagashima	Ottewill Award Lecture: <i>Polysaccharides as Colloid Stabilisers in Emulsion Polymerisation</i> Peter Lovell	A18: <i>Colloids crossing mucosal barrier: non-invasive delivery of biologicals</i> Snow Stolnik
14:30	C17: <i>SURFs and SAILS: anionic surfactants and ionic liquids with quaternary ammonium counterions</i> Paul Brown		A19: <i>The kinetics of colloidal aggregation – Effect of bimodal Hamaker constant distribution and Brownian forces</i> Grant Webber
14:50	C18: <i>Alkane microdrop collisions in surfactant free systems</i> Hannah Lockie		A20: <i>Spontaneous formation of non-spherical O/W emulsion droplets in particle stabilised systems</i> Phil Taylor
15:10	C19: <i>Water-in-Oil Microemulsions in HPLC</i> Marina Rukhadze	PC13: <i>Dual Stimuli-Responsive Microgels Based on Photo Cleavable Crosslinkers: pH-Dependent Swelling and Light-Induced Degradation</i> Daniel Klinger	A21: <i>Interactions between biosurfactants and particles as colloid stabilizing agents</i> Brent Murray

Tea Break 15.30 – 15.50

15:50	C20: <i>Rheology of explosive emulsions –viscosity, elasticity, time effects, transportation</i> Irina Masalova	PC14: <i>Carboxyl Functional Stimuli-Responsive Magnetic Particles</i> Mahbubor Rahman	A22: <i>Competitive adsorption of surfactants with non aqueous colloidal particles used in lubricant additives</i> Peter Dowding
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16:10	C21: <i>Characterizing the Electrostatic Behaviour of Single Micro-Particle Using a Plate Condenser in an Atomic Force Microscope</i>	PC15: <i>The phase behaviour of pNIPAM microgel and colloid mixtures</i>	A23: <i>Solution Conformation of Polymer-Drug Conjugates: Contrast-variation SANS as a tool to elucidate the microstructure of uni-molecular aggregates.</i>
	Jin Wang Kwek	Katie Bayliss	Alison Paul
16:30	C22: <i>Experimental force and time measurements during particle adsorption at an oil-water interface</i>	PC16: <i>Synthesis, Characterisation and Interfacial Activity of Poly(2-vinyl pyridine) Particles</i>	A24: <i>Adsorption Kinetics from Polymer/Surfactant Mixtures at an Expanding Liquid Interface</i>
	Louis Fradette	Damien Dupin	Anna Angus-Smyth
16:50	C23: <i>Growth and shrinking of Pluronic micelles in Pluronic-flurbiprofen solutions: variation of concentration and pH</i>	PC17: <i>Metallosurfactants – Self-Assembled Metal Surfaces</i>	A25: <i>Hydrodynamic stresses in colloidal aggregates under shear flow</i>
	Shirin Alexander	Peter Griffiths	Ryohei Seto
Break			
Conference Dinner 19.30 – 23.00			

*Denotes invited speaker

Microscale Patterning of Functional Materials via Direct-Write Assembly

Jennifer A. Lewis

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The ability to pattern functional materials in planar and three-dimensional forms is of critical importance for several emerging applications, including flexible electronics, photovoltaics, antennas, structural and tissue engineering scaffolds, and self-healing materials with embedded microvascular networks. Direct-write assembly enables one to rapidly fabricate diverse classes of materials in arbitrary shapes without the need for expensive tooling, dies, or lithographic masks. In this talk, the design of concentrated colloidal and nanoparticle inks with tailored rheological properties will be described. In addition, several recent advances of microscale patterning will be highlighted, including omnidirectional printing of flexible microelectrodes, conformal printing of 3D electrically small antennas, and printed origami of metallic and ceramic scaffolds with complex 3D architectures.

Aqueous Dispersion Polymerisation: A New Paradigm for the Facile Synthesis of Bespoke Organic Nanoparticles in Concentrated Solution

Prof. Steve Armes

Department of Chemistry, University of Sheffield, Sheffield, UK.

Methacrylic AB diblock copolymers are readily prepared using reversible addition-fragmentation chain transfer (RAFT) chemistry at 70°C under aqueous dispersion polymerisation conditions. The first block is a highly hydrophilic polymer such as poly(glycerol monomethacrylate) [PGMA], whereas the second block is poly(2-hydroxypropyl methacrylate) [PHPMA]. As the PHPMA chains grow, they become hydrophobic, which drives the *in situ* self-assembly of the copolymer chains.¹ This versatile approach allows the synthesis of sterically-stabilised nanolatexes of 25 to 100 nm diameter with good size control at around 10 % solids. Varying just two synthesis parameters enables the final block copolymer morphology to be varied systematically from spheres to worms to vesicles. A detailed phase diagram has been elucidated for one particular formulation, which allows the *reproducible* synthesis of nanoparticles with *predictable* morphologies. If block copolymer vesicles are targeted, the block copolymer morphology evolves during the growth of the PHPMA block, passing from spheres to worms to vesicles. Transmission electron microscopy studies of the sampled reaction solution reveal fascinating *intermediate* nano-structures that provide useful insights regarding the evolution of the copolymer morphology, particularly for the worm to vesicle transition. The worm phase leads to shear-thinning, free-standing gels at room temperature, presumably due to worm entanglements. Such gels exhibit unexpected thermo-sensitive behaviour, which appear to be related to subtle changes in the extent of hydration of the PHPMA block. Given the known biocompatibility of the PGMA and PHPMA chains, such gels may have potential biomedical applications.

1. "RAFT synthesis of sterically-stabilized methacrylic nanolatexes and vesicles by aqueous dispersion polymerization", Y. T. Li and S. P. Armes, *Angewandte Chem.*, **49**, 4042-4046 (2010).

Physics and Chemistry of Nanoparticle Self Assembly

Robert K. Prud'homme

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With widespread interest in “nano-bio”, attention has focused on strategies to make small particles from highly hydrophobic (low bioavailability) compounds. Our focus has been on “ultra fast” precipitations that involve two components: (1) rapid and tailored micromixing in an impinging jet to effect high supersaturations and nucleation rates, and (2) novel block copolymer stabilizers. The process depends critically on control of three time scales: particle nucleation and growth, block copolymer micellization, and polymer adsorption on the particle to produce steric stabilization. At the scale of “nano” several interfacial phenomena become significant in determining particle formation and stability. Curvature-induced solubility differences (Kelvin effect) drive diffusion-induced particle growth (Ostwald ripening). Crystallinity drives nanoparticle shape evolution. Curvature changes the free energy of compounds in nanoparticle cores (Laplace pressure) and limits drug loadings. And for polymer stabilized particles the soluble polymer brush layer controls the effective interfacial tension at the particle surface. The mobility of the stabilizing polymer on the nanoparticle surface controls long-term stability. Rapid, kinetically-controlled assembly enables the formation of nanoparticles with multiple active agents and multifunctional polymer stabilizers. This enables the delivery of “drug cocktails” from nanoparticles, the production of multifunctional nanoparticles that can deliver actives and imaging agents, and incorporation of targeting ligands to the stabilizing polymer corona. This world of interesting phenomena at the nano scale and the technological importance of the field make it a rich area of investigation.

Micelle Processes at Surfaces and in Solution

Colin D. Bain

Department of Chemistry, Durham University

Applications of surfactants in spraying, coating, milling, wetting, detergency, flotation, lubrication, etc., involve the transport of surfactants to surfaces on short timescales and under conditions that are far from equilibrium. Practical formulations frequently involve surfactants above their critical micelle concentrations so an understanding of adsorption kinetics on short timescales involves not only the diffusion and adsorption of monomeric surfactants but also the transport of micelles, the interchange of surfactants between monomers and micelles and potentially the direct interaction of micelles with surfaces.

Well-established theories exist for micelle processes near equilibrium. The Aniansson and Wall model provides a canonical description of exchange processes between monomers and micelles for small perturbations. The received wisdom on micelle adsorption is even more definitive: micelles don't adsorb. But do these models still apply far from equilibrium, when the monomer concentration is far below the cmc or the surface is only sparsely covered with surfactant? This talk will discuss recent modelling and experiments which suggest that the rate of breakdown of micelles is a very strong function of the monomer concentration and that there is a direct pathway for transport of surfactant from micelles to a surface when the surface coverage is low. Remaining quandaries will also be presented.

Polysaccharides as Colloid Stabilisers in Emulsion Polymerisation

Peter A. Lovell, Amil Pillay Narrainen and Ian Gray

*Materials Science Centre, School of Materials, The University of Manchester
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Polysaccharides, such as hydroxyethylcellulose and cellulose, have long been used in emulsion polymerisation since they are capable of becoming grafted to the latex particles, thus providing steric stabilisation, opportunities to control latex rheology through complexation of their hydroxyl groups and high affinity for cellulose fibres in paper coating applications. This paper will present results from studies of the competition between degradation and grafting of hydroxyethylcellulose and xyloglucan in emulsion polymerisations of a range of common monomers.

Gel permeation chromatography studies of free-radical degradation of the hydroxyethylcellulose and xyloglucan in aqueous solution initiated by 4,4'-azobis-(4-cyanopentanoic acid), potassium persulfate, hydrogen peroxide and the redox couple of hydrogen peroxide with ascorbic acid will be reported for reactions carried out in the presence and absence of monomers at concentrations below their aqueous saturation concentrations. The results will be interpreted in terms of the mechanism of polysaccharide degradation following H-abstraction from polysaccharide chains, and the competition between polysaccharide chain scission and initiation of polymerization in the presence of monomer. The results will be used to rationalise observations on emulsion polymerisations carried out in the presence of hydroxyethylcellulose and xyloglucan, and to establish the factors which control the competition between polysaccharide degradation and grafting of polysaccharide chains to the latex particles during emulsion polymerisation.

Colloidal molecules in the shape of multipod-like nanoparticles obtained from silica seeds by styrene emulsion polymerization

A. Perro^{1,2}, D. Nguyen^{1,2}, A. Désert^{1,3}, S. Reculosa¹, O. Lambert³, J.C. Taveau³, E. Bourgeat-Lami⁴, S. Ravaine², E. Duguet^{1*}

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Hybrid organic-inorganic nanoparticles with well-controlled morphology are currently of great interest for numerous applications. Synthetic routes leading to robust aggregates made of nanoparticles of different chemical natures which are associated in a controlled manner (*i.e.* number of nanoparticles and geometrical arrangement) are especially investigated as potential “colloidal molecules”.

Our strategy is based on a seeded emulsion polymerization process leading to biphasic particles, which are composed of spherical silica spheres surrounded by a varying number of polystyrene (PS) nodules. The hydrophilic surface of the silica seed particles (50-400 nm) needs to be previously functionalized. In such conditions, the nucleation/growth of the PS nodules is highly favoured at the silica surface, leading to multipod-like morphologies (bipods, tetrapods, hexapods, octopods, *etc.*). While varying different experimental parameters, it was demonstrated that the key parameters to control the pod number and arrangement are (i) the ratio between the number of silica seeds and the number of growing PS nodules, (ii) the size of silica seeds and (iii) the silane grafting density.

In particular, we demonstrated that the number of PS latex per silica seed can be calculated from the size of the silica seed by solving an equation which results from the minimization of a two-term-energy. The first one is an attraction towards the centre and the contribution of the second one produces two-body particle repulsions, which can balance the attractive central force.

Lastly, original planar biphasic colloids may be also obtained by shaping these multipod-like particles on planar substrates by taking advantage of the softness of the PS nodules, leading to triangles, squares, pentagons, hexagons, octagons, *etc.*

A key feature of our approach is that our synthetic process is reproducible, fast and may yield grams of biphasic submicronic particles (up to 90% purity).

How can we commercialize nanotechnology and where are the unique applications?

Peter Dobson

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The field of nanotechnology is not as new as many believe, and there are literally hundreds of examples of the application of colloids (now re-badged as *nanoparticles*) in everyday products. This talk will examine the successes of some of these products and look at the way that modern nanotechnology ideas have helped to shape and alter existing products. After a decade of fairly intense scientific research activity, it is time to take stock and ask the questions “So what?....where does this position the routes to real applications?”. The area is under scrutiny because many believe there is a paradigm for the prediction of the future commercialization in other emerging technologies. The public perception of “nano” has created a problem, but the scientific research to allay some of the health concerns is in itself creating exciting new opportunities, especially in healthcare and nanomedicine. The Research Councils have been working with the Technology Strategy Board to maximize the commercial and societal impact of its recent Grand Challenge nanotechnology programmes to ensure that good research is carried through application to commercialization.

Colloidal suspension for stimuli response drug release

D. Bahadur

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Colloidal suspension of Nano particulates (NPs) have been developed by various soft chemical methods. Magnetic nanostructures with sufficient biocompatibility are the best candidates for several therapeutic and diagnostic applications such as treatment for cancer through hyperthermia, targeted and sustained drug delivery, as contrast agents and other bio sensing applications. We discuss here some of these aspects based on the work carried out in our laboratory. In addition, we discuss development of suspension of multifunctional magnetic hybrid nanostructures, which may be used for a combined therapeutic and diagnostic approach. For efficient delivery of magnetic nano particulates with drug to the diseased site, magnetic fluid based release systems will be discussed with different possibilities of thermo sensitive and pH sensitive polymers, gels, liposomes and dendrimers as carrier. These encapsulates of chemotherapeutic drug, MNPs and tagging targeting moiety (like folic acid) on the surface have been investigated. Besides pH and temperature, ultra sound and AC magnetic field have been used as stimuli to trigger drug release. The synergetic effect of hyperthermia and chemotherapy with respect to some of these stimuli will be discussed.

Such nanostructures when properly functionalized can be used as effective vehicles for biological entities in vivo. In this respect we will also discuss some of the other non magnetic systems, (e.g. porous zinc oxide or layered double hydroxides) for biological applications. The mechanism of cell death during controlled experimental conditions for hyperthermia treatment of cancer will be discussed.

Fabrication methods for colloidal-scale particles

D.A. Weitz

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This talk will describe new ways to create colloidal scale particles using a variety of methods based on creating templates of the scale desired.

Continuous Miniemulsification Using Static Mixers

Ula El-Jaby, Michael Cunningham, Timothy F.L. McKenna*

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One of the major impediments to the use of miniemulsification as a means of making latex products on a commercial scale is the limited number of technologies available for the emulsification step. We have developed a technology based on the use of in-line static mixers and stabilisers generated *in situ* to produce and polymerise miniemulsions in a continuous process. By using a well-known method for generating surface active agents at the oil-water interface, we can significantly reduce the time required for the stabilisation of monomer droplets on the order of 150 nanometres from several minutes to approximately 30 seconds. Rapidly stabilising the droplets allows us to directly feed the miniemulsion to a continuous tubular reactor, where they can be polymerised in conditions identical to those of a conventional batch process.

Surfactant adsorption and self-assembly: the insights from neutron reflectivity and small angle neutron scattering

J Penfold

ISIS/STFC, Oxford

The use of the neutron scattering techniques of neutron reflectivity, NR, and small angle neutron scattering, SANS, for the study surfactant adsorption and self-assembly will be introduced and reviewed. Particular emphasis will be placed on how deuterium–hydrogen isotopic substitution is used to probe multi-component mixtures and mixed phase systems, and a range of specific examples, which illustrate the unique features of the techniques, will be presented. The examples will include NR studies of mixed surfactant adsorption, polyelectrolyte-surfactant adsorption and the spontaneous formation of multilayer structures at interfaces. It will be shown how SANS has been used to resolve and quantify the structure of surfactant mixtures forming lamellar-micellar mixed phase systems, nano-vesicles, and to probe non-equilibrium effects.

Optical-trapping-based microrheology to study non-equilibrium colloids and polymer networks

Professor Christoph Schmidt

We have developed a combination of fluctuation-based and active microrheology methods that is well suited to study non-equilibrium viscoelastic systems on small length scales and with high bandwidth. We use micron-sized probe particles, embedded in the medium to be studied, and laser optical traps to confine the particles, combined with laser interferometry to detect either their Brownian motion or the particles' response to a driving force with sub-nm accuracy and bandwidths up to 100 kHz. We have applied this technology to aging colloidal systems (laponite) and to biopolymer networks (actin) driven out of equilibrium by motor proteins.

Compositional ripening of particle- or surfactant-stabilised emulsions

B.P. Binks*, P.D.I. Fletcher and B.L. Holt

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We describe the mixing of an oil-in-water emulsion of a slightly water-soluble mobile oil (α -ionone) with a similar emulsion containing a highly water-insoluble immobile oil (squalane) for emulsions stabilised either by nanoparticles or surfactant molecules. Mass transfer of mobile oil occurs resulting in the shrinking of mobile oil drops and the swelling of immobile oil drops. Surfactant-stabilised emulsion drops swell without coalescence such that the final drop radius is proportional to the swelling ratio to the power of $1/3$. By contrast, for particle-stabilised emulsions, the swelling of the squalane-containing drops triggers coalescence causing the final drop radius to be proportional to the swelling ratio to the power of 1. Addition of excess, non-adsorbed particles to these latter emulsions suppresses the coalescence and results in a switchover from particle to surfactant behaviour.

Polymersome nanoreactors as artificial organelles

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Compartmentalisation is one of the techniques that cells adopt to enable a high level of control over (bio-)chemical processes, for instance the order in which enzymes react. In many cases, the compartment also serves to protect the cell from the action of its degrading contents, as is the case with lysosomes. It furthermore serves as a scaffold for the precise positional assembly of enzymes that work together in a multistep cascade reaction. In an effort to mimic these complex enzyme systems, many studies concerning enzyme encapsulation or assembly have been reported in the literature. The focus of this research initially was on phospholipid liposomes. However, the relative fragility of liposomes limits their potential applicability. Like liposomes, polymersomes are spherical aggregates that contain a bilayer architecture. They are formed by the self-assembly of amphiphilic block copolymers in an aqueous environment and their polymeric bilayer shows a greater stability, mainly due to the lower critical aggregation concentration of amphiphilic macromolecules. A drawback of polymersome membranes is their low permeability even to water, which hampers application as nanoreactors.

To overcome this problem, block copolymers have to be used that give an intrinsically porous bilayer when self assembled. One such copolymer is polystyrene₄₀-*block*-poly[L-isocyanoalanine(2-thiophen-3-yl-ethyl)amide]₅₀ (PS-PIAT). On dispersal in water it forms porous polymersomes that possess a relatively high degree of permeability. Small molecules can move across their membranes while larger molecules, such as proteins, cannot. In a first line of research, we have positioned enzymes at three different locations on these polymersomes, namely, in their lumen (glucose oxidase, GOx), in their bilayer membrane (Candida antarctica lipase B, CalB) and on their surface (horseradish peroxidase, HRP, see figure 1). The surface coupling was achieved by 'click' chemistry between acetylene-functionalised anchors on the surface of the polymersomes and azido functions of HRP, which were introduced by using a direct diazo transfer reaction to lysine residues of the enzyme [1]. To determine the encapsulation and conjugation efficiency of the enzymes, they were decorated with metal-ion labels and analysed by mass spectrometry. This revealed an almost quantitative immobilisation efficiency of HRP on the surface of the polymersomes and a more than statistical incorporation efficiency for CalB in the membrane and for GOx in the aqueous compartment. The enzyme-decorated polymersomes were studied as nanoreactors in which glucose acetate was converted by CalB to glucose, which was oxidised by GOx to gluconolactone in a second step. The hydrogen peroxide produced was used by HRP to ABTS to ABTS⁺. Kinetic analysis revealed that the reaction step catalysed by HRP is the fastest in the cascade reaction.

In a second line of research, artificial organelles were created. For this purpose we modified the outer surface of the polymersome nanoreactors with cell-penetrating peptides, in particular the tat sequence. As a result, the polymersomes obtained the property to enter cells. Enzymes which were encapsulated in the polymersomes could be transported into mammalian cells and perform their biological activity in a living system. This was demonstrated via the introduction of HRP, which could neutralize hydrogen peroxide and therefore protect the cell against oxidative stress [2].

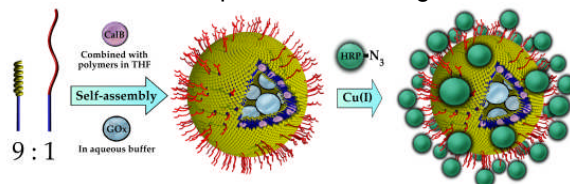


Figure 1. Positional assembly of enzymes in a polymersome

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Optical manipulation of aqueous droplets in air and in oil

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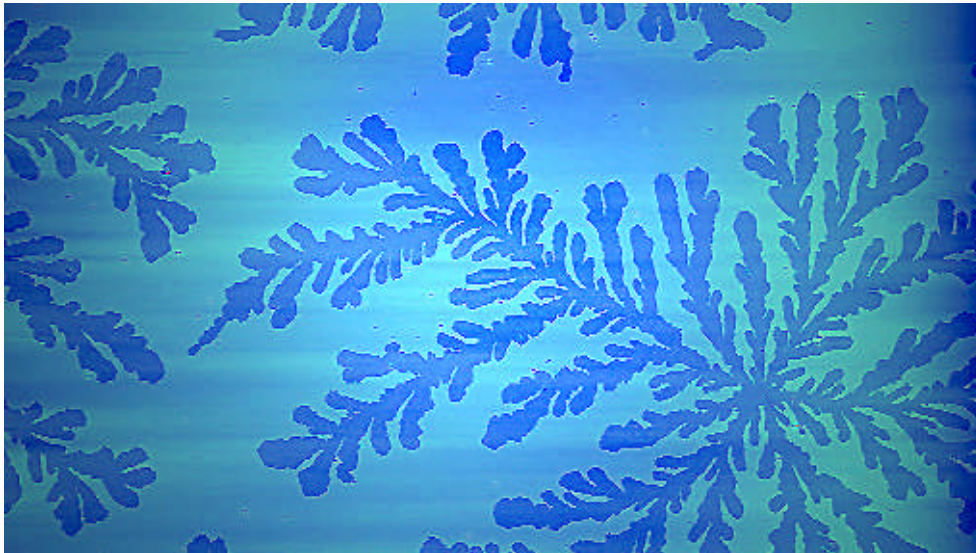
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The ability of light to trap and manipulation microscopic particles has resulted in the powerful tool called optical tweezers. These devices are sensitive force and position measurement systems in a wide range of micro and nanoscale science and enable very high localisation of trapped particles. In this talk I will discuss how optical tweezers and related optical manipulation techniques can be used to study airborne particles, both in terms of particle composition and morphology. I will show how particle interactions can be studied by examining the Brownian motion of trapped particles and also how optical tweezers can be used to potentially study aerosol mixing and other dynamical processes. I will touch on future applications of this work that will try and combine optical tweezers with other techniques, such as x-ray analysis and contact nucleation. As a counter point to these experiments I will also present data on work we have carried out on aqueous droplets in oil, which can also be manipulated by light, via an optically induced thermal process. I will discuss how a combination of this technique with microfluidic 'holes' and 'rails' opens up new possibilities for droplet microfluidics in terms of chemical and biochemical assay techniques, and more generally how microfluidic strategies might be applied back to the aerosol domain.

How do interfacial interactions influence the phase behavior and molecular ordering of molecularly thin films at solid surfaces?

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Fractal shaped solid alkane monolayer domains. Frame size: $\approx 100\mu\text{m} \times 50\mu\text{m}$
(for more info see for ref (1))

The phase transition behavior and molecular ordering of a thin film at a solid surface is affected by interfacial contributions to its free energy. This leads to a variety of interesting and unexpected phase transition, wetting and nucleation phenomena. For instance, for a thin adsorbed submonolayer film, the sharp solid/liquid (bulk) phase transition is often broadened into a phase transition region due to interfacial pre-melting (1). In certain cases the melting of thin films can lead to “running” droplets, whose direction and speed of movement can be controlled (2,3). Line tension may change the growth and shape of adsorbed nanometer size aggregates (4) and thus be relevant for heterogeneous nucleation. Even macroscopic systems can be affected by molecular interfacial processes in quite a conspicuous way: Under certain conditions, millimeter size sessile droplets of completely miscible fluids do not coalesce instantaneously because of interfacial processes at the surface between the droplets (5,6).

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Synthesis of magnetic nanoparticles for biomedical applications

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We have used different wet chemical methods to synthesise magnetic nanoparticles of different compositions, size, shapes and surface chemistries. These NPs system has been used for biomedical applications such as tracking of neural stem cells, Here are few examples:

1. Tunable shapes of magnetic nanoparticles: Fe-Pt, Fe-Pd and Fe-Pt-Pd alloys
2. Synthesis of magnetic nanoalloys from bimetallic carbonyl clusters
3. Facile synthesis of stable water-soluble magnetic CoPt: solid, nanochains/wires and hollow nanoparticles
4. Synthesis of Magnetic Co Nanoparticles by Pulsed Laser Irradiation of Cobalt Carbonyl in Organic Solution
5. Superparamagnetic Fluorescent Nickel-Enzyme Nanobioconjugates
6. Synthesis of core-shell gold coated magnetic nanoparticles and their interaction with thiolated DNA
7. Tracking transplanted neural progenitor cells in spinal cord slices by MRI using CoPt nanoparticles as a contrast agent

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Synthesis of site specific cleavable, hydrophobic Nanostructures

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Peptide-polymer conjugates are hybrid materials consisting of a peptide covalently attached to a polymer.[1] The conjugate benefits from the synergism of both components, such as high selectivity for targeting or release, which can be exploited for possible future applications in diagnostics or therapy. Their formulation to nanostructures is crucial for the application as therapeutic or diagnostic agents, e.g. if an intravenous injection of drugs is desired. In order to address hydrophobic as well as hydrophilic drugs, a very fertile method to efficiently synthesize defined nanostructures such as the mini emulsion process[2] is required.

Here we present the synthesis of site specific, protease (trypsin, pepsin) cleavable, nanoparticles in inverse mini emulsion. Different peptide sequences were synthesized employing microwave-assisted solid-phase synthesis and characterized with HPLC, NMR and MALDI-TOF MS. Capsules for encapsulation of hydrophilic compounds were prepared by interfacial polyaddition of the peptide and a diisocyanate. Furthermore the peptides were used to crosslink a hydrophobic functional polymer with standard peptide-coupling methods. Confirmation and quantification of crosslinking was obtained by the introduction of an ^{15}N -label at the N-terminus of the peptide. The reaction was performed in inverse miniemulsion generating the desired particulate morphology. After transferring the particles into aqueous medium the nanostructures were characterized with photon cross correlation spectroscopy (PCCS), scanning electron microscopy (SEM), and ^{15}N -solid state NMR. The integration of a fluorophore/quencher system, based on fluorescence resonance energy transfer (FRET) in the peptide sequences enabled the monitoring of the cleavage of the crosslinked polymeric nanostructures through recovery of fluorescence. The results underline, that the inverse miniemulsion technique is a highly suitable method for the synthesis of peptide-crosslinked and site specific cleavable nanoparticles.

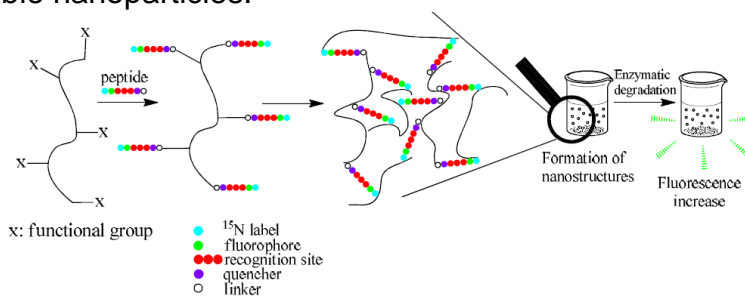


Figure 1. Synthetic route for the preparation of site specific cleavable nanostructures.

Figure 1. Synthetic route for the preparation of site specific cleavable nanostructures

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Nanoparticles bearing specific number of DNA probes for single nucleotide polymorphism detection

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Nanoparticles are increasingly being used for applications in clinical diagnostics due to their unique physical properties. Gold nanoparticles, in particular, have unique plasmonic properties allowing simplicity of detection methods. This study reported our approach of fabricating gold nanoparticles bearing a single short DNA probe that can be used as building blocks to construct nano-assemblies or as nanoprobe for gene detection. In the presence of completely matched target DNA as linker, nanoparticle dimer formation was observed. In the presence of a single sequence mismatch, however, no dimer was formed. We further applied the nanoparticle probes for genotyping mutations in the Duchenne muscular dystrophy (DMD) gene, the largest known in the human genome. Specific discrimination between wildtype and mutant sequences for a single gene mutation c.4150G>T in exon 30 of the DMD gene was achieved using a simple colorimetric detection and no false positive readout was observed. This system was also able to identify both the patients as well as the carriers of the mutation who are at-risk of transmitting the disease.

Coordination chemistry on the surface of metal and metal oxide colloidal particles

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Ligand to metal bonding on the surface of colloidal metal and metal oxide particles plays important part not only in the colloid stabilization, but also in kinetics and mechanism of the crystal nucleation and growth. This is demonstrated in synthesis of variable-sized nanoparticles of magnetite in polar chelating solvents playing the role of surfactants, and of iron triad metals in coordinating polar aprotic solvents. Colloid stabilization in these systems is presumably facilitated by solvated ions surrounding the nanoparticles as well.

Coordinated solvent can be easily displaced by polydentate hydroxycarboxylic acids such as citric, tartaric, and sugar acids, which bind to the metal on metal oxide surfaces as anionic chelating and bridging ligands. This study was done by varying the ligand structure and pH of aqueous colloids. Aqueous colloids of $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 were reacted with different ligands and monitored by the Dynamic Light Scattering and zeta-potential measurements. The isolated solids were characterized by X-ray diffractometry, TEM, thermogravimetric analysis and FT-IR spectrometry. Coordination geometry of the polydentate hydroxycarboxylic acids will be discussed.

Functionalized Titanate Nanotubes: a Potential Versatile Platform for Diagnostic and Therapeutics

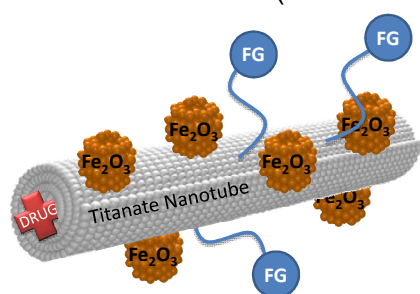
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Since the pioneer work of Kasuga *et al.*,^[1] a lot of studies have been led in the field of titanate nanotubes (TiONts) including various applications such as photocatalysis, gas sensing, etc.^[2] Recently TiONts have been considered for biomedical applications (e.g. dopamine detection, bone regeneration)^[3] and our group reported the controlled morphology, the structure and the chemical composition of titanate nanomaterials.^[4] Herein we present a novel approach using functionalized TiONts combined with iron oxide nanoparticles for both the diagnostic and the therapeutic of targeted diseases, the so-called theranostic applications.^[5]

Indeed the combination we chose consists in a nanoplatform composed of biocompatible functionalized titanate-based nanomaterials capable of carrying drugs to be delivered (cancer reactive drugs in collaboration with partner 2 or drugs



dedicated to cardiac pathologies in collaboration with partner 3) inside its constituting channel, also including surrounding iron oxide nanoparticles (Fe_2O_3) for MRI detection and various functional groups (FG in the presented scheme) such as radioactive elements (for TEP or SPECT imageries) or fluorescent compounds for fluorescence microscopy techniques and flow cytometry. To have TiONts fully dispersed a covalent coupling of

functionalized PEGs is realized onto the hydroxyl groups present at their surface. Moreover this biofunctionalization shifts the IEP towards a more acidic pH so that the PEGylated TiONts become stable at a physiological pH.

The interest of these nanoparticles associated with the radiotherapy is currently evaluated on a model of glioblastoma known to be radioresistant. TEM data show that up to 80% of the different cells types (glioblastoma cells SNB-19 and U87-MG, but also cardiomyocytes, CHO...) internalized TiONts without sign of cytotoxicity (MTT assays). These observations suggest possible coupling of both endocytosis and diffusion internalization process. Our results suggest that the further developments of these TiONts may provide a new useful tool for research and clinical therapy in the field of oncology and cardiovascular diseases.

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Formation Mechanism of Anisotropic Nanoparticles Composed of Bismuth, Antimony and Tellurium

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With the advent of nanotechnology, the field of thermoelectric (TE) materials has been rejuvenated, and what was once thought of as an area of research with insurmountable challenges has now become one of the most promising technologies to extend our current energy sources. Nanoparticles (NPs) have proven useful in these materials because the small particle size causes scattering of the heat carrying phonon along the crystal boundaries, effectively allowing the thermal conductivity to be reduced while maintaining the electrical conductivity as high as possible. This causes the overall efficiency of the material to be increased, which is expressed by the dimensionless figure of merit, ZT . With this in mind, several researchers have attempted to create efficient TE materials with nanostructuring. Among the various TE compounds or alloys under study for room temperature TE applications, some of the most promising p-type materials are Bi-Sb-Te alloys, which are predicted to have one of the highest ZT values for bulk scale materials. However, the synthesis of Bi, Sb and Te containing NPs is still challenging from the standpoint of ability to control the composition, structure and morphology.

The polyol synthetic technique is one that has proven very versatile in synthesizing NPs with controllable size, shape, composition, and structure, and in our own research we have demonstrated that this general approach could lead to a wide variety of Bi, Sb and Te based NPs with tunable shape and composition simply by changing the nature of the capping species used in the synthesis. Because of the importance in synthesizing these materials with controllable characteristics we present here a study on the mechanisms that contribute to the formation of the different observed NP shapes and composition. In this research, we focus on the effect of metal complex formation, the stability and decomposition of precursors on the formation of NPs. The ability to tune the morphology and composition of NPs based on changing synthetic parameters and addressing the underlying mechanistic details of the NP formation is the objective of this work.

Chemical Imaging Through Tissue: X-Ray Excited Optical Luminescence Chemical Sensors

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We discuss a novel technique for chemical imaging in tissues using rare earth doped $\text{Gd}_2\text{O}_2\text{S}$ nanoparticle X-ray phosphors. The technique provides both the chemical sensitivity of spectrochemical indicators and the tissue penetration and imaging ability of X-rays. Fluorescence indicator dyes display excellent chemical sensitivity towards a wide range of analytes; however conventional fluorescence imaging is of limited utility for thick tissue samples (>1 mm) because the excitation light scatters as it propagates through the tissue causing poor image resolution. X-rays are far less scattered by tissue, but conventional X-ray transmittance imaging provides only limited chemical information compared to optical techniques. We describe a hybrid method which uses X-ray excited optical luminescence (XEOL) as a light source for spectrochemical analysis. An indicator dye-coating modulates the luminescence spectrum of the phosphor in a chemically dependent manner. A narrow X-ray beam is used to excite only phosphors within the beam. This method of creating a local light source circumvents the problem of source localization in conventional fluorescence tissue imaging. An image is acquired by raster scanning the X-ray beam with respect to the sample and acquiring spectra at each position. XEOL chemical sensors have applications for measuring local acidosis, hypoxia, and degradation of coupled silver Nanoparticle layers in tissues. The Nanoparticle sensors may also be used as MRI contrast agents.

Fluorescent core-shell nanoparticles for Ca^{2+} -sensing

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Calcium ions (Ca^{2+}) act as universal second messengers in many cell types including T-lymphocytes and platelets. Measurement of intracellular Ca^{2+} in such cells therefore represents a potential indicator of e.g. viral load and disease activity or of the mechanism of platelet coagulation. These hypotheses can be tested by using fluorescent sensor nanoparticles (NPs).

NPs, in which analyte-sensitive fluorescent probes are encapsulated, are effective tools for monitoring intracellular processes. The changes in e.g. emission intensity, wavelengths or lifetime of the indicator fluorophore upon interaction with the analyte allow quantitative information about the Ca^{2+} concentration. The nanoparticle matrix provides a relatively biocompatible medium for the introduction of the sometimes toxic sensor probe molecules into the cellular environment and encapsulation of the probe molecule provides effective shielding from potential interferences. A key feature is the co-immobilisation of a reference fluorophore acting as an internal standard and thus giving an analyte-insensitive fluorescence signal. This enhances the reliability and accuracy of the measurements. Furthermore, the encapsulation of a large number of sensor molecules into sub-micron sized particles ensures facile optical detection while allowing ingress into the cell with minimum physical perturbation caused.

We present a novel type of ratiometric Ca^{2+} -sensitive NPs consisting of a silica core coated with a shell of dextran. A rhodamine-based reference dye is covalently bound to the silica core, whereas the dextran shell is labelled with the Ca^{2+} -sensitive probe Fluo-4. The nanoparticles have an average hydrodynamic diameter of 95 nm, good colloidal stability and show a 2.9-fold increase in fluorescence intensity upon binding to Ca^{2+} ions. The apparent dissociation constant of 520 nM is well suited for measurements in the physiological range.

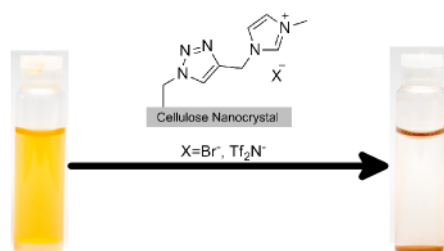
Functionalised cellulose nanowhiskers

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In our group, we have been investigating several pathways to activate the surface of cellulose nanowhiskers. These include surface azidation followed by an azide-alkyne click reaction resulting in a very high degree of substitution and the introduction of alkene groups, followed by a thiol-ene click reaction. The aim of our work is to gain a better understanding of the surface reactivity of cellulose nanowhiskers and to explore pathways that allow higher extents of modification or open up the use of a wider range of reactants. In this presentation, I will present recent work in our group on the introduction of pH-responsive fluorophores with internal standard, enabling the measurement of pH without the need of calibration or measuring the exact amount of nanoparticles added, and the introduction of imidazolium groups, which enable the ion exchange with a large array of anions. Applications of the modified nanowhiskers currently under investigation will also be presented. The image below shows the removal of an anionic dye from water by binding to imidazolium modified cellulose nanowhiskers (DS 0.36, max DS possible 0.5).



In the search of 3-D bulk metamaterials

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In my talk I will review some research activities on optical bulk metamaterials at photonics and optical spectroscopy group at the Center for Materials Research, Norfolk State University. Photonic metamaterials are rationally designed, artificial structures with pre-defined dispersion relation, which can be achieved at the certain arrangement of metallic nano-inclusions in dielectric matrix and possessed the properties unattainable in the nature. Two materials parameters are responsible for the interaction of electromagnetic radiation with the matter: dielectric permittivity ϵ and magnetic permeability μ , which are related to the refractive index n through known formula: $n = \sqrt{\epsilon\mu}$. In 1968, Russian physicist V. Veselago suggested that if ϵ and μ both will have negative sign, then n will be also negative. The idea had revolutionized the fields of electrodynamics and photonics, giving new perspective to the classical interaction of light with matter and enabling scores of unparalleled physical phenomena, including optical cloaking of invisibility, sub-wavelength imaging and etc.

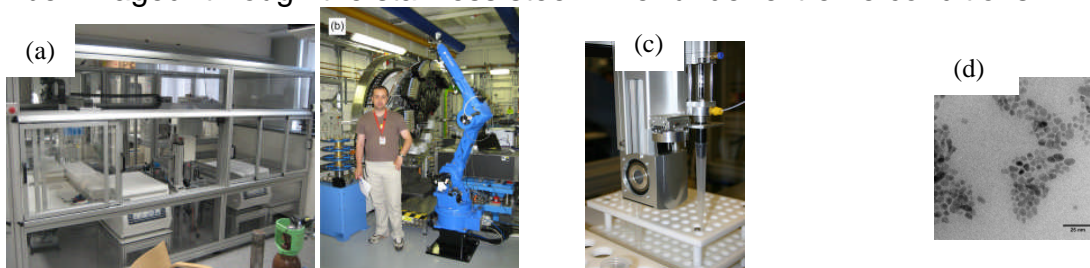
However, despite of recent tremendous progress in both theory and experiment, the research field is hindered by a lack of inexpensive large-size three-dimensional metamaterials. One way to overcome this problem is to utilize bulk dielectric templates, which nanoporous space can be filled with metals. Recently, we have demonstrated that an array of silver nanowires embedded into a flat alumina membrane matrix with 35nm-diameter pores behaves as a metamaterial with hyperbolic dispersion, characterized by different signs of the electric permittivity tensor elements. The theory predicts number of interesting physical phenomena for such specimens associated with the broad band singularity of photonic density of states, which will be discussed at the conference.

Continuous and Controlled Green Syntheses of Inorganic Nanoparticle Libraries

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Novel supercritical (sc-) fluid based routes to ceramic nanoparticles are described. The sc-water flow system produces highly crystalline doped dispersed nano-powders in a single step that possess very high surface areas (typically $>150\text{m}^2\text{g}^{-1}$). Due to the effect of both pressure and temperature during syntheses, the method also enables manufacture of nano-materials that are difficult or impossible to make using more conventional techniques. The precise control of conditions in the flow system allows us to influence product characteristics (e.g. size, shape, composition). This process has been used for the manufacture of nano-bioceramics, medical nanoparticles, nano-precursors for solid oxide fuel cell materials, battery materials, doped titanias (dielectrics and photocatalysts) and printable ceramic inks. Dr Darr will also provide details of a “High Throughput Nano-Materials Discovery” project [EPSRC reference EP/D038499/1] which encompasses aspects of nano-materials synthesis, automation, high-pressure engineering, and process control, reaction chemistry, parallel photocatalyst screening (hydrogen production from water), analytical science and intelligent computing. The idea is to use a rapid combinatorial approach to synthesize and screen for new phases of “difficult to make” materials which will display superior electronic and related properties. Other robots in use include those for property testing and automation of sample measurement in extreme environments (high energy x-rays, etc. The talk will also cover our recent development related to scale-up synthesis via a pilot plant and state-of-the-art X-ray tomographic experiments in which the hydrothermal nanoparticle nucleation regions can be “imaged” through the stainless steel mixer under extreme conditions.



- (a) RAMSI (Rapid Automated Materials Synthesis Instrument) robot for automated nanoparticle synthesis, cleanup and printing, (b) a new High Resolution PXRD Beamline robot at Diamond Beamline I11 for analysis of nanoceramics libraries and (c) close up of robot arm on RAMSI showing a mounted pipette for printing ceramic slurries and (d) surface functionalized magnetite showing packing of individual particles.

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Network analysis on the applications of magnetic nanoparticles for healthcare

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The current interplay between Physics, Chemistry, Engineering and Medicine could not be better exemplified than by the development of magnetic nanoparticles, which embodies a flourishing field that has moved quickly from just promising applications to an increasing number of ready-to-use technologies over the last decade. This advancement has been especially remarkable in biomedicine, where the achievement of bespoke magnetic nanoparticles has lead both to a significant improvement of well established techniques and groundbreaking inventions for the diagnosis and treatment of certain types of diseases. Obviously, the vast deployment done so far has left a sizeable trail of publications and patent documents that can be tracked through any of the available journal citation databases. The study of this complex bibliometric network constitutes a way to understand the origins of this recent research area, how it has been built and subsequently expanded as well as to glimpse the most likely future trends.

The present work reveals the outcomes of gathering, processing and interpreting the network formed by over three hundred thousand articles published in the field of magnetic nanoparticles collected from the Web of Science^{®1} database. The structure of the resulting network and the relationship between biomedical applications and the other most relevant areas in this topic is discussed. Other interesting findings related to collaboration and co-citation subnetworks are also highlighted. Finally, main paths representing the flow of knowledge throughout the whole network are identified.

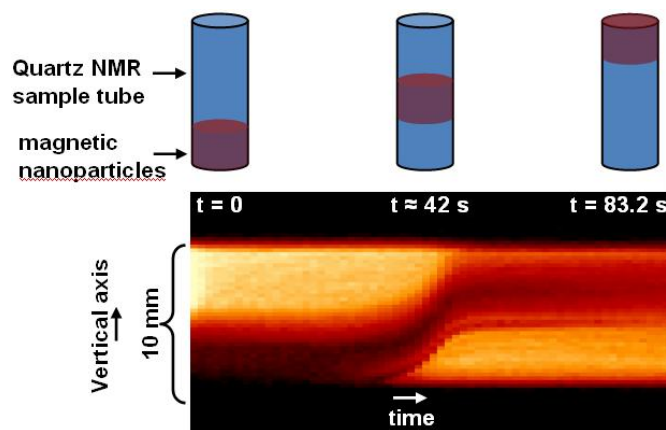
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Superparamagnetic Nanoparticles for Drug Delivery

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The use of magnetic fields for the delivery of chemotherapeutics bound to superparamagnetic nanoparticles offers a promising method for the non-invasive treatment of inoperable tumours. Studies of inflow magnetic targeting of superparamagnetic nanoparticles in plastic microcapillary films, representative of the human blood vessels, with different magnetic field geometries has yielded a computer model to optimise capture conditions [1]. We have demonstrated that superparamagnetic magnetite nanoparticles fabricated by an easily scalable method can be driven and tracked in real time at high velocities *in vitro* using MRI hardware [2]. Force balance calculations are consistent with the magnetic properties of individual 10 nm diameter particles that move collectively as micron sized agglomerates with hydrodynamic diameter similar to that inferred from zero-magnetic-field dynamic light scattering measurements. Magnetotactic bacteria are currently being explored as a potential future scalable source of monodisperse magnetic nanoparticles for therapeutic and biosensing applications.



2-D MRI manipulation of superparamagnetic iron oxide nanoparticles

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Selection of nanocrystalline oxides cores for magnetic fluid hyperthermia

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Magnetic fluid hyperthermia is based on the conversion of magnetic energy to heat mediated by loss processes, namely

- hysteresis power losses, originating in the irreversibility of the magnetization process
- Néel relaxation, conditioned by the spontaneous rotation of the magnetic moments of the particles,
- friction losses due to the Brownian rotation of the magnetic particles as a whole.

From the point of view of achieving the highest possible heating power it is thus necessary to adjust the parameters of the AC magnetic field to the characteristics of the system of particles or vice versa to tailor their properties to the available or admissible parameters of the AC field facility. Further regardless of the mechanism, the magnetic heating in the vicinity of T_c gradually decreases and it is switched off when the transition temperature is achieved. Therefore if the Curie temperature is suitably adjusted, this behaviour can be used as a mechanism of self-control and local overheating of the healthy tissue can be prevented. These intentions will be discussed on appropriately selected materials, namely

- magnetically soft magnetite
- magnetically hard cobalt ferrite
- cobalt-zinc ferrite solutions
- lanthanum – strontium manganese perovskite

with respect to their magnetic properties and the specific use in magnetic heating.

Functionalisation of iron oxide nanoparticles for biomedical applications and dendritic and phosphonate approaches to develop T₂ contrast agent for MRI

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Superparamagnetic iron oxide nanoparticles (NPs) with appropriate surface coating are widely used for numerous *in vivo* applications and in particular for MRI contrast enhancement. In the biomedical field, most studies are performed for improving the materials biocompatibility and ensuring multifunctionalization (targeting, imaging...), but only a few investigations have been carried out improving the quality of the magnetic NPs, their size distribution and studying the effect of their functionalization on their structural and magnetic properties. Indeed particle size, surface chemical structures and the nature of interactions of the organic coating with the NPs surface appear as critical parameters determining the blood half-life, opsonization, biokinetics and biodistributions of magnetic nanocrystals. Therefore, the design of the coating and the nature of the interaction of the coating with the NPs surface are more and more key points to address.

The main bioactive molecules grafted at the surface of iron oxide NPs will be described as well as strategies for conjugation of molecules and their effect on parameters such as the colloidal stability, biodistribution... Then a synthesis way based on dendritic and phosphonate approaches will be presented: phosphonate groups ensure a strong anchoring of dendron at the NPs surface with preservation of magnetic properties, and dendrons, in addition to their small size, are very promising as the diversity of functionalization brought by the arborescent structure simultaneously may solve the problems of biocompatibility, low toxicity, large *in vivo* stability and specificity.

Iron oxide NPs synthesized by co-precipitation¹ and thermal decomposition² were coated with three dendrons bearing PEG chains or carboxylate or amine-functionalized PEG chains to improve colloidal stability, graft fluorescent molecules and investigate cell interactions.^{3,4} Cell viability tests, relaxivity values, biodistribution studies and in-vivo IRM experiments have demonstrated the low toxicity of these dendronized nanoparticles and their interest as contrast agent.^{3,5}

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Magnetically responsive (nano)biocomposites and their applications

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Magnetic nano- and microparticles have already found many important applications in various areas of biosciences, medicine, biotechnology, environmental technology etc. These smart materials exhibit different types of response to external magnetic field. In most cases they can be described as composite materials, where the magnetic properties are caused by the presence of iron oxides nano- or microparticles. Such materials can be efficiently separated from difficult-to-handle samples and targeted to the desired place, applied as contrast agents for magnetic resonance imaging or used to generate heat during exposure to alternating magnetic field.

In addition to magnetic composites based on synthetic or inorganic materials, a large amount of magnetic biocomposites has been developed and used. In many cases magnetic fluids can be used to convert diamagnetic biological materials (e.g., microbial and algae cells, plant-derived materials etc.) into their magnetic derivatives. Alternatively the cells can be magnetically modified by binding of maghemite or magnetite microparticles on the cell surface, by specific interactions with immunomagnetic nano- and microparticles, by the biologically driven precipitation of paramagnetic compounds on the cell surface, by covalent immobilization on magnetic carriers, by cross-linking of the cells or isolated cell walls with a bifunctional reagent in the presence of magnetic particles or by entrapment (together with magnetic particles) into biocompatible polymers.

Magnetic biocomposites have been successfully used as adsorbents for the removal of both organic and inorganic xenobiotics, such as dyes, pesticides, heavy metal ions and radionuclides. Magnetically modified living microbial cells can serve as whole cell biocatalysts. Magnetic modification of biological materials enables to prepare stimuli responsive materials with a great potential for future applications.

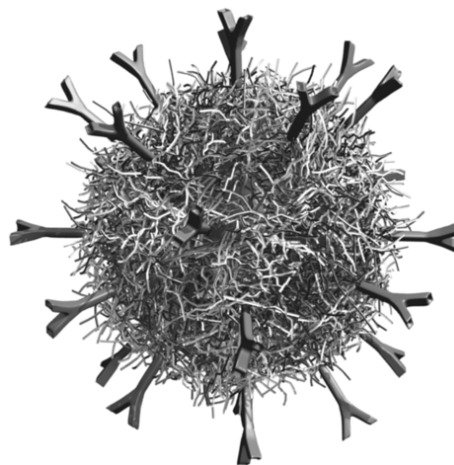
Targeted Delivery of Encapsulated Therapeutics using Nanoengineered Capsules

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Targeted delivery of drugs to specific cells in the body has the potential to revolutionise the treatment of many diseases. An emerging technique to deliver drugs is to immobilise the drug inside a nanocapsule, whereby the body is protected from potentially harmful side effects of the drug, while also preventing the drug from being degraded by the body. This technique has potential to treat a range of diseases, from HIV to cancer. To achieve this goal a number of key areas must be addressed in the design of the drug carrier, including the loading and release of drugs, as well as functionalisation with targeting molecules. Such nanoengineered capsules can be assembled using the layer-by-layer deposition of interacting polymers onto a sacrificial template particle. This technique allows for fine control over the properties of the capsule by altering the number of layers deposited, the material deposited at each layer, and also by controlling the assembly conditions. We have demonstrated that a number of therapeutics, such as DNA, proteins, peptides and anti-cancer drugs can be encapsulated within the LbL polymer shell and released in an active form both *in vitro* and *in vivo*.

One major challenge has been functionalising and targeting low fouling capsules specifically to cancer cells. We have recently developed a 'click' chemistry approach to functionalise capsules with targeting molecules, such as antibodies (Ab). Using these capsules we have demonstrated that Ab functionalised capsules specifically bind to cancer cells, even when the target cells are less than 0.1% of the total cell population. This precise targeting offers significant promise for drug delivery applications.



Liposome preparation using a hollow fiber membrane contactor - Application to spironolactone encapsulation

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In recent years, it has become more and more evident that the development of new drugs alone is not sufficient to ensure progress in drug therapy. A promising strategy involves the development of suitable drug carrier systems such as colloidal systems. In this study, we present a novel liposome preparation technique suitable for the entrapment of pharmaceutical and cosmetic agents. This new method was based on membrane contactor principle and used for the first time a hollow fiber module. The module conception increases the membrane surface and allows a uniform flow which may make easily the extrapolation of the results for an industrial production. In order to investigate the process, key parameters influence on the liposome characteristics was studied. It has been established that the vesicle size distribution decreased with the organic phase pressure decrease, the phospholipid concentration decrease and the aqueous to organic phase volume ratio increase. Liposomes were filled with a hydrophobic drug model, spironolactone, which could be used for a paediatric medication. The mean size of drug-free and drug-loaded liposomes was respectively 113 ± 4 nm and 123 ± 3 nm. The zeta potential of drug-free and drug-loaded liposomes was respectively -43 ± 0.7 mV and -23 ± 0.6 mV. High entrapment efficiency values were successfully achieved (93 ± 1.12 %). Transmission electron microscopy images revealed nanometric sized and spherical shaped oligo-lamellar vesicles. The release profile showed a rapid and complete release within about 5 hours. Additionally, special attention was paid on process reproducibility and long term lipid vesicles stability. Results confirmed the robustness of the hollow fiber module based technique. Moreover, the technique has a potential for continuous production of nanosized liposome suspensions at large scale, Thus it appears as a promising way to achieve important benefits in the logic of process intensification strategy.

Preparation of controlled particle-stabilized emulsion droplets using Rotary Membrane Emulsification

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Over the last decade, there has been a large interest in designing monodisperse encapsulating structures based on emulsion templates that can control the delivery of actives, in response to changes in their environment. Although many systems have been developed, very few actually reach the manufacturing stage, primarily due to the complexities in producing these highly functional capsules that are required.

Membrane emulsification is an attractive approach as it produces monodisperse emulsions (Figure 1) and can easily be scaled up. In this process the oil phase is pushed through a porous membrane into the continuous phase containing a dispersion of the particles. As the droplets grow from the pores the particles adsorb to the oil-water interface and provide colloidal stability to the newly formed interface.

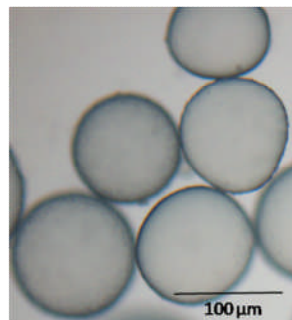


Figure 1: Silica stabilised emulsion droplets produced using Rotary Membrane Emulsification.

In this study it is illustrated that under optimal conditions highly stable emulsion droplets, with a narrow droplet size distribution can be produced using silica colloids [1]. The effects of numerous mechanical and chemical properties have been investigated to demonstrate the control over the mean droplet size.

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FACS Based High Throughput Screening Systems for Gene Libraries in Single and Double Emulsions

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Throughput of screening system is the most limiting step of directed enzyme evolution and crucial for finding improved enzyme variants. Most often screening is performed inside wells of microtiter plates and can be applied to almost any enzyme for which there is an enzymatic assay, but it limits the size of gene library that can be screened to up to 10^4 . *In vitro* compartmentalization technology (IVC) where fluorescent enzymatic reaction is performed inside water microdroplets of single and double emulsions, enables screening of gene libraries at very high rates of 10^7 droplets per hour, using fluorescence activated cell sorter (FACS). Despite IVC's general application potential there are still a lot of problems in applying this technology for screening industrially important enzymatic activities in emulsion systems¹.

These problems will be addressed and discussed with respect to results that we obtained during developing FACS based screening systems for glucose oxidase (GOx) in single and double emulsions. One of the developed screening systems represents a novel fluorescent assay for glucose oxidase (GOx) that can fit to requirements of FACS screening in double emulsions. Other ultrahigh-throughput screening system is based on fluorescent labelling of yeast cells expressing GOx in single emulsions and afterwards sorting of labelled cells by FACS². Performance of both screening systems was checked by screening GOx error prone PCR mutant libraries containing 10^7 cells with $\sim 10^5$ of different GOx variants. GOx variants with increased expression level and increased activity were found (1.2 times decreased K_m and a 2.7 fold increased k_{cat} compared to wild type GOx).

Further improvements of emulsion based HTS technology for screening of higher enzymatic activity and possibilities of applying developed screening systems for other enzymes (oxidases, glycosidases) and sorting devices (microfluidics) will be discussed.

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Microparticles with Bimodal Nanoporosity Derived by Emulsion Templating

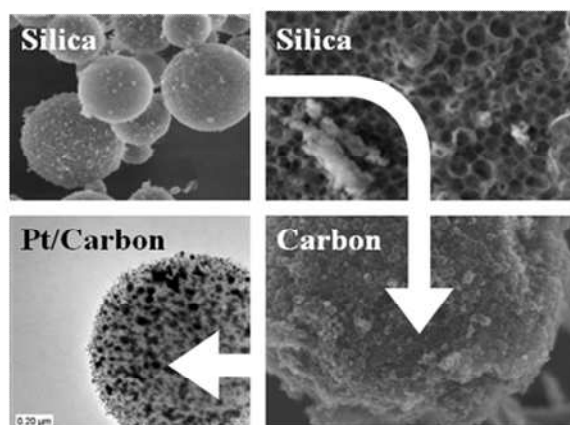
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Microfluidics allows for the generation of small micrometer sized monodisperse droplets. Such droplets can be used as tiny reactors for material synthesis or analytical applications on a large scale. In this study we report data on using droplet microfluidics for fabrication of mesoporous silica particles with porosity that varies between a few nanometers and a few tens of nanometers. Aqueous droplets containing silica precursor and surfactants are formed in an oil continuous phase. The water is then expelled out of the droplets leading to solidification of the silica. The concentrated surfactants form structures, which are templated by the oxide forming a network of pores. Varying the conditions like surfactants type and concentrations and/or presence of electrolytes allows obtaining a wide range of pore morphologies. Certain surfactant compositions lead to sharp drop of the interfacial tension, which leads to formation of microemulsions. Tuning of the microemulsion phase that is used for templating, may result in biporous particles.

The obtained silica particles are then used as template to fabricate mesoporous carbon or carbon-Pt microparticles using a “lost-wax” technique (see the figure below.) These particles have shown very promising properties as electro-catalysts for fuel cells.



Colloid flow control in sub-micrometer channels and detection by laser scattering

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Single particle flow control, counting and sizing in fluidic specimens is of paramount importance in environmental, industrial and clinical analysis, on-chip particle synthesis and biological sciences. ^[1] Micro- and nano-fluidics ^[2] are emerging technologies that rely on biocompatible and low cost materials and mass production fabrication processes and allow the exploitation of tiny liquid volumes and low analyte concentrations. On the other hand laser-light-scattering is a well established detection technique that offers a non-invasive tool for the counting of micro- and nano-particles such as polymer colloids, blood cells and viruses. ^[3]

We introduce a new approach for the fabrication of hybrid polydimethylsiloxane (PDMS)/glass microfluidic chips equipped with arrays of sub-micrometer channels (with minimum feature size down to 600 nm) of tuneable cross section and aspect ratio. ^[4] We are able to control the flow of polymer colloids (i.e. polymethylmethacrylate and polystyrene) in our microfluidic chips by means of a computerized pressure-based flow control system. Imaging and detecting the colloid flow direction through the sub-micrometer channels is achieved by laser-light-scattering in a restricted region of a single channel. We demonstrate the possibility of sizing populations of colloids with different dimensions down to 50 nm and propose the presented approach as a cheap and rapid tool toward the *in situ* filtering of colloids.

The improvement of the presented technology, for example with the exploitation of nanofluidic channels, could open the way for the on-chip sizing of colloids with dimension of down to ten nanometers thus offering on-the-fly capability to optimize colloid reaction synthesis and non-invasive screening of colloid interactions and aggregation in quasi 1-dimensional confined systems.

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Micromanipulation and release properties of biomineralised double-shell microcapsules

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The purpose of this work is to develop novel double-shell microcapsules, whereby the inner shell defines the release profile of the encapsulated active, and the outer shell acts as protector and initiator of the active release via reaction to mechanical or environmental triggers.

Initial studies focused on the development of poly(methylmethacrylate) (PMMA) microcapsules containing hexyl salicylate as a model oil. The capsule wall thickness was varied and characterised using transmission electron microscopy (TEM), and the subsequent effects on the mechanical strength and release properties of the capsule were studied via micromanipulation¹ and active release analysis².

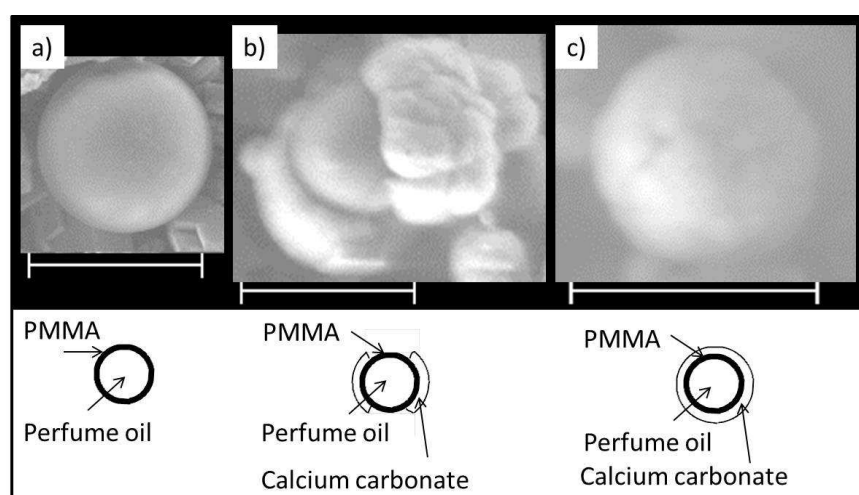


Figure 1. SEM images and schematics of a) single wall PMMA microcapsule, b) end-capped PMMA-calcium carbonate microcapsule, and c) double-shell PMMA-calcium carbonate microcapsule (20 μm scale bar).

The surface of the inner PMMA microcapsule (Figure 1. a)) was then seeded and subsequently coated with a layer of calcium carbonate to form a second wall. This biomineralisation procedure was initiated via nucleation of the polymer surface with calcium carbonate, followed by end capping (Figure 1 b)) and finally full surface coverage by calcium carbonate resulting in the second wall formation (Figure 1 c)). The change in both the strength and release properties of the resulting double-shell capsules were then analysed via micromanipulation and active release studies, and compared with previous results.

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Complex emulsions as a template of new hybrids particles for bionanotechnology applications

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The colloidal particles are not only under evaluation in various biomedical applications, but they are really used in various biomedical levels¹: (i) They are used in rapid diagnostic tests based on agglutination process². (ii) Cationic particles (i.e magnetic latexes) are principally used in nucleic acids extraction and concentration. (iii) Cell sorting and identification using magnetic or fluorescent particles, (iv) Viruses extraction and detection via hydrophilic and charged magnetic particles. (V) General particles (mainly carboxylic in surface) are used in immunoassays and specific capture of single stranded DNA fragments³.

In addition, magnetic hybrid particles prepared from double emulsions based process are now explored in various in vivo applications such as in magnetic resonance imaging.

In vitro biomedical applications, the specificity and the sensitivity of the targeted application efficiency are directly related to the surface particles properties and to the accessibility of the immobilized biomolecules. The interactions between biomolecules and reactive particles are strongly dependent on the colloidal and surface properties of the dispersion, and the physico-chemical properties of the biomolecules. In this direction, considerable attention has been paid to the preparation of magnetic latex particles for biomedical applications. Indeed, these composites particles are commonly used in immunoassays as solid phase supports for the immobilization of biomolecules such as oligonucleotides, proteins or antibodies. The main advantage of colloidal magnetic particles in nanobiotechnologies is due to their separation upon applying an external magnetic field⁴.

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Short-molecule stabilisation of indium tin oxide nanoparticles for highly stable colloidal dispersions

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Indium tin oxide (ITO) nanoparticles play a very important role in many fields of application, especially in electronic devices due to their good conductivity in combination with transparency. Besides the gas phase deposition processes carried out today, solution-based coating and printing techniques would be highly attractive for the fabrication of ITO coatings, for they would offer high flexibility and low cost and could also be applied e.g. to flexible polymer substrates. A prerequisite for the fabrication of transparent ITO coatings from dispersion is high stability of the nanoparticles against agglomeration. Depending on the type of dispersion medium (hydrophobic or hydrophilic), electrostatic, steric or electrosteric forces are utilised to prevent the particles from agglomeration. The strength of interaction between the particles strongly depends on the particle size. In the case of nanoparticles < 50 nm in size, the adsorption of short-chained organic molecules at the particle surface is sufficient to prevent the particles from agglomeration. This so-called small-molecule stabilisation strategy, resulting in a very thin organic shell of the nanoparticles, is a highly attractive concept, as the effective volume of the particles is not influenced by a shell, which in principle enables the preparation of highly concentrated dispersions. Furthermore the intrinsic properties of the particles are not isolated by an organic shell and can be maintained.

The main goal of this work is to gain a deeper understanding of the interrelation of the adsorption of the stabiliser molecules and the deagglomeration and stabilisation of the particles. Indium tin oxide nanoparticles < 10 nm serve as a very interesting and application-relevant system. Through a straightforward post-synthetic stabilisation strategy, we managed to achieve stable colloidal ITO dispersions with completely freestanding nanoparticles in a variety of media ranging from water to hydrophobic solvents. These dispersions appear highly suitable for the low-temperature fabrication of thin films for different kinds of application like printable electronics.

Fabrication of biodegradable poly(lactic acid) particles in flow focusing glass capillary devices

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Poly(DL-lactic acid) (PLA) particles with a diameter in the range from 12 to 100 μm were fabricated in flow focusing glass capillary devices shown in Figure 1. The disperse phase was 5% (w/w) PLA in dichloromethane (DCM) containing small amount of Nile red and the continuous phase was 5% (w/w) poly(vinyl alcohol) in Milli-Q water. The two immiscible liquids were introduced from the two ends of the same square capillary in opposite directions and both liquids were collected and exit through the inner circular capillary. The disperse phase was hydrodynamically flow focused by the continuous phase in the tapered section of the circular capillary, which caused the disperse phase to break into drops inside the collection tube. PLA particles were formed by DCM evaporation at room temperature. In order to prevent wetting of the collection tube with the disperse phase, the hydrophilicity of the glass surface was enhanced by 2-[methoxy(polyethyleneoxy)propyl]trimethoxysilane. Experimentally, we show that the droplet size is influenced by the operating conditions and orifice size, as shown in Fig. 1. The drop formation occurs near the orifice in the dripping regime (Fig. 1a-b) and farther downstream in the jetting regime (Fig. 1c). The drops formed in the jetting regime are significantly bigger than those formed in the dripping regime and have a broader size distribution.

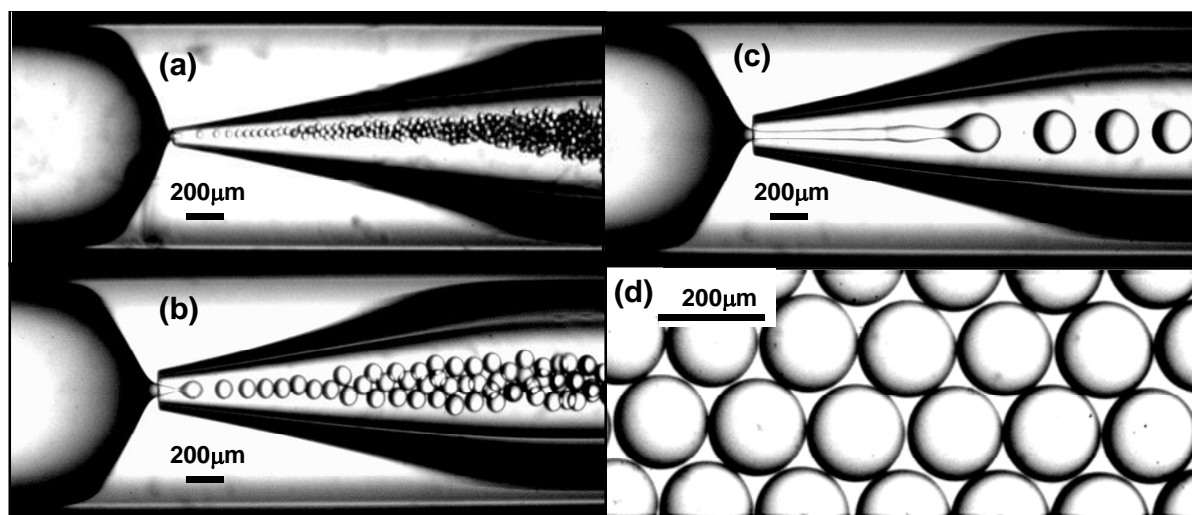


Fig. 1. (a) $Q_c=0.5 \text{ mL h}^{-1}$, $Q_d=0.003 \text{ mL h}^{-1}$, $d_{\text{orifice}}=60 \mu\text{m}$, $d_{\text{droplet}}=33 \mu\text{m}$. (b) $Q_c=5 \text{ mL h}^{-1}$, $Q_d=1 \text{ mL h}^{-1}$, $d_{\text{orifice}}=130 \mu\text{m}$, $d_{\text{droplet}}=100 \mu\text{m}$. (c) $Q_c=6.5 \text{ mL h}^{-1}$, $Q_d=0.7 \text{ mL h}^{-1}$, $d_{\text{orifice}}=130 \mu\text{m}$, $d_{\text{droplet}}=230 \mu\text{m}$. (d) Collected monodispersed droplets.

The work was supported by the Engineering and Physical Sciences Research Council (EPSRC) of the United Kingdom (grant reference number: EP/H029923/1)

Crystallization of binary colloidal monolayers with adjustable configurations at the air-water interface

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Colloidal monolayers with high order and increased complexity beyond plain hexagonal packing geometries are useful for 2D templating of surface nanostructures and lithographic applications.

Here, we present a method for the crystallization of binary colloidal monolayers featuring a close-packed monolayer of large spheres (L) with a superlattice of small particles (S) at the air water interface using a Langmuir trough.^[1] The fraction of the respective particles at the interface can be determined from the surface-pressure area isotherms and used to precisely adjust the stoichiometry of the two particle types at the air-water interface.

This leads to a high degree of control over the occupation of the interstitial sites in the close-packed layer of large spheres by the small colloids. Thus, large areas of binary 2D crystals with a single small colloid in the interstitial sites (LS₂ configuration), triplets of small particles (LS₆) and bridget triplet structures (LS₉) structures are prepared in a controlled way (Figure 1). The process allows the formation of binary crystals over a wide range of particle size ratios $d_{\text{small}}/d_{\text{large}}$ from 0.19 to 0.40.

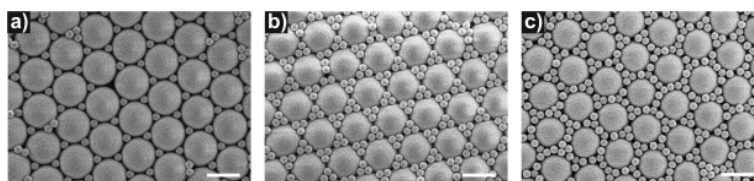


Figure 1. Binary monolayers consisting of 1063 nm and 225 nm poly-styrene colloids with LS₂ (a), LS₆ (b) and LS₉ configuration.

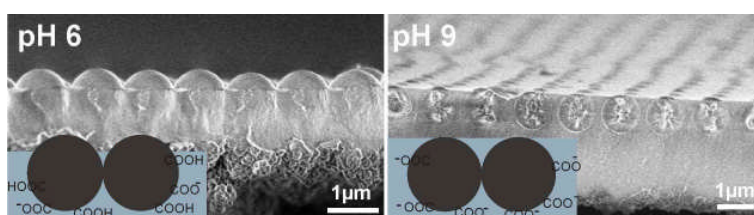


Figure 2. Interfacial polymerization of butyl cyanoacrylate to directly image the contact angle of the colloids at the interface.

The pH value of the subphase can be used to enhance the crystallization process by changing the contact angle of the particles at the interface, leading to different volumes of the interstitial sites available for the small colloids. An interfacial polymerization of butyl cyanoacrylate is used to directly image the contact angle of the colloids at the interface (Figure 2). Transfer to solid substrates is achieved by a surface lowering technique. A variety of substrates with arbitrary topographies can thus be decorated with colloidal monolayers. Applied to lithographic processes, such monolayer architectures allow the generation of complex patterns, not accessible with conventional close-packed monolayers.

Hydroxyapatite nanoparticle-amored biodegradable polymer microspheres fabricated via Pickering emulsion route

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HAp is one of the calcium phosphates and the main mineral of bones and teeth in vertebrate, and artificially synthesized HAp has been extensively used in a variety of applications, such as biomaterials, ion exchangers, adsorbents and catalysts by exploiting their biocompatibility and adsorbability with many compounds. Recently, we have reported the preparation of oil-in-water Pickering-type emulsions using hydroxyapatite (HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) nanoparticles as a particulate emulsifier in the absence of any molecular surfactant [1].

In this study, we describe the first synthesis of HAp nanoparticle-biodegradable polymer nanocomposite microspheres via Pickering emulsion route [2-5]. The HAp nanoparticles were employed as a particulate emulsifier in order to prevent flocculation of emulsion droplets/microspheres as well as to give high cell adhesive property to the biodegradable polymer microspheres obtained. Cell adhesion experiment indicated that the microspheres showed high cell adhesiveness and should be useful for a variety of biomedical applications including drug delivery system, cell carrier and scaffold. The synthetic method described in this study needs neither molecular surfactant nor polymeric stabilizer, which is usually used to synthesize/stabilize the microspheres in media and has possibilities to cause allergy-like reactions and carcinogenicity at the same time.

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Novel method of producing highly uniform silica particles using inexpensive silica sources

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In the last few years there has been increasing interest in the production of porous inorganic materials with high surface area. Such materials have potential application in various fields of catalysis, separation, sorption, bioreactor, sensors and so on. Silica is an inorganic material that does not swell and with its good mechanical and thermal stability it can be used in various solvents and have wide applications. In the literature silicon alkoxide or tetraethoxysilane are mainly used as silica sources. The main drawback of using such materials is that they are expensive and therefore production of large quantities of silica would not be cost effective.

In this work silica droplets were successfully produced using The Dispersion Cell with a hydrophobic nickel membrane attached on the bottom of the cell (Fig. 1 a,b). Inexpensive sodium silicate and sulphuric acid were used as silica source (dispersed phase) and kerosene containing 2% Span 80 was used as continuous phase.

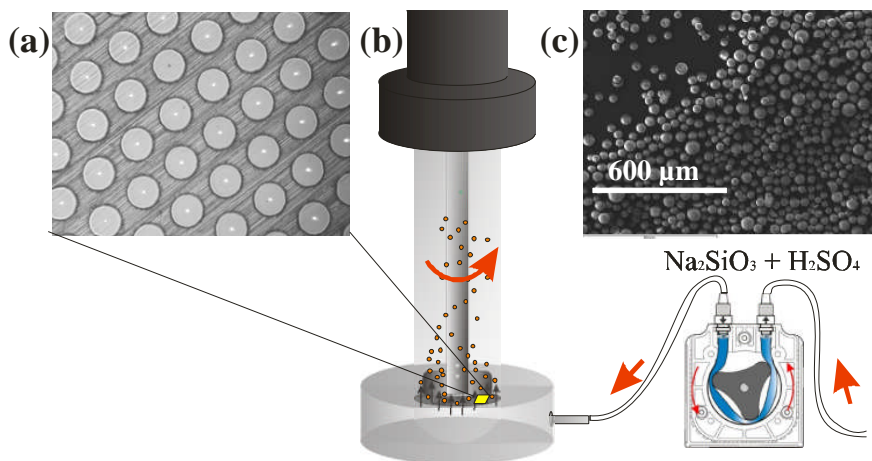


Fig. 1. (a) Hydrophobic nickel membrane with 15 μm pores and (b) Dispersion Cell both kindly provided by Micropore Ltd. UK. (c) SEM of calcined silica particles

By changing the shear stress on the membrane surface liquid silica droplets in the range between 50 and 160 μm were produced. After solidification of silica the particles were washed and dried at room temperature followed by calcination at 550°C. After final drying the produced silica particles were in the range between 30 and 70 μm (Fig. 1c). BET specific surface area of the produced silica after calcination was found to be 750 m^2/g while the average pore diameter was 1.3 nm.

The authors wish to acknowledge the financial support of the UK Engineering and Physical Sciences Research Council. The work was undertaken as part of the DIAMOND project into Decommissioning, Immobilisation And Management Of Nuclear wastes for Disposal.

Multilayer microcapsules based on supramolecular structures produced from bovine serum albumin and high methoxy pectin

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Microcapsules with multilayer shells were produced using supramolecular structures made from bovine serum albumin (BSA) and high-methoxy (HM) pectin. Two supramolecular structures were used: spherical soluble complexes of BSA-HM pectin and semi-flexible BSA fibrils. At pH 4, the fibrils are positively charged, while the complexes are negatively charged. By alternately adsorbing complexes and fibrils onto an emulsion droplet, microcapsules with different number of layers were formed. The microcapsules were characterized in terms of their size distributions, zeta potentials, morphology and mechanical strength. SEM images show that with increasing number of layers, the thickness of the shell increases, leading to stronger microcapsules. The rheological properties of oil/water interfaces stabilized by the supramolecular structures were characterized using shear and dilatational rheology. It was observed that interfaces stabilized with BSA/pectin soluble complexes have a higher surface dilatational elastic modulus and surface shear elastic modulus, than those stabilized by BSA fibrils. Both supramolecular structures form interfaces which are mechanically stronger than those stabilized by native BSA monomers. This implies that these structures are more effective for creating microcapsules with strong shells. The microcapsules produced by layer-by-layer adsorption of soluble complexes of BSA-HM pectin and BSA fibrils described here can be applied in a food system.

Nanoemulsification via Ultrasound

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Nanoemulsions have found increasing attention in recent years due to their unique properties caused by their nanoscale drop size and their wide range of application. Despite this, an in-depth investigation of different aspects of nanoemulsification has not been reported yet. In this contribution, the underlying mechanisms of drop formation via ultrasound and shelf stability of nanoemulsions are discussed.

A range of silicon oils with viscosities in the range of 0.65-100cSt and hydrocarbon oils with different chain lengths were used as model oils and sodium dodecyl sulphate (SDS) was used as surfactant. The drop size variations were studied during sonication (formation stage) and post sonication (growth stage). Sonications were conducted under isothermal and non-isothermal conditions. Isothermal sonication was found to be a pre-requisite to obtaining fine nanodrops. Non-isothermal sonication of emulsions containing low-boiling point oils, such as hexane and octane, resulted in extensive formation of cavities and their propagation in the emulsion (Figure 1). The results show a U curve for the final drop size vs. viscosity ratio (viscosity of the dispersed phase to that of the continuous phase), a pattern not reported previously (Figure 2). The average drop size decreases sharply with increasing viscosity ratio for values smaller than 1, but reaches a plateau for values between 1 and 3. This U trend was theoretically reproduced using the theory developed by Bentley and Leal (Figure 2). Also, it was found that monomodal drop size distributions (DSD) were formed during sonication of low viscosity oils while binary DSDs formed for oils with higher viscosity (Figure 3). This clarifies that the breakup mechanism changes from bursting at low viscosity ratios to end pinching at high viscosity ratios.

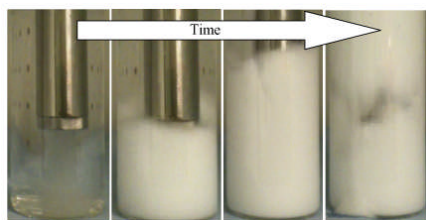


Figure 1. Extensive cavitation during sonication of water/SDS/hexane.

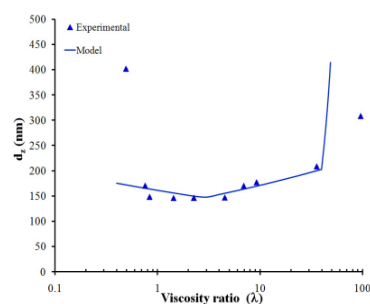


Figure 2. Variation in drop size vs. Viscosity ratio (0.5 vol% O/W ratio and 1.0 g/l SDS).

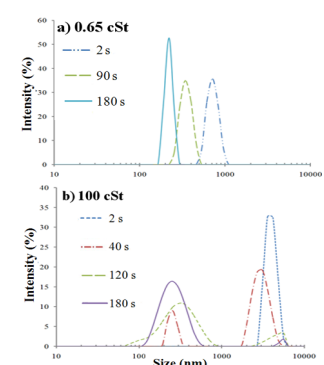


Figure 3. DSDs of emulsions produced with a) 0.65cSt and b) 100cSt.

Furthermore, it was found that Ostwald ripening (OR) and coalescence simultaneously contribute to destabilization of drops during both formation and growth stages.

Uniform Drops by Microchannel Emulsification

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In recent years, there has been increased interest in the formulation of uniform emulsion droplets using a wide range of techniques such as membranes and microchannels. In such systems drop rupture is usually controlled by shear. In this research, droplet formation under the influence of buoyancy force in a single microchannel is studied. A single microchannel device was simulated by injecting the dispersed phase liquid (n-alkane) into a static continuous phase comprising various concentrations of sodium dodecyl sulfate (SDS) in water. The effect of important process parameters such as the flow rate of the dispersed phase, the type of oil used as the dispersed phase liquid, the microchannel diameter, and the concentration of surfactant, on the droplet size and size distribution was investigated using images captured with a high-speed camera (Fig.1). It was found that droplet diameter initially increases with increasing dispersed phase flow rate, up to a critical value, and then reduces at higher feed flow rates. The polydispersity of the resulting micro-droplets continues to increase with dispersed phase flow rate. At extremely low feed flow rates, where the buoyancy force is the main cause of drop detachment, drops were obtained with the maximum uniformity. The surfactant concentration significantly affected drop size and uniformity. At high surfactant concentrations, however, the drop size depends only on the feed flow rate (Fig.2.). With regard to the effect of channel diameter on droplet size, it was found that using needle with smaller diameter gives smaller droplets but at the expense of higher polydispersity.

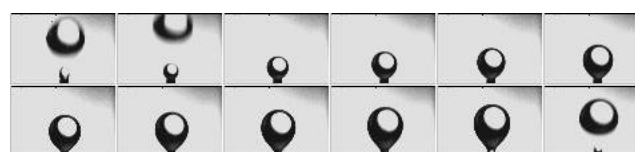


Fig.1. Formation of droplets.

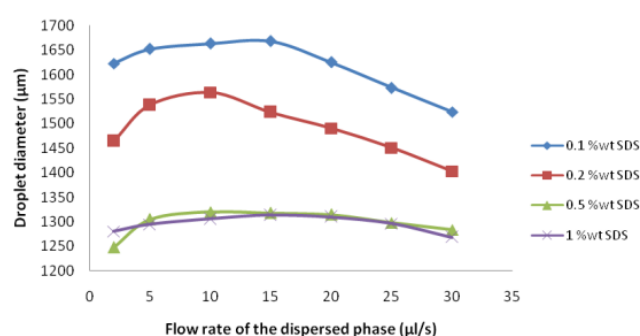


Fig.2. Drop size variations with dispersed flow rates for different concs. of SDS

Gold Nanoparticles-Based Point-of-Care Diagnostics

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Point-of-care (POC) diagnostics are expected to revolutionalise the health care industry by diagnose diseases directly of patients and the general public. The key advantage of POC diagnostics is that they are rapid, simple, cost-effective and accurate devices that can diagnose diseases of interest at a point of need with minimal infrastructure. The technology is also expected to improve the quality of life of individuals in developing countries, where people are suffering due to the lack of advanced diagnostic tools. POC diagnostics have further the potential to rapidly diagnose diseases at an early stage of infection.

Mintek, through DST/Mintek Nanotechnology Innovation Centre, has established active research groups focusing on designing and developing various POC tests for both animal and human diseases. Advanced noble metal nanoparticle systems, in particular gold nanoparticles are produced in our laboratories in large quantities and used extensively as probes in developing robust lateral flow and electrochemical diagnostic POC tests. Due to the stability and robustness of gold nanoparticle systems, several detection platforms can be used to detect or monitor various diseases or analytes to a point of meeting industrial demand. The progress made today and future prospects in developing gold nanoparticles-based POC tests will be presented.

Manipulating fluids for fabricating functional materials

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The processing and manufacture of many colloidal systems, such as solid dispersions, and emulsions, involves fluids; the ability to manipulate fluids therefore enables generation of complex colloidal systems. Advances in microfluidics suggest new ways to engineer colloidal systems with unprecedented degree of control. By employing drops and jets as templates, materials with complex structures have been generated with high uniformity. The ability to continuously and reliably generate these structures makes microfluidics ideal not only for fabricating conventional materials more efficiently, but also for exploring new types of materials. By combining the microfluidic approach with existing techniques in colloidal science, novel functional materials are formed. I will describe approaches for forming monodisperse single and multiple emulsions using microfluidics and introduce ways to use these emulsions as templates for generating functional materials, which include particles, capsules, and vesicles for encapsulation and release of actives, sensor applications, and material synthesis. In particular, I will describe how double emulsions can be used to generate robust polymersomes with both single and multiple compartments. I will conclude the talk with some challenges in applying these techniques and describe current efforts to meet these challenges.

Remotely Controlled Hydrogel Sponges

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The aim of the work is to synthesize thermo-responsive sponge-like structures with oil micro-drops locked within their pores. The change of temperature will lead to the variation of hydrogel local properties (like porosity, pore diameter), and consequently to the releasing of the encapsulated oil content. Poly-N-isopropylacrylamide (PNIPAM) hydrogel was used to synthesize such structures due to its ability to undergo volume expansion/contraction at the LCST. The oil content was incorporated into the hydrogel structure before polymerization by forming O/W emulsion with the solution of monomers.

In order to effectuate “remote control” of the polymer volume change, citric acid stabilized Fe_2O_3 nanoparticles were incorporated into the hydrogel structure. Upon application of an external electromagnetic field, the magnetic nanoparticles will heat up locally and inducing a transition from the expanded to the collapsed state of the polymer.

The hydrogel microstructure and oil dispersion within it will be investigated by SEM and confocal microscopy, respectively. The kinetics of the oil content releasing from the micro-sponges was investigated by time-dependent UV/VIS spectrophotometry.

Fabrication of Colloidal Grid-Pattern Network by Two-Step Convective Self-Assembly

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Patterning of colloidal particles into ordered structures is a fundamental technique for various applications, including optical materials, photonic crystals, and sensors. In a typical approach, physically or chemically pre-modified substrates are utilized to assemble particles into a desired configuration. However, these approaches involve a sequence of complicated manufacturing processes and require costly facilities. On the other hand, bottom-up approaches provide one with simple and inexpensive routes to fabricating colloidal structures.

In the present study, we explored a “template-free” approach to arranging colloidal particles into a network pattern by a convective self-assembly technique, which is one of the attractive self-organization processes. In this approach, which we call “two-step convective self-assembly (Fig.1),” a stripe pattern of colloidal particles is first prepared on a substrate by immersing it in a suspension (Fig.2a).^[1] The substrate with the stripes is then rotated by 90° and again immersed in the suspension to produce stripes perpendicular to the first ones, resulting in a grid-pattern network of colloidal arrays (Fig.2b). The width of the colloidal grid lines can be controlled by changing the particle concentration while maintaining an almost constant spacing between the lines. Our method is applicable to various types of particles, including silica, gold, silver, and polymeric particles. In addition, the wide applicability of this method was employed to create a hybrid grid pattern.^[2] A possible application of the grid pattern is transparent conductive materials.

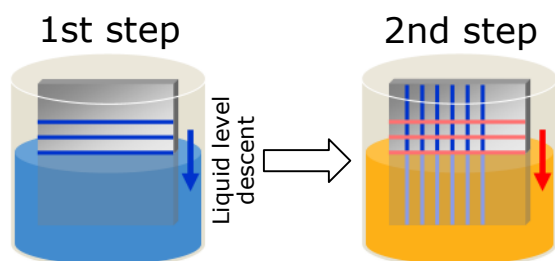


Fig. 1. A schematic of two-step convective assembly method for the fabrication of grid patterns.

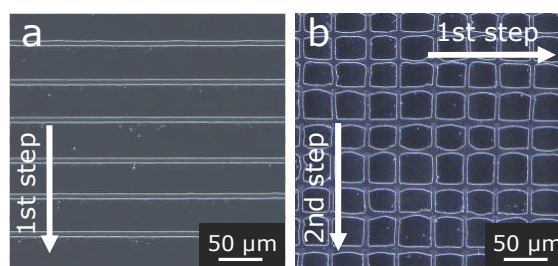


Fig. 2. Optical micrographs. a) Stripe pattern of 120 nm silica particles. b) Grid pattern of 120 nm silica particles.

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Liquid Marbles Stabilized by Particle Assemblies with Liquid-Repellent Character

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Colloidal particles have been known to be adsorbed at fluid interfaces and stabilize dispersed systems consisting of two immiscible fluids, represented by emulsions of oils and water¹. Dispersed systems of air and liquids can be also prepared using colloidal particles; liquid-in-air materials (liquid marbles, dry liquids) are formed if particles are relatively liquid-phobic, while air-in-liquid materials (foams) are made if particles are relatively liquid-philic. We have shown nearly spherical particles of oligomers of tetrafluoroethylene, which are physically agglomerated in air, possess so-called re-entrant structures that suspend air-liquid surfaces between the particles and generate high liquid repellency due to composite surfaces of air and the particles². The liquid-repellent particulate agglomerates stabilize oil-in-air materials such as oil marbles and dry oils.

Here we report that fused spherical glass beads made by heat treatment also show liquid repellency as a result of the formation of air-bead composite surfaces. The wetting transition of liquids on the bead assemblies in air occurs between the heterogeneous wetting (metastable Cassie-Baxter state) and the complete wetting (Wenzel state), depending on the bead surface chemistry, liquid properties and distance of beads in the assemblies. Liquid marbles are stabilized as a result of adsorption of the assemblies with liquid-repellent surfaces.

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Dynamic forces between sterically stabilized oil droplets: How important is the polymer brush?

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Polymeric stabilisers are common in many processed products ranging from pharmaceuticals and engine lubricants to formulated foods and shampoos^{1,2}. In particulate systems, steric stabilization provides a repulsive force that arises from the compression of the polymer brush, which screens the influence of attractive surface forces, such as the van der Waals force. This mechanism has dictated polymers design and selection for more than thirty years, and yet the mechanisms behind steric stabilization in emulsions systems may be fundamentally different or even counter intuitive compared to particulate systems. For the interactions between two drops, we show that the interplay between drop deformation, hydrodynamic drainage and steric forces combine to make their behaviour and emulsion stability much less sensitive to polymer architecture and yet a far more complex interaction than in rigid systems.

We present direct force measurements between two oil droplets coated with an amphiphilic tri-block co-polymer as a function of collision speed using Atomic Force Microscopy (AFM). At slow collision speeds we show the contributions to the observed forces show little dependence on the steric force law and are far more dependent on the drop deformation. At higher collision speeds, the observed force is sensitive to the amount of drainage of liquid through the brush. Simple constitutive models for both force² and drainage³ behaviour of the steric layer have been incorporated into an existing physical model⁴ to describe the interplay between droplet deformation, surface forces and hydrodynamic drainage to quantitatively analyze the AFM force measurements. These results demonstrate the importance of accurately understanding the role of deformation when involving steric stabilization in soft matter systems.

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Self-assembly in solution of silica-based hybrid materials: contribution of *in-situ* SAXS studies

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Surfactant templated mesoporous silica powders have been extensively studied in the past 15 years by exploiting the self-assembly properties of amphiphilic molecules in aqueous medium. The large success of these systems mainly relies on the apparent simplicity that enables to design porous networks with different architectures and pore sizes. However, a better control of the final nanostructure (2D-hexagonal, 3D-cubic) requires a deeper understanding of the interaction mechanisms between the templating agents and the network-forming species.

This work will show our latest experiments using *in-situ* Small Angle X-ray Scattering (SAXS) performed with highly brilliant synchrotron radiation to follow the formation mechanism of templated silica powders in the presence of different types of surfactants (non-ionic triblock copolymers, non-ionic fluorinated surfactants, cationic surfactants with different polar head groups) and silica precursors. This type of experiments give access to a lot of information about the cooperative self-assembly of these systems and the nanostructure formation. We will emphasize how the inorganic precursor affects the micelles in solution (prior to, during and after hydrolysis of the precursor) and how the micelles shape is linked to the final nanostructure of the hybrid material.

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Confined drying of polymer solutions

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We developed an original tool for the rapid screening of phase diagrams of polymers and surfactant solutions. Our technique is based on *the controlled drying of a droplet solution in a confined geometry* (Figure 1). The surfaces of the wafers are hydrophobic thanks to an appropriate coating, to avoid the pinning of the contact line of the droplet. The confinement casts a well-defined timescale τ to the drying kinetics, mainly governed by the wafer's area. Indeed, water removal only occurs through a diffusive process from the droplet to the edge of the wafer.

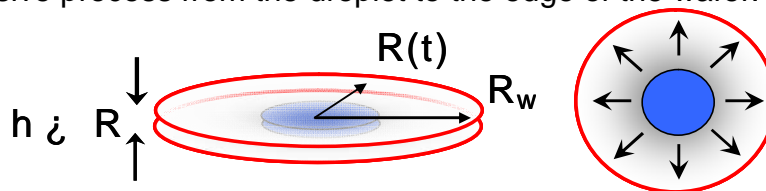


Figure 1: the sample cell consists of two circular glass plates (diameter ~8cm) between which a liquid droplet is squeezed; the gap is controlled by thin linear spacer (~75 μ m)

We studied the drying of an aqueous solution of a tribloc copolymer (Pluronic, P104) thanks to three different techniques: microscopy combined with crossed-polarizer, fluorescent microscopy and Raman imaging. The first technique allows us to follow the drying kinetics of our model system (Figure 2). We also investigated the evolution of the droplet area as a function of time and for several experimental conditions, and compare these results to simple 2d models. Our results point out that the solution mainly evaporates as pure water (no activity), up to stop abruptly at a final concentration of ~ 80%wt.

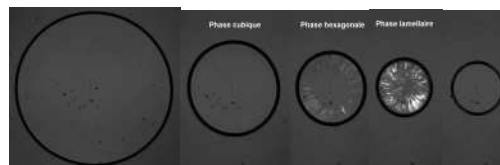


Figure 2: Typical snapshot of evaporation with crossed-polarizer. A succession of isotropic, cubic, lamellar, hexagonal and isotropic mesophases can be identified.

Fluorescent microscopy allows us to track tracers inside the droplet, and to identify unambiguously hydrodynamic recirculations probably due a Marangoni solutal effect. Finally, space and time resolved Raman spectroscopic measurements performed during drying. This technique thus permits to draw quantitatively, using a single confined drop, the phase diagram of the copolymer solution, with an accuracy of about 3%. This is especially interesting, for concentrated regimes where the solution is extremely viscous and hard to handle. Our next goal is to investigate using our tools, more complex systems (metallic nanoparticles/copolymers), and to form interesting organized mesophases, that may present unusual optical properties.

Neutron Reflectivity Study of the Calcite-Water Interface

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The interface of CaCO_3 (calcite) and water is of paramount importance in a number of key academic and industrial areas such as scale deposition in domestic and industrial situations and controlled growth of biogenic skeletons. We have investigated this interface and adsorption of key organic compounds to it using neutron reflection. This technique has proved to be an outstanding approach for the study of several particular solid/liquid interfaces allowing investigation of surface layers with molecular precision, but we believe this is one of the first times this technique has been applied to this important interface.

Here we present results from adsorption at the calcite-water interface, particularly irreversible adsorption of polyacrylate with a simultaneous increase in surface roughening with the sodium salt. This surface roughening could be reduced by using the polyacrylate calcium salt. A diffuse layer of up to 200 Å thickness with increasing polyacrylate concentration was observed.

In addition, bilayers of aerosol-OT (AOT) adsorbed from water as a function of aerosol-OT concentration and added electrolyte were observed (see Figure 1). At high AOT concentrations, significant off-specular scattering was observed which can be interpreted as an adsorbed lamellar phase with conformal roughness, reminiscent of the equivalent system on silicon/silica.

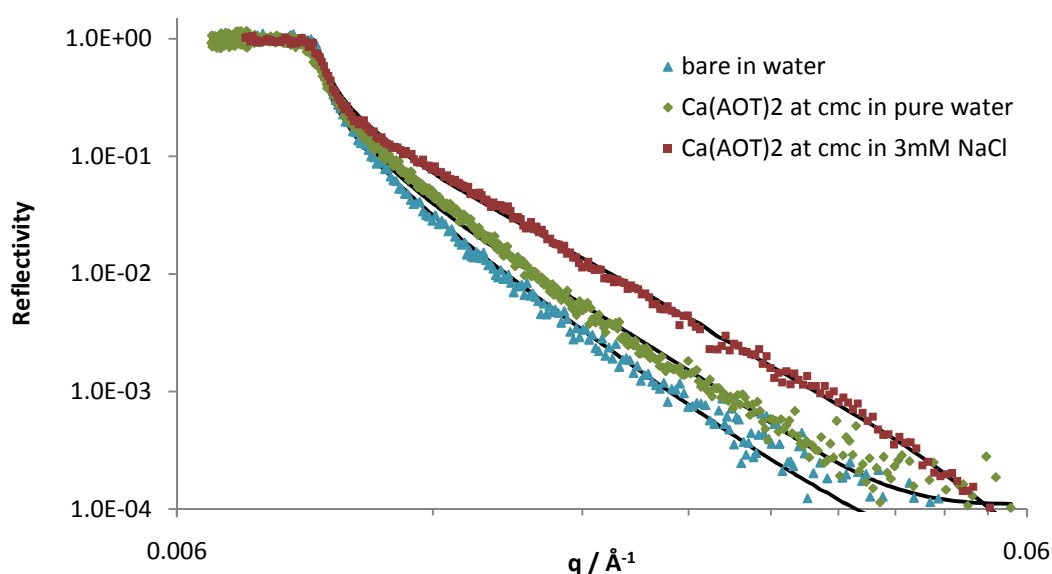


Figure 1 Neutron reflectivity profiles of bare calcite-water interface (blue), adsorbed Ca(AOT)_2 in pure D_2O (green) and with adsorbed Ca(AOT)_2 in 3 mM NaCl (red); solid lines are fits to the data

Structure of PEO in ethylammonium nitrate and adsorbed at the silica interface

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The structure of poly(ethylene oxide) (PEO) dissolved in bulk ethylammonium nitrate (EAN) has been determined using small angle neutron scattering as a function of concentration. These measurements reveal that the radius of gyration of PEO in EAN is smaller than in water, suggesting that EAN is a poorer solvent. The morphology of PEO adsorbed at the silica – ethylammonium nitrate interface has been investigated using colloid probe AFM force curve measurements. Steric repulsive forces were measured, confirming that PEO is able to compete with the ethylamine cation and adsorb to the silica surface. The range of the repulsive interaction increases with polymer molecular weight (e.g. from 1.4 nm for 0.01 wt% 10 kDa PEO to 40 nm for 0.01 wt% 300 kDa PEO) and concentration (e.g. from 16 nm at 0.001 wt% to 78 nm at 0.4 wt% for 300 kDa PEO). Fits to the force curve data could not be obtained using standard models for a polymer brush, but excellent fits were obtained using the mushroom model, suggesting the adsorbed polymer films are compressed and relatively poorly solvated, consisted with the SANS data.

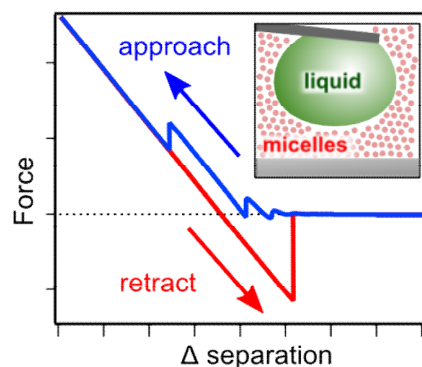
Interactions between oil droplets in concentrated surfactant phases

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Oscillating structural forces arise when nanoscale colloids are confined at high concentration between two approaching surfaces. As layers of colloid are squeezed out, changes in osmotic pressure cause alternating regions of repulsion and attraction – effectively the high-concentration limit of the depletion interaction. In this work, direct measurements of such oscillatory structural forces between the soft interfaces of two emulsion droplets are presented. The intervening structuring phases used comprise micelles or microemulsion droplets. Quantitative comparison with a theory encompassing the role of surface forces and deformation indicates that the deformable nature of droplets allows them to act as far more sensitive probes than solid spheres. In addition, the responsive nature of soft surfaces can give rise to unexpected path-dependent behaviours not encountered in rigid systems, suggesting a reversible aggregation/flocculation for emulsion droplets and, potentially, spatial ordering within concentrated soft matter phases.



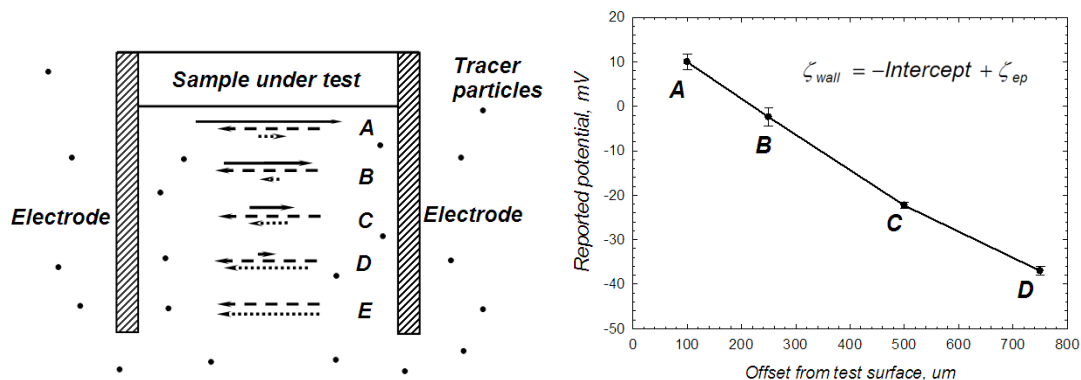
Discussing the measurement of surface zeta potential using laser doppler electrophoresis

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The measurement of surface zeta potential using laser doppler electrophoresis is experimentally investigated and discussed with emphasis placed on methodology and results. The technique measures the surface potential of a single sample surface placed between the electrodes of a specially modified dip cell by recording the overall electrophoretic and electroosmotic motion of tracer particles at various displacements (**A-D**) normal to the test surface and the electrophoretic motion only (**E**) far from the surface. A simple model is then fitted to calculate the fluid velocity at the wall slipping plane and thence the zeta potential, via the Smoluchowski relation.



The technique and experimental methodology is explored by means of a number of worked experimental examples. These include the overall accuracy, precision of the technique at high and low surface charge, tracer particle concentration, tracer zeta potential with respect to the surface potential, pH titrations of various surfaces showing excellent agreement with literature values from other techniques such as streaming potential and electro-osmotic (capillary) flow, the effects of buffer concentration and thermal trends to investigate the effect of temperature on both the tracer particle in the presence of the surface and of the surface itself.

Profiling dispersion concentration and settling with an *in situ* acoustic backscatter system

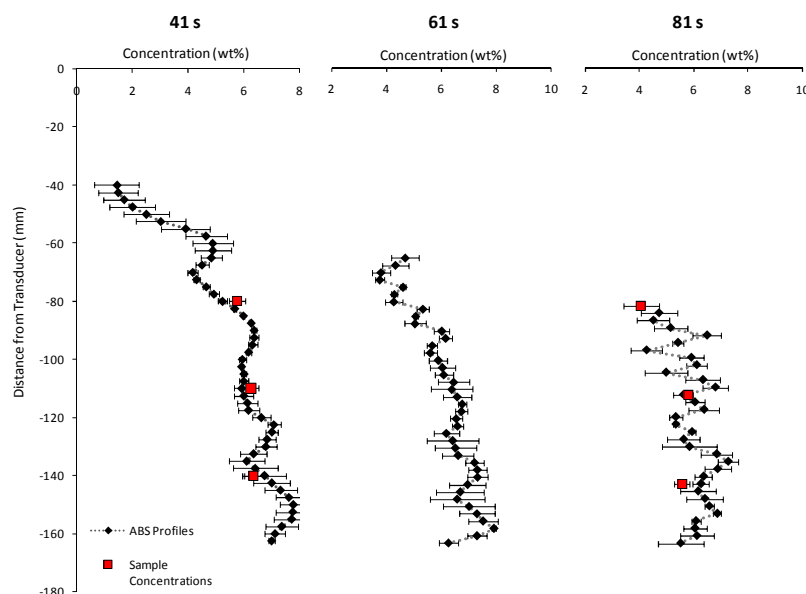
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Understanding dispersion mixing and settling characteristics is critically important to many processing operations commonly encountered in industries from pharmaceutical manufacture to mineral processing and water treatment. Traditionally, standard laboratory measurement of stability is done through scanning light transmission methods, while any in-line or *in situ* monitoring by concentration sampling. A possible alternative is the use of ultrasonics, where transducers can be fitted *in situ*, negating the need for sampling, while the ability to penetrate optically opaque dispersions make it ideal for high concentration systems. Work reported here, investigated the use of a multi-frequency Acoustic Backscatter System (ABS) to profile dispersion concentration segregation and settling for application in various industrial systems. The great advantage of ABS is the ability to conduct full depth profiles from a single point measurement; however, quantitative analysis of particulate concentration is limited to dilute regimes. We sought to investigate these instrumental limits, by comparing ABS responses through a 1 m tank to theoretical expectations, which highlighted the influence of interparticle scattering and adsorption on profile measurements. Because of these effects, a qualitative method was established to measure concentration by correlating the gradient of acoustic attenuation through dispersions. This gave the ability to assess the segregation of a settling sludge system over time, showing a build up in bulk concentration due to hindered settling effects. In addition, differential analysis allowed a full concentration profile down the settling column to be tracked over time.



Passive microrheology : non intrusive measurement of the emulsions stability

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This work presents a new technique of the passive microrheology for the study of the microstructure properties of soft materials like emulsions. Our technology uses Multi Speckle DWS (MS-DWS) set-up in backscattering with a video camera. It allows to measure the mean displacement of the microstructure particles in a spatial range between 0,1 and 100 nm and a time scale between 10^{-1} and 10^5 seconds. Different parameters can be measured or obtained directly from the Mean Square Displacement (MSD) curve like a fluidity index, an elasticity factor, a viscosity factor, a relaxation time, a MSD slope.

This technique allows to monitor the evolution of the microstructure, the restructuration after shearing, the variation of the viscoelastic properties versus temperature, pH, the physical stability of emulsion or suspension.

This work focuses on the measurement of viscoelastic properties evolution of emulsions to follow their stability. The results will show the advantages of using a non intrusive method to detect nascent destabilisation of the microstructure before rheology or visual method.

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NMR as an Analytical Tool to Characterize Dispersions

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High resolution NMR spectroscopy is one of the most powerful analytical tools used to probe details of molecular structure and dynamics. Such instrumentation requires very high resolution and uses extremely large, powerful magnets. However, the need for portable and unusual NMR has been evident for the past decade. With the advent of small, powerful permanent magnets a commercial instrument using low resolution NMR is already available to measure the surface area of suspensions. However, it is feasible to measure other characteristics of dispersions such as diffusion, from which size can be estimated. Further, it is possible to directly measure volume fraction and, potentially, the molecular weight of polymers. One important practical application is the ability to determine competitive adsorption and/or displacement of polyelectrolytes, macromolecules and surfactants at interfaces. The theory underpinning these new approaches to dispersion characterization will be described in detail and the factors affecting reduction to practical implementation will be discussed together with examples of each measurement. In addition, there is a synergy between NMR diffraction and both small angle light scattering (SALS) and ultra-small angle neutron scattering (USANS). This aspect will also be briefly reviewed.

Wettability and Behaviour of Solid Particles in Thin Liquid Films, Foams and Emulsions

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Solid colloidal particles can spontaneously attach to air-water or oil-water interfaces and act as an effective stabiliser of foams and emulsions. The contact angle of solid particles at the liquid interface determines their ability to stabilise/destabilise such disperse systems. We investigate the behaviour of micrometer and sub-micrometer solid particles in free standing liquid films by the so-called Film Calliper Method (Horozov et al., *Langmuir* 2008, **24**, 1678) and measure their contact angles. In this method, the films are observed in monochromatic reflected light and the thickness profile of the film meniscus is reconstructed from the interference pattern. It is used to obtain the three-phase contact angle of bridging particles (simultaneously attached to both film surfaces) in real time without the need of sophisticated equipment or complex calculations. The applicability of the method for measuring the particle contact angle at air-water and oil-water interfaces in the absence or presence of surfactants is demonstrated. The obtained results are linked to the stability and properties of particle-stabilised foams and emulsions.

Interactions between Hollow Silica Shells using Total Internal Reflection Microscopy (TIRM)

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Micron-sized hollow spheres have a broad array of potential uses in industrial applications. Both nano- and micro- hollow spheres find growing importance in advanced material science as they are key to innovative advancements in various applications, for example, drug delivery and other biological systems, ultrasound contrast agents and as cosmetic, catalyst supports and dye capsules *etc.* The capsules synthesized are constructed by tougher and more durable materials, such as polyelectrolytes, polymers, silica or metals. The efficiency of transportation of these shells within their respective systems is highly governed by the interactions amongst the hollow shells and other substances within their environment. Therefore, a more fundamental understanding of how the forces differ between solid particles and hollow shells is essential if significant improvement to transport efficiency is desired. This project focuses on the investigations of hollow silica shells.

The differences between a solid silica particle and a shell may be subtle, where conventional force measurement equipments include the Surface Force Apparatus (SFA) and the Atomic Force Microscope (AFM) do not have the appropriate sensitivity to probe such differences in forces. Total Internal Reflection Microscopy (TIRM) has been shown to be ideal to study systems using a range of solid particles with suitable sensitivity. Therefore, this light scattering technique was employed in this project to examine the dissimilarities in force behaviors between a solid particle and a hollow shell configuration. A few attributes that are unique to hollow shells may possibly include: 1) the retardation of Van der Waals forces; 2) shell deformation and 3) increased mobility of the shells. Hollow silica shells were synthesized using sol-gel method and they were mechanically characterized using the AFM. This presentation aims to discuss some preliminary TIRM results using the synthesized hollow shell-plate configuration.

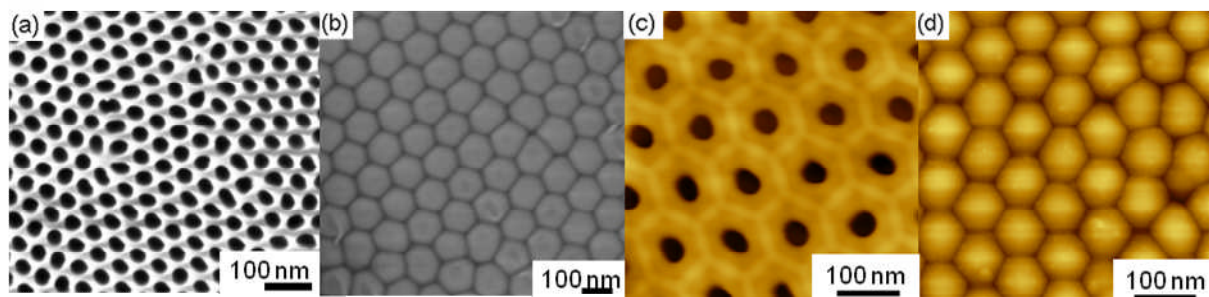
From Wenzel to Cassie: what are the wetting properties of anodized alumina?

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Nanoporous alumina has been subjected to a variety of studies due to its potential applications within industry, ranging from protective coatings of electronic devices to a material used both as a nanoporous template and membrane in nanofluidics studies. It is therefore important to know and understand the wetting properties of the alumina surface, and how these properties may change if the fabrication procedure varies. This study has investigated the wettability of both the nanopores and nanodomes produced by the anodization of aluminum. The figures a and c below show the structure of the nanopores by SEM and AFM, respectively; figures b and d are SEM and AFM micrographs of the alumina nanodomes. By changing the parameters of the anodization process we can control (with narrow pore/dome distribution) the size of the nanopore/nanodome, ranging from 10-100 nm for the pores and 20-200 nm for the domes. From static contact angle (CA) measurements (on the range described above), it was found that for both the pores and domes the CA of water on these structures increased from $<10^\circ$ to 80° and from 30° to 85° , respectively. We found that the Cassie-Baxter equation¹ could not explain the trend we observed for the nanopore studies due to the constant solid surface fraction i.e. the porosity remained relatively constant. From the linearity of the relationship, the Wenzel model² was used to explain the wetting behaviour of the pores. It has also been concluded that there is a two-tier roughness affecting the wetting of the domes with a possible transition from Wenzel to Cassie due to air being trapped in between the domes as the features increase in size.



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Determination of Pore Space of a Highly Monodisperse O/W Emulsion Using NMR Diffusometry

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Emulsion systems are widely used in many commercial products in food, pharmaceutical, and cosmetic industries. They are also interesting to study the pore structure and connectivity. There are many non-NMR techniques which have been used to study these systems such as light scattering and optical and electron microscopy. However, for a highly concentrated emulsion a technique that can probe non-invasively and can be used in a concentrated emulsion is needed. Thus, NMR pulsed field gradient stimulated echo (PGSE NMR) method or NMR diffusometry is introduced [1].

A highly monodisperse oil-in-water (O/W) emulsion has been produced from polydimethylsiloxane (PDMS) and Milli Q water with surfactants by a microfluidic method. After creaming, the highly concentrated emulsion has been studied using PGSE NMR looking at both the PDMS and water in the pore spaces around the PDMS droplets. Q-space data shows distinct minima which are directly related to the pore size distribution in the emulsion [2, 3]. Moreover, a nano-silicate particle (MQ resin, R3) was embedded into the PDMS droplets at concentration up to 50%wt. The MQ resin-PDMS emulsions are stable for a month or more.

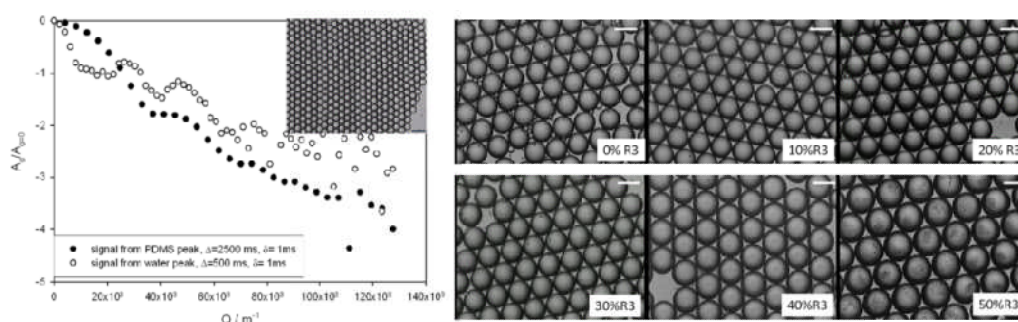


Figure 1: Attenuation plots of PDMS and water signals of a highly monodisperse PDMS in water emulsion (left) and pictures of embedded MQ resin in PDMS droplets from 0-50%wt, scale is 100um (right)

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Spreading of surfactant solutions over hydrophobic substrates

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Kinetics of spreading of aqueous surfactant solution droplets over highly hydrophobic substrates proceeds in one slow stage at concentration of surfactants below some critical value and in two stages if the surfactant concentration above the critical value: the fast and relatively short first stage is followed by a slower second stage. It is shown that the kinetics of spreading at concentrations below critical and the second stage at concentrations above critical are determined by a slow surfactant molecules transfer on a bare hydrophobic substrate in front of the moving three phase contact line (autophilic phenomenon). The latter process results in an increase of the interfacial tension of the hydrophobic solid surface in front and the spreading as a result. It is proven that in spite of that the latter process results in a decrease of the total free energy of the droplet and, hence, the adsorption of surfactants molecules on a bare hydrophobic substrate in front of the moving three phase contact line is a spontaneous process. The duration of the first stage of spreading in the case of the surfactant concentration above the critical correlates well with the duration of adsorption of surfactant molecules onto liquid-air interface. The latter allows assuming that the adsorption on the liquid-air interface is the driving mechanism of spreading during the first fast stage of spreading at surfactant concentrations above the critical. It is discussed why the first stage does not present in the case of surfactant concentrations below the critical concentration in spite of the longest duration of adsorption in this case.

This research was supported by MULTYFLOW, EU project, Engineering and Physical Research Council, UK and Syngenta, UK.

Real-time monitoring of complex moduli from micro-rheology

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We describe an online method for analyzing passive micro-rheology data which allows real-time monitoring of frequency dependent complex moduli¹. The most commonly available way to convert displacement data into a modulus requires a Kramers-Kronig transformation², introducing high frequency artifacts, and necessitating the predetermination of experiment duration. We instead implement a coarse-graining algorithm to reduce a long time series measurement into an online multi-scale correlation, and use a transformation method which preserves experimental noise³. The resulting algorithm is fast, simple, uses very little data storage and is artifact free.

Firstly, it was applied to a kinetic Monte Carlo simulation of a particle in a harmonic potential, approximating optical tweezers / particle tracking measurement⁴. Good agreement was found between theoretically predicted moduli. High frequency artifacts were not observed, and coarse-graining was demonstrated to not introduce any artificial effect. Secondly, experimental data obtained using optical tweezers, silica microspheres and solutions of polyethylene glycol at different concentrations were similarly analysed. Good agreement was seen between tabulated viscosities and bulk rheology measurements.

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SURFs and SAILs: anionic surfactants and ionic liquids with quaternary ammonium counterions

Paul Brown

Small-angle neutron scattering (SANS) and surface tension have been used to characterize a class of surfactants (SURFs), including surfactant ionic liquids (SAILs). These SURFs and SAILs are based on organic surfactant anions (single tail dodecylsulfate (DS), double chain AOT and the tri-chain TC) with substituted quaternary ammonium cations. This class of surfactants can be obtained by straightforward chemistry, being cheaper and more environmentally benign than standard cationic SAILs. A surprising aspect of the results is that, broadly speaking, physico-chemical properties of these SURFs and SAILs are dominated by the nature of the surfactant anion, and that chemical structure of the added cation plays only a secondary role.

Langmuir, 2011 Manuscript ID: la-2011-00387n.R1 accepted

Alkane microdrop collisions in surfactant free systems

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Collisions between oil micro-drops in aqueous systems, particularly those without surfactant stabilisers, continue to present open questions. Specifically, the understanding of the surface forces in very thin film between these deformable interfaces and the origin of the negative charge at the oil-water interface remain areas of inquiry. Experimentally, the measurement of drop interactions is challenging due to geometric changes to the interfaces with film pressure increases, fluidity of both organic and aqueous phases and the propensity for coalescence at close separation. These measurement challenges have been overcome through the development of an accurate technique for measuring micro-drop interactions using Atomic Force Microscopy (AFM), with drops positioned on tailored self assembled monolayers.¹ For interactions between tetradecane drops at low electrolyte concentrations the existing mathematical theory^{2,3} describes the force-distance cycles for a range of drop collisions measured experimentally, where a film of over 5 nm is maintained. Experimental and theoretical agreement in surfactant-free systems confirms the physical understanding of the effects of hydrodynamics, surface forces and deformation with only the hydroxide ion providing the surface charge for a stabilizing electrical double layer force. At higher concentrations, where a very thin film forms during the interaction, significant hysteresis is observed between approach and retract of drops, suggesting a dynamic physical change occurring in the confined aqueous film.

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Water-in-Oil Microemulsions in HPLC

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Reverse micelles represent one of the normal membranous structures in cells. The biological processes occurring in a reverse micellar system mimic the membranous environment. Water located in the core of reverse micelle exhibits at least two structures. Water that is close to the barrier molecules i.e. surfactants, reveals more density, is less free and forms hydrogen bonds less, than the molecules in free (pure) water. There are only scanty literary data about application of reverse microemulsions as mobile phases in liquid chromatography notwithstanding such interesting structure of water core [1,2].

The goal of the presented work was study of influence of different factors e.g. concentration of surfactants Brij-30 and AOT, content of water, also pH of water pockets on the chromatographic behavior of some drugs.

The chromatographic measurements were carried out with a micro-column liquid chromatograph, "Milichrom-4". The chromatographic column was a Silasorb C₂ stainless steel column. Detection wavelength was 250 nm.

Results show that retention factors of samples are influenced by surfactant type and concentration, also by water pH and presence of different ions in the water core. It was revealed that more hydrophobic compounds are eluted early in comparison with polar solutes by mobile phase hexane-water-Brij-30 mixture. In contrast to this elution order of the model compounds is reversed by using of mobile phase with AOT. Introducing of the different ions results in the different changes in chromatographic retention of the model compounds.

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RHEOLOGY OF EXPLOSIVE EMULSIONS –VISCOSITY, ELASTICITY, TIME EFFECTS, TRANSPORTATION

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Explosive emulsions are highly concentrated w/o emulsions (up to 90 volume % of dispersed phase), where dispersed phase comprises the over-cooled, highly concentrated inorganic salts solution. Rheological properties of these emulsions demonstrate the variety of effects including non-Newtonian behavior, yielding at low shear stresses and the effect of rheopexy occurs at low shear rates. Viscous properties and yielding was studied in detail, including droplet size, oil phase concentration dependencies and estimation of pumping characteristics taking an account refinement of droplets as a function of pumping speed. The important feature of rheological behavior of these emulsions is the absence of wall slip as was proven using experiments with varying gaps in rotational flows and different pipe diameters. The normal stresses in shearing were also measured. Normal force in the low-shear-rate domain does not depend on shear rate. This was explained in the frames of the Reynolds mechanism of dilatancy, while at a high shear rate the Weissenberg mechanism of normal stresses as the consequence of elasticity becomes dominant. The two-step model of flow of the emulsions under study was proposed, based on the whole complex of experimental evidences including direct microscopic observations. It was demonstrated that at low shear rates, the flow of emulsions proceeds by rolling larger drops over smaller ones, while the dominant mechanism of flow above some shear stress threshold is droplet deformation. Three levels of time effects related to the evolution of rheological properties of the emulsions were found: rapid viscoelastic process (at time scale of the order of 0.01s), rheopexy due to structure rearrangements in flow (at the time scale of the order of 100s) and slow aging due to crystallization of the over-cooled phase (at the time scale of several weeks). Finally the problem of modeling long distance transportation of the emulsions (corresponding to their technological applications) was discussed. This problem is related to the choice of the appropriate rheological equation for flow properties and the analysis of shear-rate and shelf-life stability of the emulsions. The results of the calculations were confirmed by real industrial applications.

Characterizing the Electrostatic Behaviour of Single Micro-Particle Using a Plate Condenser in an Atomic Force Microscope

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A small parallel plate condenser with Indium-Tin Oxide (ITO) glass covers as electrodes was made to characterize the electrostatic behaviours of glass particles (105 to 150 μm) on an Atomic Force Microscope (AFM) cantilever under an applied electric field. The forces acting on the particle in the electric field were analyzed at various positions between the ITO glass covers. At distances near to the bottom ITO glass cover, the interplay of forces due to the intrinsic particle charge, the induced charge by the electric field, and its image charge in the ITO glass resulted in a quadratic relationship between the force and the applied voltage. However, the relationship became linear when the charged particle was placed in between the glass covers. The predominance of the intrinsic particle charge on the electrostatic force was confirmed when the force acting on an uncharged particle placed in between the glass covers was found to be insignificant. By evaluating the forces on the charged particle, the intrinsic charge on the surface of the particle can be estimated. It was also observed that a low surface conductivity of the particle can affect the distribution of surface charges resulting in a reduced response to the applied electric field. The small plate condenser would have potential in evaluating the electrostatic behaviours of single powder particles with various surface properties and serve as an alternative method to the conventional Faraday's pail.

Experimental force and time measurements during particle adsorption at an oil-water interface

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The replacement of traditional molecular surfactants by nano- or micrometer-sized solid particles in emulsification processes offers many advantages and raises new opportunities in the process industry. The emulsion stabilization mechanism with solid particles can be visualized in three steps: 1) the particle first approaches and reaches the fluid/fluid interface; 2) the particle adsorbs and gets trapped at the interface; 3) the adsorbed particles form a network that stabilizes the emulsion. At the moment, the state of knowledge does not allow for process design mainly because of the lack of information about the overall stabilization mechanism. In this work, the colloidal probe technique, a particular atomic force microscopy method, is used to measure the adsorption force and time of model spherical micrometer-sized glass beads at a planar interface of silicone oil and water. Force curves reveal that capillary forces and viscosity of the phases are found to be the factors governing the adsorption mechanism. While the oil viscosity has no significant effect on the adsorption force measured, it does affect the adsorption time linearly, whereas particle size, wettability and ionic strength of the water solution strongly impact both force and time. These results are compared with oil/water emulsions prepared with mineral oils of various viscosities and glass particles of different surface wettabilities. While strongly adsorbed particles tend to stabilize the emulsion, increasing the viscosity of the oil phase has the opposite effect, confirming the individual roles and the combined effects of viscosity and particles wettability during the formation and stabilization of solid-stabilized emulsions.

Growth and shrinking of Pluronic micelles in Pluronic-flurbiprofen solutions: variation of concentration and PH

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Solubility of highly hydrophobic drugs such as flurbiprofen for oral dosage forms has been challenging and different strategies have been applied in order to increase the adsorption and bioavailability of these drugs. Flurbiprofen is a very effective anti-inflammatory drug which is used to treat pain, swelling, and stiffness caused by osteoarthritis and rheumatoid arthritis.

Polyethylene-polypropylene-polyethylene tri-block copolymers have shown significant potential as drug carriers, in particular for encapsulation of hydrophobic drugs. Because of the hydrophobic character of PPO blocks, multi-molecular micelles form above the critical micellisation concentration (CMC) and critical micellisation temperature (CMT). In this paper we discuss the use of Pulsed-field gradient stimulated-echo nuclear magnetic resonance (NMR) and surface densitometry to study the effect of drug addition and pH variation on micellisation behavior of Pluronic triblock copolymers (P103, P123, and L43). At various flurbiprofen concentrations, a substantial increase in the hydrodynamic radius of Pluronic P103 from 6nm to 15nm (with the highest drug content) was found by PFGNMR. From these data we can also know that the addition of flurbiprofen increases the aggregation number, fraction of polymer micellised and fraction of drug interacting with the polymer. These data clearly show that nearly all of the flurbiprofen is localized within the polymer micelles as desired for targeting, improved solubilisation and controlled release. The pH triggered behavior of the Pluronic-drug solutions was also studied and a strong pH dependent was observed when raising the pH above the pKa of flurbiprofen. The data showed that above pH 4.5, drug is gradually released from the micelles as a result of its improved solubility, leading to shrink of the micelles and decreased in the polymer micellisation. The size and aggregation number of the micelles, the quantity of the block copolymers and of the flurbiprofen have a great influence of using these Pluronic copolymers in possible application to drug deliveries.

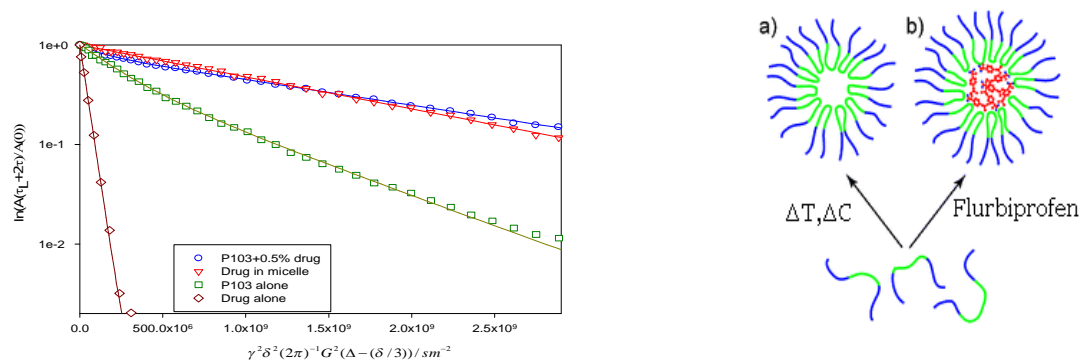


Figure 1: Attenuation plots for 5%w/w P103, 0.5% w/w Flurbiprofen in D₂O/d₆-ethanol (90:10). The data was taken from the CH₂ resonance at $\delta \sim 3.6$ ppm for P103 and the attenuation of the Flurbiprofen aromatic group at $\delta \sim 7.5$ ppm.

New interactions between aqueous droplets dispersed in oil

Michael O'Sullivan* , Anya Howe, Stuart Clarke, and Alex Routh

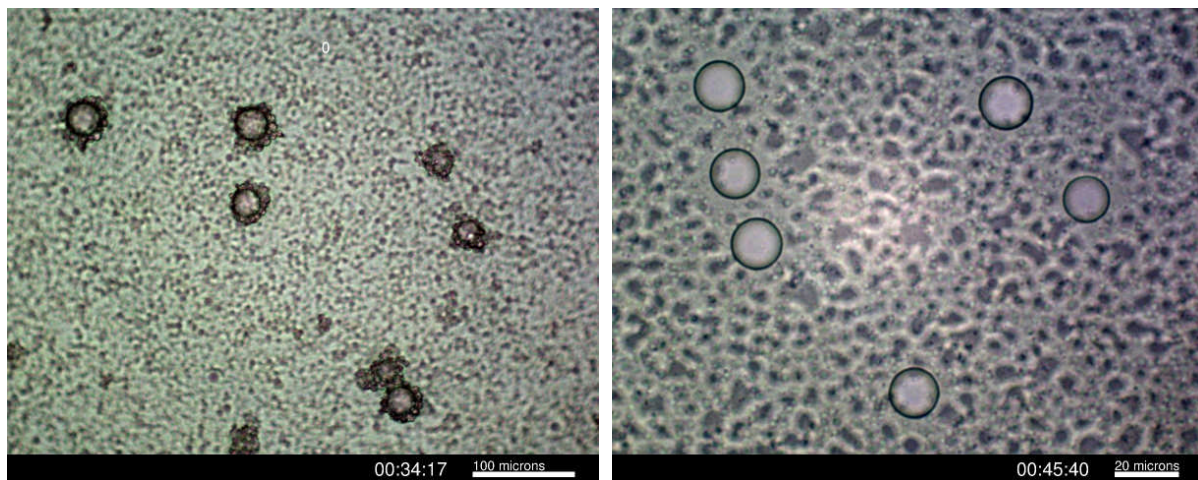
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A new attractive interaction between aqueous droplets dispersed in oil, in the presence of surfactant, has been observed. The interaction depends upon differences in both droplet size and internal solute concentration.

If the small droplets possess a higher solute concentration, they stick to the larger droplets and withdraw water from them. The attractive interaction, however, is not observed if the smaller droplets' solute concentration is lower than that of their counterparts.

Repulsive interactions are attributed to the presence of surfactant. Arguments analogous to those used to explain the depletion potential in terms of an overall Gibbs energy balance are considered for the attractive interaction.



Small salty droplets stick to larger, less salty ones (left), while no such interaction occurs if the large drops are saltier (right).

New Route to highly concentrated polymer dispersions and structure-property relationship of their films

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The production of high concentration of fine particles of isotactic polypropylene; PP, by a dispersion route is challenging due to particle coalescence issues. We report a new method in which PP particles are generated by an extrusion route. Here, PP is processed in the presence of another PP immiscible polymer such as an epoxy resin yielding PP particles in epoxy resin continuous phase. After processing the polymer blend is exposed to a solvent that only dissolves the epoxy resin. This results in a dispersion of fine PP particles in a solution of epoxy resin. We show that by manipulating the processing conditions and chemical compositions the PP particle size can be varied from sub-micron to several microns. Factors influencing particle size are discussed and it is found that the principal parameters are degree of co-reaction between the PP and epoxy resin and the viscosity ratio of the two polymers. A comparison of the experimentally obtained particle size is made with the theoretical predictions reported in the literature.

When these PP dispersions are formulated into liquid coating composition and cross-linked at elevated temperatures, the derived films have a rich and complex multiphase morphology/structure. The morphology can be linked to improvements in the film mechanical property. In addition due to the relatively low surface energy of PP we observe that the derived films show surface enrichment of PP and ways to exploit this phenomenon is discussed.

Synthesis and characterization of PNIPAM/SiO₂/Fe₃O₄ microparticles for controlled Delivery

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Composite microparticles consisting of polymer PNIPAM (poly-Nisopropylacrylamide), nanoparticles Fe₃O₄ and SiO₂ were prepared by the Pickering emulsion polymerization. PNIPAM is known as a temperature-sensitive polymer which changes its hydrophobic/hydrophilic character with temperature. At low temperatures (below the lower critical solution temperature (LCST) ~32 °C), the amide groups interact strongly with water molecules through hydrogen bonding and the polymer swells. At higher temperatures (above LCST), the hydrogen bonds between water and the amide groups are disrupted, water molecules are expelled from PNIPAM and polymer shrinks. Magnetite (Fe₃O₄) is a superparamagnetic material and it generates heat by the Brown-Neel relaxation in the presence of radiofrequency alternating magnetic field. In this work Fe₃O₄ is distributed in PNIPAM and composite microparticles are formed. Radiofrequency heating of magnetite causes the increase of the entire microparticle temperature above LCST and thus changes in structure (shrinkage). The process of shrinking and swelling of microparticles is controlled contactless by the nanoparticles of magnetite. Silica (SiO₂) nanoparticles which construct a shell of the composite microparticles can be modified by the process of silanization and thus form a specific surface for substrate adhesion. Composite microparticles of PNIPAM/SiO₂/Fe₃O₄ form an externally controlled system for targeted delivery of different drugs or nanoparticle carriers. In the present work we show a parametric experimental study of magnetite concentration on the shape, size, shrinkage ratio and heating ability of final microparticles.

One-step Preparation of Functional Colloidosome Microcapsules

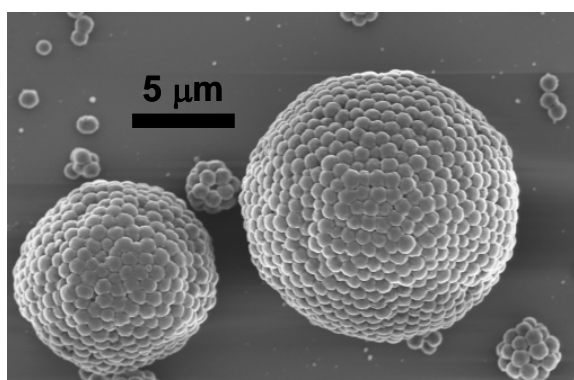
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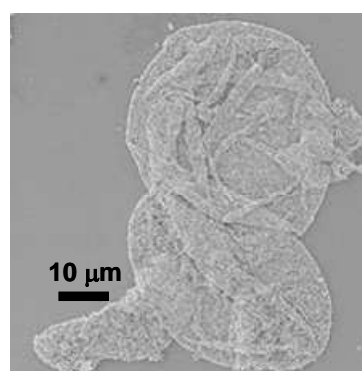
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Recently, solid-stabilised emulsions have been increasingly used as templates for the preparation of microcapsule structures, often referred to as colloidosomes. Several methods have been reported for locking adsorbed particle monolayer on the surface of emulsion droplets to prepare a robust shell for the intended microcapsules. Most processes require at least one additional step after emulsification of the system for this purpose, including addition of an adsorbing polymer/polyelectrolyte to the continuous phase, annealing at elevated temperature, etc.

This presentation will describe our recent efforts to design one-step processes for the preparation of such colloidosome microcapsule structures. I will focus on two recently developed methods that result in the preparation of colloidal shells strengthened by either precipitation or cross-linking of a polymer on the surface of the particles forming the shell. I will also describe how these two methods can be used to provide functionalities to the colloidal shells by using polymers or particles that are responsive to their physico-chemical environment (such as pH or temperature changes).



(a)



(b)

Scanning Electron Micrographs of colloidosome microcapsules with shells consisting of (a) an inner polymer layer onto which a monolayer of pH-responsive particles is attached and (b) a monolayer of core-shell nanoparticles with their pH-responsive polymeric shell cross-linked on the droplet surface.

Competition at the nanoparticle surface: one polymer, two surfactants, many possibilities

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Environmental pressures are driving detergent formulations to become ever-more sophisticated blends of stabilisers; new formulations of drugs require elaborate stabilisation as they pass from manufacturer to patient; cosmetics and paints increasingly mix colloidal dispersions of different origins into the one final product. The stability of the dispersion in each of these multicomponent systems poses significant problems and the interactions of hydrosoluble neutral polymers with surfactants and their adsorption onto particles is key for the understanding of the mechanism of colloidal stability.

The interactions between poly(vinyl pyrrolidone), PVP, sodium dodecyl sulfate, SDS, and a non-ionic alcohol ethoxylate surfactant have been previously investigated [1]. It was demonstrated that the alcohol ethoxylate does not bind to PVP and desorbs bound SDS from the polymer. We report the effect of non-ionic alcohol ethoxylate surfactant, $C_{13}E_7$, on the PVP/SDS/silica system as studied by photon correlation spectroscopy, solvent relaxation NMR and SANS. Our results confirmed that, in the absence of SDS, $C_{13}E_7$ is non-interacting and does not affect the layer thickness of the adsorbed PVP. As SDS is added, the layer thickness increases due to Coulombic repulsion between micelles in the polymer layer. When $C_{13}E_7$ is progressively added to the system, it forms mixed micelles with SDS, the total charge per micelle reduces so the repulsion between micelle and silica surface that would otherwise cause the PVP to desorb is reduced. Thus, the polymer layer appears to be more strongly adsorbed but also more stretched (Figure 1). The structural conformation of the layer was also investigated by SANS.

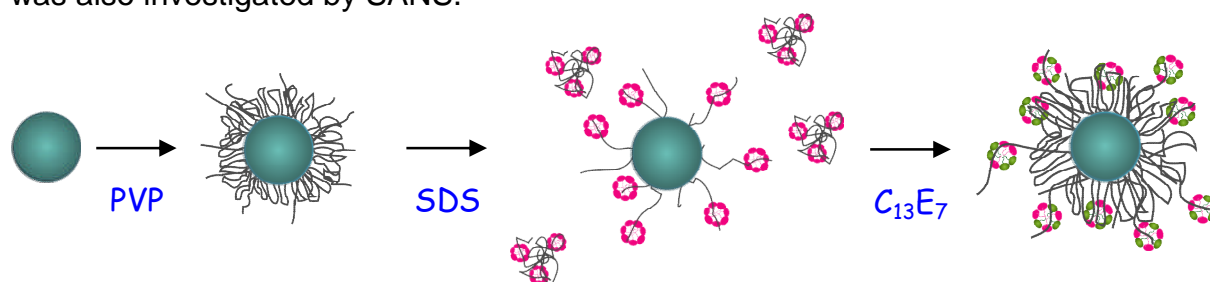


Figure 1. Schematic representation of the adsorbed polymer layer with sequential surfactant addition.

1. Y. Li, R. Xu, D. M. Bloor, J. Penfold, J. F. Holzwarth, E. Wyn-Jones, *Langmuir*, **2000**, 16 (23), 8677–8684

Covalently Cross-linked Colloidosomes

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Model poly(glycerol monomethacrylate)-based macromonomers have been used to prepare sterically-stabilised polystyrene latexes by either aqueous emulsion or alcoholic dispersion polymerisation, affording mean latex diameters of approximately 107 nm or 1188 nm respectively as judged by dynamic light scattering. Such PGMA₅₀-PS latexes have appropriate surface wettability to stabilise 25-250 µm oil-in-water Pickering emulsions, depending on the latex concentration and oil type. Colloidosomes were formed by covalent cross-linking of the hydroxyl-functional stabiliser chains from *within* the oil droplets using a polymeric diisocyanate (tolylene 2,4-diisocyanate-terminated poly(propylene glycol) [PPG-TDI]. This oil-soluble cross-linker was confined within the oil droplets, allowing colloidosomes to be prepared at 50 vol % solids without any aggregation (see K. L. Thompson et al., *Macromolecules*, **2010**, 43, 10466). The resulting microcapsules survive removal of the internal oil phase using excess alcohol, unlike the non-cross-linked Pickering emulsion precursor. These observations confirm the robust nature of these covalently-stabilised colloidosomes. A method for controlling the permeability of these colloidosomes by exploiting the solvent properties of binary oil mixtures has also been evaluated. Finally, microcapsule permeability has been explored via dye release experiments. Less permeable microcapsules can be obtained by deposition of polypyrrole onto the colloidosome exterior.

Double crosslinked pH-responsive microgels for intervertebral disc repair: Design and properties

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Degeneration of the intervertebral disc (IVD) leads to chronic lower back pain. There is an urgent need for a minimally invasive approach for repairing damaged IVDs. Previously, we demonstrated the potential for using conventional, single crosslinked, pH-responsive microgels to restore the mechanical properties of damaged IVDs[1]. The microgel particles swelled due to a pH increase[2]. Although the gelled dispersions of single crosslinked microgels were able to support biomechanically meaningful loads their potential use was limited by the likelihood of the particles migrating under load. The present study resulted from the requirement to prevent particle migration by introducing crosslinking between the microgel particles (double crosslinking). The double crosslinked microgels are different in structure and properties to those previously reported. They are also injectable. The new family of double crosslinked pH-responsive microgels discussed here (See Fig. 1) have tunable modulus values and high yield strains. The fundamental colloid and polymer science principles that govern the mechanical properties of the double crosslink gels will be discussed. These new microgels are expected to have a number of regenerative medicine applications for load bearing soft tissue repair, including IVD repair.

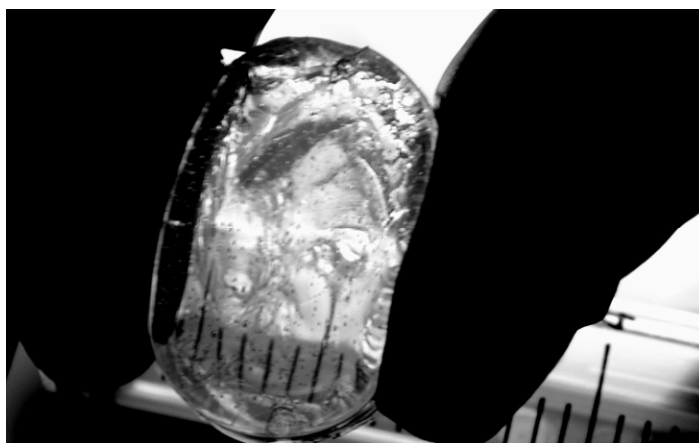


Fig. 1. Injectable pH-Responsive double crosslinked microgel.

1. T. J. Freemont and B. R. Saunders, *Soft Matter*, 4, 919, 2008.

2. B R. Saunders, N. Laajama, E. Daly, S. Teow, X. Hu and R. Stepto, *Adv. Coll. Interf. Sci.* 147, 251, 2009.

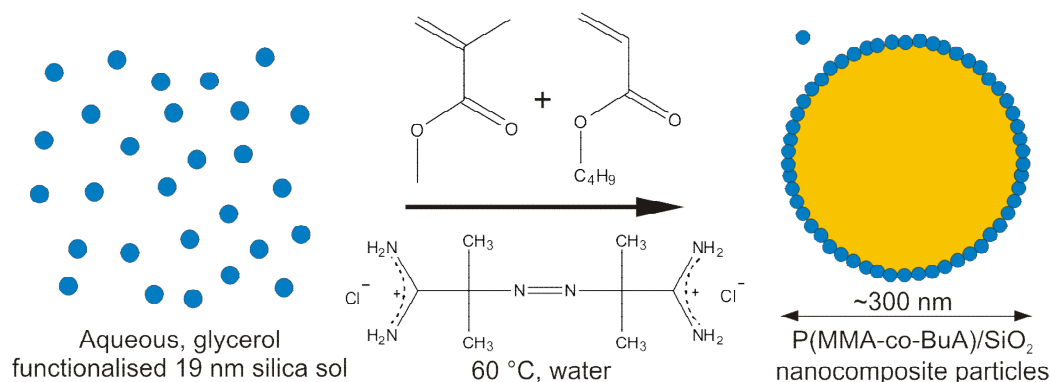
All-acrylic film-forming colloidal polymer/silica nanocomposite particles prepared by aqueous emulsion polymerisation

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The efficient synthesis of all-acrylic, film-forming, core-shell colloidal nanocomposite particles is reported. This route involves *in situ* aqueous copolymerization of methyl methacrylate with *n*-butyl methacrylate in the presence of a glycerol-modified ultrafine silica sol using a cationic azo initiator. It is shown that relatively monodisperse nanocomposite particles can be produced with typical diameters of 200 - 300 nm and silica contents of up to 30 wt. %. The importance of using a glycerol-functionalised silica sol is highlighted and it is demonstrated that systematic variation of parameters such as the initial silica sol concentration and initiator concentration affect both the mean nanocomposite diameter and the silica incorporation efficiency. The morphology of the nanocomposite particles comprises a copolymer core and a particulate silica shell, as determined by aqueous electrophoresis, small angle x-ray scattering, x-ray photoelectron spectroscopy and electron microscopy. Moreover, it is shown that films cast from *n*-butyl acrylate-rich copolymer/silica nanocomposite dispersions are significantly more transparent than those prepared from the poly(styrene-co-*n*-butyl acrylate)/silica nanocomposite particles reported previously.^{1, 2} A particle formation mechanism is proposed to account for the various experimental observations made when periodically sampling such nanocomposite syntheses at intermediate comonomer conversions.



1. A. Schmid, S. P. Armes, C. A. P. Leite and F. Galembeck, *Langmuir*, 2009, **25**, 2486-2494.

2. A. Schmid, P. Scherl, S. P. Armes, C. A. P. Leite and F. Galembeck, *Macromolecules*, 2009, **42**, 3721-3728.

Biodegradable pH-responsive hollow polymer particles: triggered particle swelling, gel-formation and disassembly

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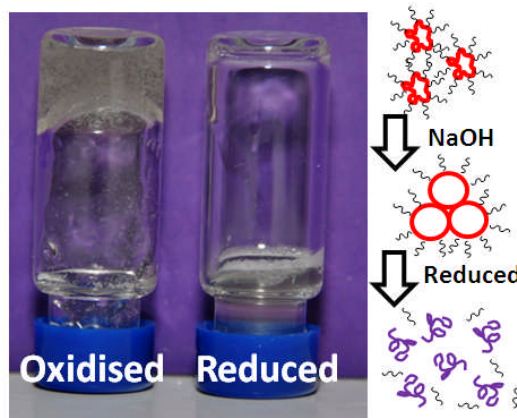
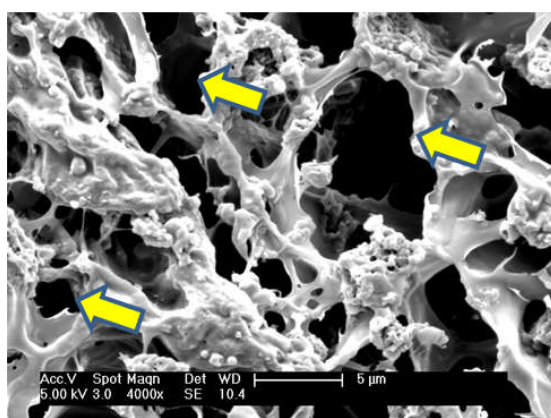
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Hollow particles are of interest due to their potential applications in drug delivery, catalysis, electronic materials, lightweight fillers, artificial cells, vessels for confined reactions, gene delivery, encapsulation of cosmetics and paints. Current methods for producing hollow polymer particles typically involve colloid templating. Particles produced using these methods are often at very low concentrations and require thorough purification to remove harmful reagents such as HF. The requirement for the particles to be loaded following synthesis can also add further complication. The need for a more simple and versatile process is clear.

The new method introduced here is a simple, two-step process for generating hollow polymer particles which are both pH and redox sensitive. A linear amphiphilic co-polymer is dissolved in a co-solvent and emulsified. Diffusion causes precipitation of the co-polymer at the droplet/water interface. The hollow shells produced can be functionalised with thiol groups to induce redox sensitive intra-particle crosslinking.

The hollow poly(methyl methacrylate-co-methacrylic acid) particle dispersions generated swell as the pH is increased to form stable particle gels which can be disassembled by adding reducing agents. This gelation behaviour is highly tune-able and can be adjusted by modifying the initial linear co-polymer composition, and degree of thiol functionalisation.

The similarity of the process to conventional solvent evaporation means that active loading can be undertaken during the precipitation step. This removes the requirement for complicated loading processes. Dissolution of the particles under reducing conditions breaks down the crosslinks. This means that the only product of degradation is the linear co-polymer, which can be excreted naturally from the body, making this system highly applicable in vivo.



Preparation of durable biomembrane-mimetic hydrogels by water channel confined photocrosslinking of complex fluids

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Hydrogels have attracted a lot of interest as biomaterials for use in drug delivery and regenerative medicine. Comparatively fewer studies directed at their development and evaluation for use in soft electronics or energy transducing materials have been reported. The lack of use of synthetic hydrogels for non-biomedical applications has been attributed to their insufficient environmental and mechanical stability to operational conditions frequently encountered for many technological applications. To this end, we have work to develop a synthetic approach for the preparation of a durable biomimetic chemical hydrogel that can be reversible swollen in water. An aqueous dispersion of a diacrylate end-derivatized PEO-PPO-PEO macromer, a saturated phospholipid and a zwitterionic co-surfactant self-assembles into a multilamellar physical gel at room temperature as determined by X-ray scattering. The addition of a water soluble PEGDA co-monomer and photoinitiator does not alter the self-assembled structure and UV irradiation serves to crosslink the acrylate end groups on the macromer with the PEGDA forming a network within the aqueous domains as determined by FT-IR. The physical gel converts to an elastic self-supporting chemical gel. Storage under ambient conditions (air at room temperature) causes dehydration of the hydrogel, to 5 wt %, which can be reversed by swelling in water (to achieve 85 wt % water content). The fully water swollen gel remains self-supporting but converts to a non-lamellar structure. As water is lost the chemical gel regains its lamellar structure. Incubation of the hydrogel in nonpolar organic solvents that do not dissolve the uncrosslinked lipid component (hexane) allow for swelling without loss of structural integrity.

Auto-stratification in latex coatings

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The vertical distribution of particles within a dried film has a large impact on the final film properties. The mechanism by which the particles in a film come into close packing during solvent evaporation has an important role to play in the final film morphology. As the solvent evaporates from the top surface, causing it to descend, the particles can develop non-uniform concentration across the vertical height of the film, depending on the diffusion rate. This process is described by the associated Peclet number, which in this case is the ratio between the evaporation rate and the particle diffusion. When the Peclet numbers of the components are such that the diffusion of one type of particle is dominant during drying, but the transport of the other component is dominated by the evaporation rate of the solvent from the film/air interface, a system is set up such that one component dries uniformly, yet the other is collected by the descending interface. This results in segregation. A key aspect of this mechanism is that it is independent of orientation as gravity does not play a role.

Experimentally this phenomena can be observed through the controlled evaporation of water from drying films of two types of latex particles, each with a different particle radius. Volume fractions of particles of each component were evaluated both on the surface and through the cross-section of the films using Atomic Force Microscopy, GARField NMR and Confocal Microscopy.

By applying the principles of classical diffusion mechanics to hard sphere system, driven by a chemical potential gradient, a theory for this novel method of segregation during drying of a two component film has been derived. The diffusion behaviour of the particles has been modelled numerically as a coupled PDE system using a modified FTCS scheme, showing a significant segregation.

Ultrafine Translucent Nano-latexes via Semicontinuous Microemulsion Polymerisation

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Polymeric nano-latexes have received a great deal of attention because of their potential applications such as ultrathin films and drug delivery nanocarriers used for crossing various biological barriers within the body. Semicontinuous microemulsion polymerisation is a novel and powerful technique that can produce concentrated nano-latexes using a low concentration of surfactant. In this technique, the volume growth rate of particles is controlled at a very low value by the rate of monomer addition (R_a). As a result, particle formation is enhanced and particles with narrow size distribution are produced.

There are some controversial issues regarding effects of surfactant concentration $[S]$ and R_a on the particle size and distribution in semicontinuous microemulsion polymerisation. This is partly because the completion of particle nucleation, and the role it plays in elucidation of underlying mechanisms of polymerisation, has not been considered in literature. In this research, we closely monitored particle nucleation in the course of addition.

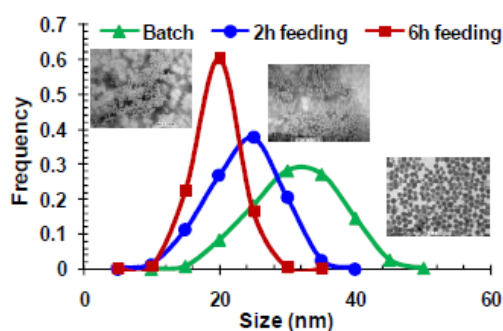


Figure 1. PSDs for different addition times.

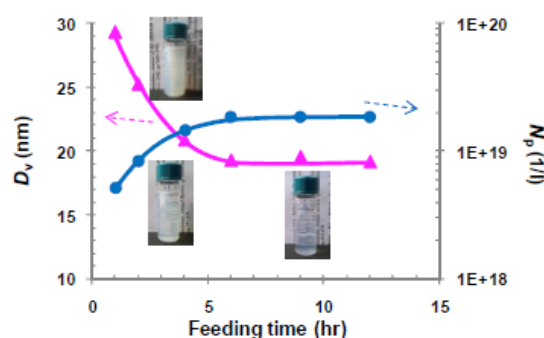


Figure 2. Particle size and number variations with R_a

Figure 1. PSDs for different addition times. **Figure 2.** Particle size and number variations with R_a

Particle formation and growth in the semicontinuous microemulsion polymerisation of styrene were studied using various monomer feed rates (R_a) and surfactant concentrations ($[S]$). Polymeric nanoparticles as small as 10 nm were produced. The size of particles as well as the particle size distribution (PSD) at the end of nucleation could be easily manipulated by adjusting the rate of monomer addition. A lower R_a (i.e. higher addition time) leads to formation of smaller particles with a narrower distribution (Figure 1). The number of particles is almost two orders of magnitude greater than that produced by conventional batch polymerisation. Increasing $[S]$ can increase the number of particles by providing more micelles for particle formation and prolonging the nucleation period. However, the interesting result was that PSDs at the end of nucleation were found to be independent of $[S]$. At extremely low values of R_a or very high $[S]$, a minimum particle size could be achieved (Figure 2). The weight-average molecular weight (M_w) as well as the number of chains per particle of the nanolatex decreased with the rate of monomer addition.

Dual Stimuli-Responsive Microgels Based on Photo Cleavable Crosslinkers: pH-Dependent Swelling and Light-Induced Degradation

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The aim of this work is the preparation of dual stimuli-responsive microgels to exhibit a pH-dependent volume phase transition due to ionizable groups in the network-forming polymer and the ability to complete particle disintegration upon irradiation due to light-cleavable crosslinking points. The particular combination of the mentioned stimuli is designed to exhibit two different degradation profiles. In both cases, particles are highly swollen for pH values higher than the pKa of the microgels, whereas decreasing pH leads to deswelling of the networks. Disintegration of the collapsed particles by direct irradiation represents a one step degradation profile. In contrast, by transferring the collapsed particles to phosphate buffer solution slightly swollen particles are obtained, which subsequently can be degraded by application of UV-light, therefore characterizing a two step swelling/degradation profile. With regards to potential delivery applications, a slow release based on diffusion out of the slightly swollen network can either be combined or replaced with a fast on-demand release upon irradiation. This versatile behaviour represents a great potential for the loading and release of active compounds.

Our approach to realize the described concept is based on two considerations. First, incorporation of methacrylic acid groups into gel networks represents a well established approach to achieve the desired pH-dependent swelling behavior. Free radical copolymerization of HEMA and MAA in inverse miniemulsion leads to anionic PHEMA-co-PMAA hydrogel nanoparticles. Second, light-induced particle degradation is realized by using photo labile crosslinkers containing *o*-nitrobenzyl moieties. The fast and quantitative reaction upon irradiation with UV-light in various solvents and even the solid or macromolecular state render those moieties highly interesting for the described concept. Especially, the tunable enhanced absorption for wavelengths of $\lambda > 300$ nm enable photoreactions to be carried out in a controlled manner and under mild conditions.

Carboxyl Functional Stimuli-Responsive Magnetic Particles

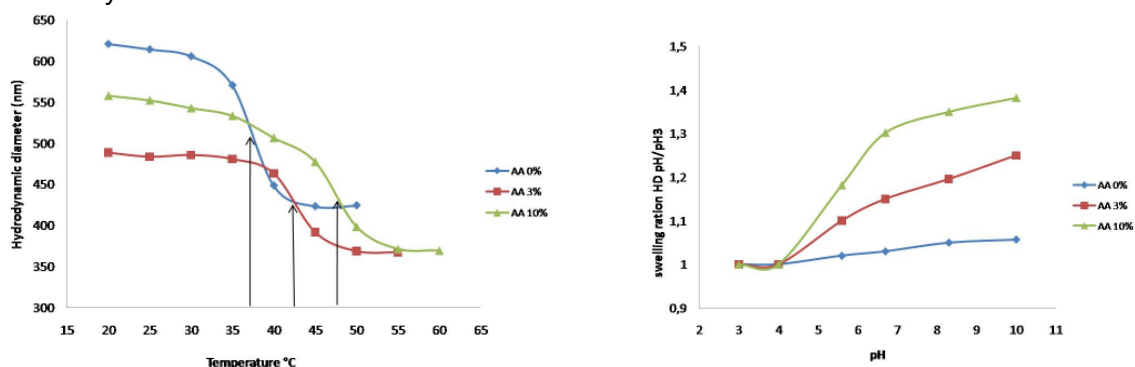
Md Mahbubor Rahman*, Hatem Fessi and Abdelhamid Elaissari

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As a smart material magnetic particles have gained much interest because of their promising application in different fields such as separation, controlled drug delivery, catalysis carriers, and etc[1-2]. Proper surface functionality and colloidal stability of magnetic particles is the key requirement for biomedical applications to interact physically or chemically with biological entities such as enzymes, nucleic acids, antibodies. The particles having magnetic and temperature responsive property are of great interest for better use in controlled switching biotechnology. Poly(N-isopropylacrylamide) PNIPAM with functional monomer has been utilized for magnetic particles surface coating because of its coil to globule transition with temperature. To date, most of the reported works are related to PNIPAM based functional hydrogel or non-magnetic core-shell particle preparation. Only few reports have been dedicated to functional magnetic PNIPAM particles elaboration, particularly, carboxyl functional magnetic P(NIPAM-co-AA) particles. Here we report the synthesis and colloidal properties of carboxylic acid functional pH and temperature responsive magnetic submicron particles. Divinylbenzene (DVB) cross-linked magnetic seed particles were prepared by emulsion polymerization in the presence of oil-in-water magnetic emulsion as a seed. Thereafter, onto these cross-linked magnetic particles, P(NIPAM/AA/MBA) shell was prepared by seed polymerization. Reasons behind the choosing of carboxylic acid groups are pH sensitivity and prone to easy covalent link formation with other molecules or post modification.

The hydrodynamic diameter, electrokinetic properties and colloidal stability of the prepared particles in terms of pH, temperature and salt concentration were characterized. On the basis of the results, it was found that the colloidal stability of the magnetic particles depend on both of the temperature and electrolyte concentration of the dispersion medium. The magnetic particles stability increases due to the functionalization with acrylic acid (AA) containing PNIPAM. There was a considerable effect of pH on the particles hydrodynamic size and electrophoretic mobility but not significant effect on colloidal stability of particles at room temperature. As depicted in the following figures, it was also found that the presence of acrylic acid in the PNIPAM chains affects the volume phase transition and increases pH sensitivity.



1. S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. Vander Elst, R. N. Muller, *Chem.Rev.*2008,108(6),2064
2. M.M.Rahman, A. Elaissari in A.M.vVan Herk and K. Lanfester (ed), *Adv.Polym.Sci.*, 2010,233,237

The phase behaviour of pNIPAM microgel and colloid mixtures

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Depletion interactions give rise to phase separation in colloid-polymer mixtures at sufficiently high concentrations of both species. Similarly a fluid-solid phase separation is expected for binary hard sphere (BHS) mixtures; however in practice it appears such mixtures are very prone to form metastable (jammed) states. Recently it was shown that the addition of microgel particles can induce depletion attractions between colloidal particles [1]. These colloid-microgel mixtures are of particular interest, as the stimuli responsive nature of the microgels enables us to reversibly tune particle interactions by changing external parameters.

Here, temperature responsive pNIPAM microgel particles are used to induce depletion attractions between polystyrene latex spheres. Such microgels can be modelled as hard spheres with a polymer brush-like outer layer [2]. Mixtures with a microgel / polystyrene size ratio of 0.11 showed a fluid-solid phase separation, in good agreement with predictions for BHS. Gel states were obtained on further increase of concentration, around the position of the predicted metastable BHS fluid-fluid binodal, echoing previous claims of the significance of a hidden fluid-fluid phase boundary as the precursor to gelation. It thus appears that the slight deformability of the microgel particles reduces the tendency for mixtures to remain in jammed states. Nevertheless the mixtures did tend to form gels more easily than mixtures of the same polystyrene spheres with linear polymer coils at a similar polymer / colloid size ratio.

1. For example: Fernandes, G. *et al.* **Langmuir** (2008) 24, 10776

2. Scheffold, F. *et al.* **Phys. Rev. Lett.** (2010) 104, 128304

Synthesis, Characterisation and Interfacial Activity of Poly(2-vinyl pyridine) Particles

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Sterically-stabilised, lightly cross-linked poly(2-vinylpyridine) latexes (P2VP) were prepared by aqueous emulsion polymerisation. These near-monodisperse P2VP particles were characterised in term of their size, critical pH for latex-to-microgel swelling, overall degree of swelling and surface charge. Viscosity and static light scattering studies showed that 0.11 wt.% divinyl benzene cross-linker was required to fully cross-link the P2VP latex. Rheological behaviour of the acid-swollen P2VP microgels prepared at differing cross-linking densities confirmed that the Batchelor equation for hard spheres is obeyed for volume fractions below 0.30, but the Krieger-Dougherty model is more appropriate for higher volume fractions due to strong particle-particle interactions. The characteristic time scale for microgel swelling is of the order of tens of milliseconds and depends on the particle size. On the other hand, the kinetics for deswelling is up to two orders of magnitude slower, due to the formation of an external 'skin' of deprotonated P2VP. P2VP latex particles can adsorb at the solid/liquid, liquid/liquid and gas/liquid interfaces. Acid-induced swelling leads to rapid desorption from the liquid/liquid and gas/liquid interface. Thus such particles act as pH-responsive Pickering emulsifiers or foam stabilizers. In the latter case, this behaviour was confirmed by monitoring the coalescence of millimetre-sized air bubbles using a high-speed camera. At neutral/alkaline pH, bubble coalescence was suppressed due to the adsorbed monolayer of P2VP latex at the air/water interface. However, on lowering the pH to around 2, rapid coalescence occurs due to desorption of the P2VP particles in their protonated microgel form from the air/water interface.

Metallosurfactants – Self-Assembled Metal Surfaces

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Metallosurfactants represent a class of surfactant in which the polar headgroup of the surfactant contains a *d*- or *f*- block metal complex as an integral structural component. The incorporation of transition metals into a surfactant structure facilitates new functionality, such as catalytic activity, to be concentrated at interfaces. Further, the self-assembly of metallosurfactants provides a simple means of preparing well-defined aggregates of metal complexes with nuclearities equal to the aggregation numbers of the micelles themselves, and these are beginning to find application in for example, magnetic resonance imaging, templating of mesoporous materials and homogeneous catalysis. The critical micelle concentrations for a set of homologous series of metallosurfactants have been determined, and show classical behaviour in terms of the hydrophobe size, but some interesting and unusual trends with headgroup character. The morphology of micelles formed by these materials has been determined by small-angle neutron and X-ray scattering. On addition of oil and cosurfactant, the formation of classical *o/w* metallomicroemulsions may be induced, whose structure is sensitive to the nature of the surfactant headgroup and the cosurfactant, but *w/o* microemulsions are significantly harder to formulate. These observations considerably extend our understanding of the relationships between chemical structure and micelle morphology for these interesting molecules.

Surface force measurements between titania surfaces prepared by atomic layer deposition in aqueous electrolyte and CTAB solutions

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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 (~5) and significantly larger dispersion forces. As such the balance between the repulsive hydration forces and the van der Waals attraction at short range should differ considerably between silica and titania. However it is challenging to find titania surfaces that are sufficiently smooth to allow the short range forces to be investigated. Using Atomic Layer Deposition (ALD), we have produced suitably smooth titania surfaces (RMS roughness ~1nm) by coating silica colloids 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. Further, we have examined the adsorption of CTAB to titania using optical reflectometry and observed slow adsorption below the cmc as previously seen on silica. We will also report on the measured surface forces between titania surfaces in CTAB solutions.

Phases in Coexistence in a Mixture of Neutral Hard Colloidal Spheres and a Depletion Agent

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The semi-grand canonical ensemble theory within the free volume approximation was applied to construct the composite Helmholtz free energy density function of a mixture of uncharged hard colloidal spheres and a depletion agent which may be rods or discs in its liquid and solid phases. Differing from the usual means of resorting to the pressure and chemical potential, we employ the free energy density minimization method [G.F. Wang and S.K. Lai, Phys. Rev. E **70**, 051402 (2004)] to calculate the phase diagram of this kind of the colloidal mixture. The method crosshatches the domains (rather than the phase boundaries) of homogeneous single phases, namely gas, liquid and solid, as well as these phases in coexistence. The calculated coexistence domains do exhibit the well-known triangular area of coexisting gas-liquid-solid three phases, but it has to be realized as some kind of a kinetic amalgamation of sets of two coexisting phases. A remarkable finding in our study is that, for any initial concentrations of colloids and depletion agent that fall inside the triangular area, the minimized coexisting (gas, liquid and solid) phases are just the vertices of the triangle, but the spatial volume of each phase is different generally. It would thus be interesting if laboratory experiments at the same quantitative level as those reported for the colloid-polymer mixture [F. Renth, W.C.K. Poon and R.M.L. Evans, Phys. Rev. E **64**, 031402 (2001)] can be carried out to confirm this theoretical prediction [S.K. Lai and Xuhui Xiao, J. Chem. Phys. **132**, 044905 (2010)].

Work supported by the National Science Council, Taiwan (NSC99-2112-M-008-001)

Janus Composite Colloids

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Controlling micro-structure of a colloid is important to gain additional performances of composite materials. Janus colloids with compartmentalized regions onto the surface are promising. It is challenging to develop methodology for large scale synthesis of such composite colloidal materials, whose structure and composition can be tuned. I will present some results achieved in our group.

Janus colloids have been fabricated by simultaneous biphasic grafting of different polymer brushes onto the two parts of a Pickering colloid at a liquid/liquid emulsion interface by atomic transfer radical polymerization. The two parts of a colloid at a Pickering emulsion interface are separated into two phases, which can be synchronously modified by ATRP in the two phases. Janus non-spherical colloids are prepared by asymmetric wet-etching the colloids which are frozen at the interface. Recently, we have developed seeded emulsion polymerization toward large scale production of Janus composite colloids with two components distinctly compartmentalized onto the same surface. Meanwhile, microstructure can be tuned.

Besides spherical colloids, we have recently proposed a method by materialization of an emulsion interface toward Janus hollow spheres, whose shell is biphasic onto interior and exterior surfaces, respectively. Materials can be preferentially and selectively loaded inside the cavity from their surroundings. Furthermore, by crushing these Janus hollow spheres, Janus nanosheets are derived, which can be used as effective solid emulsifiers to collect chemical spills.

Angew. Chem. Int. Ed. 2008, 47, 3973-3975; **Chem. Commun.** 2009, 3871-3873; **Chem. Commun.** 2010, 4610-4612; **Macromolecules** 2010, 43, 5114-5120; **Angew. Chem. Int. Ed.** 2011, 50, 2379-2382; **Chem. Commun.** 2011, 1231-1233.

Suspension processing and suspension engineering rheology

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Billions of tonnes of material are processed in the form of suspended particles, worldwide, and on a very wide range of scales. In order to scale-up, control and optimize such processes way better than we do, we need to be able to model them; just as processes involving simple fluids and now, increasingly, molten polymers are modeled.

Real processes involve complex and arbitrary loadings, deformations and flows. For example, a material might be subject to differential compression (i.e. filtration) while being sheared in one or more directions. Such a combination of shear and differential compression occurs not just in many solid-liquid separation processes, but also when a thin particulate coating, of a set of granules or a ceramic monolith is dried, whence the response to mixed loading can be cracking.

The general scheme for process modeling is in place (see e.g. Lester et al. 2010 [1] for details). The pressing problem now is to develop in tandem experimental methods for characterizing the constitutive behaviour of suspensions [2] in two and three dimensions and equations for interpreting, representing and encoding the data [3].

To be useful, constitutive equations have to fulfill many requirements and to pass many tests. For example, they need to be able to deal with yielding, shear-thinning, shear-banding, order-of-magnitude changes in volume-fraction, etc.. It will be suggested that hyper-elastic constitutive equations formulated in terms of the Hencky or “natural” strain measure have the versatility required potentially. Preliminary work has shown that these look to be capable of capturing most of the key features of suspension behaviour, including some of those that have been puzzling hitherto.

1. D.R. Lester, M. Rudman, P.J. Scales, Macroscopic dynamics of flocculated colloidal suspensions, Chem. Eng. Sci., **65**/24, 16362-6378, DOI: 10.1016/j.ces.2010.09.006.

2. The focus of attention is on aggregated suspensions, since colloidally-stable systems seem rather rare in industry and the environment.

3. The topic was discussed extensively at a workshop, organized by A.D. Stickland, held at University of Melbourne in late 2010, aimed at developing a road-map for future research. The speaker has benefitted considerably from discussions with the participants.

Interaction and Attachment of Particles and Bubbles in an Aqueous Environment

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The interaction of particles and bubbles in aqueous environments is an important feature of many industrial processes, for example in mineral separation by 'flotation'. Despite its importance, the attachment process and the variables controlling it are still not well understood.

In our experiments we directly observed particle–bubble interaction and attachment at the microscale. We analyse this empirical data and compare it to predictions generated from theoretical models that include inertial contributions.

Experiments were carried out in a glass cell filled with water, in which glass particles were dropped onto a larger captive air bubble. The equipment was configured so that the particle path toward, around, and away from the bubble was totally unimpeded. By recording on high-speed digital video, relevant parameters could be directly estimated — e.g. particle velocities, and the duration of particle sliding over the bubble surface.

Particle trajectories showed a significant deviation at separations much larger than their own diameter, due to the hydrodynamics. Comparison with theoretical predictions indicated that the bubble surface exhibited intermediate mobility. Theoretical predictions for an immobile bubble surface were practically symmetrical about the bubble's equator, while asymmetry was apparent in the theoretical predictions for a mobile bubble surface. The most pronounced asymmetries were seen in the experimental results.

Particles dropping more centrally were observed to slide over the surface of the bubble. In several cases the sliding particle 'jumped in' toward the bubble. We interpret this as the precise moment of attachment, enabling direct estimation of the threshold duration to achieve attachment, *i.e.* "induction time". Among the observed events were rotation of the particle upon jumping in, and particle jump-in below the bubble's equator. We attribute these 'anomalous' behaviours to surface non-uniformity.

Phase separation in mixtures of silica particles of two sizes, dispersed in dimethylformamide, on the addition of polystyrene

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Phase separation, induced by attractive depletion interactions through the addition of non-adsorbing polystyrene, in dispersions of charged silica particles (30 and 200 nm diameter), in dimethylformamide, has been studied, firstly for each particle size separately, and then for mixtures of the two sizes. The latter studies, to our knowledge, is the first investigation of ternary mixtures of two sizes of particles plus polymer. Two monodisperse polystyrene samples were used, having number-average molar masses of 115,000 and 543,000. The repulsive electrostatic interaction between the silica particles was reduced through the addition of up to 40 mM lithium chloride.

With the larger silica particles alone, beyond a critical added polymer concentration, a solid-like, aggregated particle phase separated out from the coexisting (stable) vapor-like phase. With the smaller particles alone, with increasing polymer concentration, first a colloidal liquid phase separated and then, at an even higher polymer concentration a solid-like, aggregated particle phase was again observed¹. These results agreed well with recent predictions for charged particle – polymer mixtures.

For the ternary systems, the total particle volume fraction was kept fixed. For certain volume ratios of the large to small particles, three co-existing phases were formed at equilibrium, and in others two. However, an unexpected, novel observation was the manner in which the three-phase systems evolved with time: initially a two phase (solid + vapor) system formed within minutes, but over a longer timescale (hours), the third, liquid-like phase separated from the solid phase².

1. J. Zhou, J. S. van Duijneveldt and B. Vincent, *Langmuir*, 2010 26 9397

2. J. Zhou, J. S. van Duijneveldt and B. Vincent, *Phys.Chem.Chem.Phys*, 2011 13 110

Stimuli-responsive capsules for instantaneous delivery

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Drug delivery is a method of using pharmaceutical compounds more effectively, so as to only target affected regions of the body, reducing side-effects, or to control the release of the chemicals so that they will be effective for a longer time. One method of drug delivery is micro-encapsulation, whereby compounds are trapped inside micrometer-sized containers and either slowly released through pores or quickly released by rupturing. However, micro-encapsulation systems could benefit greatly from enhanced functionality and versatility. This is offered by the colloidosome; a self-assembling, hollow spherical structure made from adjoined nanoparticles, which is capable of slow, controlled release of compounds. In this study, a novel pH-responsive colloidosome delivery system for small molecules is proposed, utilising pH-sensitive polymers and crosslinking agents to attach the nanoparticles to one another. This allows the colloidosomes to respond to changes in pH, causing them to expand or contract to contain and release compounds more or less rapidly. The formed capsules were investigated using optical, fluorescence and scanning electron microscopy and were proven to be effective at encapsulating and storing dextran sugar molecules and releasing them in response to a pH stimulus. Such controlled release colloidosomes may be useful in drug delivery applications in the future, as some diseases locally alter pH levels, or have other potential applications in the fields of cosmetics, agriculture and nutrition.

Physico-chemical networks: enzymatically cross-linked chitosan/gelatin hydrogels

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The self-assembly properties of naturally-derived polymers are exploited in numerous technological applications and are also fascinating materials to study from a fundamental viewpoint. Understanding the mechanisms involved in the self-assembling process provides tools to tune these processes in order to obtain materials with desired structural and dynamic properties.

Our interest lies in the application of hydrogels as scaffolds for tissue replacement. For medical applications, biopolymers offer numerous advantages over their synthetic counterparts. In this work, gelatin and chitosan were combined due their wide availability and useful biological properties by using an enzymatic 'glue': transglutaminase. Gelatin is a well-known example of a self-assembling system, which changes from a disordered sol phase to an ordered gel phase with temperature. The gel phase arises from the formation of triple-helices due to partial refolding of the gelatin. In this work, we seek to use this sol-gel transition as a tool to control the enzymatic cross-linking of gelatin and chitosan. In the presence of gelatin helices, the access to binding sites is affected and thus it is possible to direct the spatial distribution of the cross-links, compared to the same process in the sol state. Rheological characterization of the gels obtained shows a distinct difference between the hydrogels crosslinked in the gel phase and the sol phase, with the former showing higher shear moduli. We propose that cross-linking conducted in the sol phase (at 37°C) produces a higher proportion of non-elastic active junctions, e.g., closed loops, while in the presence of the physical network (at 21°C) the chemical junctions are more ordered, giving rise to a stiffer network.

Recent Advances in Oleic Acid-Based Gemini Surfactants

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Gemini surfactants, consisting of two monomeric surfactants linked with a spacer, are an important class of functionalised amphiphilic molecules. The use of gemini surfactants, instead of conventional monomeric ones, allows for the reduction of the total consumption of surfactants in chemical products owing to their excellent adsorption and molecular association capabilities in aqueous media. This indicates that gemini surfactants are environmentally friendly materials. Nevertheless, the number of commercially available gemini surfactants is very limited. This is because the synthesis of gemini surfactants is generally more complicated than that of monomeric surfactants, and therefore, the costs associated with the synthesis and purification of gemini surfactants are prohibitive. In order to facilitate the widespread use of gemini surfactants in a variety of applications, the development of low-cost strategies for the synthesis and purification of gemini surfactants is essential.

On the basis of this background, oleic acid-based gemini surfactants have been developed by our research group. Oleic acid is the basis of human sebum and stratum corneum cell lipids, and hence, it is a biocompatible, ecological, and relatively low cost material. Indeed, it is possible to modify the cis double bond with various kinds of hydrophilic headgroups through relatively simple chemical reactions. It is also possible to introduce a hydrocarbon chain at the terminal carbonyl group via the amide or ester bonding. These two synthetic strategies allow for the design of a wide variety of gemini surfactants, as well as for control of the hydrophobicity of the surfactants by variations in the hydrocarbon chain length and the type of headgroups. In this presentation, we present recent developments in such surfactants from the standpoints of their syntheses, aqueous solution properties and potential applications.

Colloidal particle stability in inkjet inks

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The ability to generate, manipulate and deposit tiny droplets (of 20 – 50 μm diameter i.e. equivalent to volumes of 4 – 65 pL) precisely and efficiently is highly appealing. This technology, commonly known as the inkjet technology, is currently dominated by the desktop printing industry. To extend this technology to other applications, such as printed electronics, flat display panels, drugs deposition, etc, requires a better scientific understanding of the inkjet printing process. Particularly, the stability of ink particles throughout the whole process is paramount and understanding how the different aspects of the printing process influence particle aggregation will allow for great improvement in the printing process. This includes the ability to print a wider range of materials as well as to incorporate higher solids content within the ink, which at the moment is typically below 5 vol %.¹

A particular aspect of inkjet printing is the temperature difference that exists between the point of ink injection and the substrate where the ink is deposited. This temperature difference, which can reach up to 60 °C², can be detrimental to the stability of the high solids-loaded ink. This is particularly crucial at the printing nozzle as particle flocculation will lead to nozzle clogging. Therefore, the aim of this work is to investigate the behaviour of particles in a range of ink mediums as a function of temperature, allowing the study of critical flocculation temperature for the chosen particles. This understanding on particle stability will aid in the design of a better high solids content ink, up to 40 vol %, in the relevant ink solvents.

¹ Calvert P, Chemistry of Materials, 2001, 13, 3299.

² Fakhfour V *et al.* Micro and Nanosystems, 2009, 1, 63.

Novel hydrogel composites containing pH-responsive microgels

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Microgels are crosslinked polymer particles with the ability to swell when exposed to an outside stimulus such as pH or temperature. These particles swell and form physical gels which are strong, highly flexible and have high water contents. In biological systems, it would be possible to inject such systems to provide a load-bearing matrix. This could provide a minimally invasive solution to problems such as degenerated intervertebral discs (IVDs). However, due to the physical gel nature of the gels, when exposed to pressure or fluid, they naturally migrate and redisperse as individual particles. This problem severely limits their potential application for IVD repair.

By adding a co-monomer, we have achieved an adaptable system that maintains the advantages of using a microgel whilst fixing the particles in place. Depending on the co-monomer, it is possible to create microgel composites with the ability to preserve the mechanical properties of the microgel and a fluid-to-gel transition which can be triggered physiologically after injection. We show that the mechanical behaviour of these hydrogels can be tuned using co-monomer selection. We further show that it is also possible to utilise the co-monomers in very small quantities to form double network gels that are highly flexible with high swelling ratios, as seen in Fig. 1.

By changing the type and amount of co-monomer, it is possible to form and tune hydrogel composites that are able to utilise the advantages of using microgels to form strong and flexible gels that could be viably used in the body for IVD repair. The structure-property relationships governing this new class of responsive hydrogel composites are discussed.

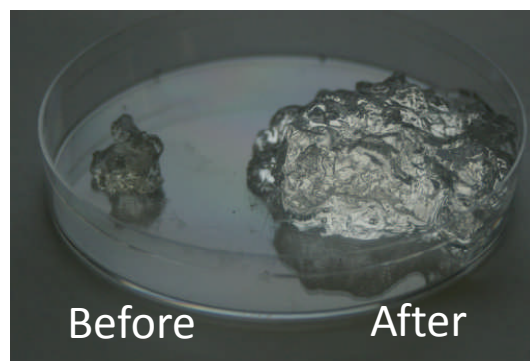


Fig.1. pH-responsive microgel crosslinked with added small-molecule co-monomer before and after 1 week swelling at pH = 7.4.

Many-body effects on depletion interactions

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We investigate the “classic” problem of depletion by ideal chains in a model system of hard-sphere colloids. However, unlike most other approaches, we do not resort to the popular, but rather crude, Asakura-Oosawa (AO) approximation. Instead, we study two different model systems:

- (i) Colloids in polydisperse polymer solutions. Here, we develop an analytic theory, based on a continuum chain model. Assuming spherical symmetry of the polymer field around each colloid, combined with a local approximation, compact expressions can be derived for many-body interactions between the spheres. We also develop the corresponding (but more approximate) pairwise additive interaction. By invoking these expressions in simulations, we show that many-body effects have a profound importance, on phase diagrams as well as structure.
- (ii) Colloids in monodisperse polymer solutions. Here, we use a more “direct” approach, wherein the colloid-polymer potential of mean force, PMF(c-p) is obtained from a single sphere + single chain simulation. The PMF(c-p) is then numerically fitted to a simple analytic expression. With this as input, we can use classical density functional theory (DFT) to exactly calculate the PMF(c-c) such “effective” polymers (ideal particles interacting with colloids via our fitted PMF(c-p)) induce between two colloids. Furthermore, polymer-DFT allows us to calculate the corresponding *exact* PMF(c-c), in the presence of explicit (“real”) ideal chains. At least when the colloids and the chains have equal “size” (which is the case we have focused on), the agreement between the PMF(c-c) produced by explicit and “effective” chains is essentially quantitative! This result is by itself unexpected and quite remarkable. We then proceed to simulate phase diagrams of a dispersion containing colloids and our “effective” polymers. As our “effective” polymers are explicitly included in the simulations, we automatically capture many-body effects. Our results are compared with predictions from the much more approximate AO model.

Toward Soft-Brain Materials with Topological Colloidal Array in Discreet Wrinkle Space

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Wrinkles or folds are ubiquitous—from skin, brain, leaf to cloth they are a commonly observed phenomenon in our life. When membranes are exposed to compressive strains, they typically respond already at rather low stresses by a so-called buckling instability. These wrinkle patterns have received attention in various fields, research and are important building blocks for diverse applications. Spatial periodicity causes unique optical, electronic or acoustic properties due to wave interference phenomena. Here, we discussed the fabrication of unique wrinkle patterns using polydimethylsiloxane (PDMS) as elastomeric substrate covered by a hard layer coating.

We have succeeded construction of complex topological wrinkle patterns inspired by the brain wrinkle, using new 3D axial stretching method. These various wrinkle patterns offers the opportunity to creating hierarchically organized surface and various polystyrene (PS) nanoparticle and DNA fiber arrays.

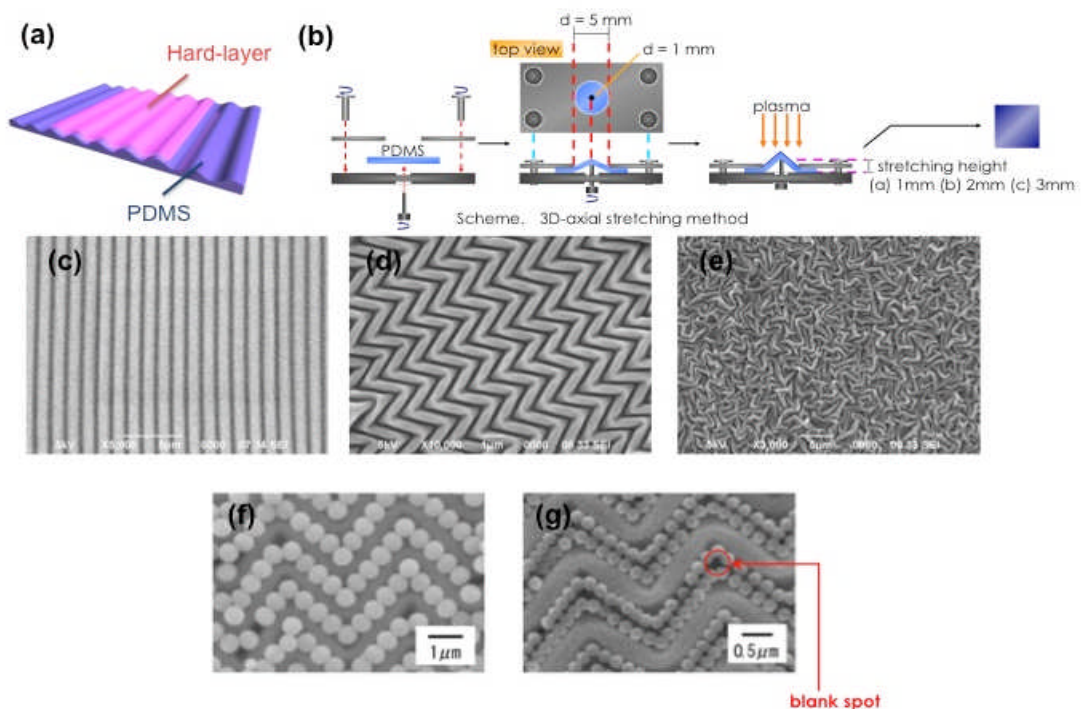


Fig. (a) Schematic illustration of wrinkle structure. (b) Schematic illustration of 3D-axial stretching method. (c, d, and e) SEM images of various wrinkle structures: (c) stripe, (d) herringbone and (e) brain-like shape. (f and g) SEM images of topological PS particle arrays: (f) D=500 nm and (g) D=188 nm.

DNA-loaded calcium alginate nanoparticles

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Gene therapy has attracted major attention due to the broad range of diseases that can be treated by repairing or replacing non-functional genes. Efficient gene therapy requires that DNA is incorporated in a suitable vehicle that protects it against degradation and mediate transport of the genetic material over extra- and intracellular barriers. Calcium-alginate gel particles show good potential to be used as DNA carriers, as they are biocompatible, allow an efficient DNA entrapment and facilitate the release of the genetic material from the endosomes.

In order to allow cellular uptake, the particles carrying the DNA have to be small, preferably in the sub-200 nm range. A plethora of methods is available to produce nanoparticles, for instance, the use of nanoemulsions as templates. Since DNA is sensitive to shear and high temperatures, mild emulsification methods, such as the phase inversion temperature (PIT) method, are better used. In the PIT method, the nanoemulsions are formed by exploiting the characteristic temperature dependence of nonionic surfactants containing ethylene oxide headgroups. Furthermore, the interactions between DNA and these surfactants have been shown to be slightly repulsive.

Here we report on the formation of DNA-calcium-alginate nanoparticles, precipitated in W/O emulsion droplets of controlled size. A purification method was also developed to recover the formed nanoparticles from the emulsion. The DNA-loaded nanoparticles were characterized with respect to their physicochemical properties, e.g. size and size distribution, DNA loading efficiency and release rate.

Amphiphilicity Determines Nanostructure in Protic Ionic Liquids

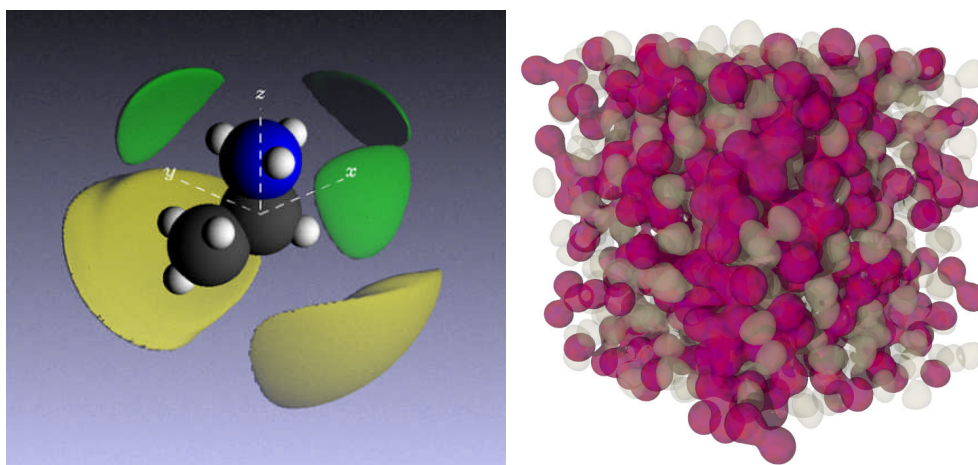
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The bulk structure of the two oldest ionic liquids (ILs), ethylammonium nitrate (EAN) and ethanolammonium nitrate (EtAN), is elucidated using neutron diffraction. The spectra were modelled using empirical potential structure refinement. The results demonstrate that EAN exhibits a long-range structure of solvophobic origin, similar to a bicontinuous microemulsion or disordered L_3 -sponge phase, but with a domain size of only 1 nm. The alcohol (-OH) moiety in EtAN interferes with solvophobic association between cation alkyl chains resulting in small clusters of ions, rather than an extended network.

Studies on the Deposit Microstructure formed from Drying Sessile Drops containing Dispersed Phases through Changes in Marangoni Flows and Rheology and the Consequences for Biodelivery Enhancement

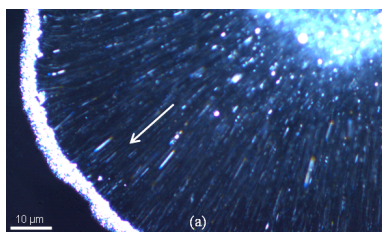
M.A. Faers^{1*}, K. Tsangaris¹, R. Pontzen¹, A. Bismarck².

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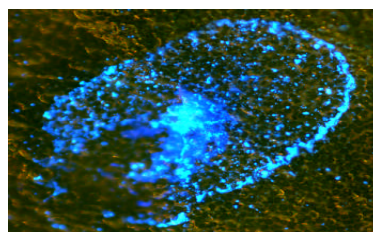
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Annulus deposits formed from drying sessile drops containing dispersed particles have received much attention since Deegan *et al* (Nature **389** (1997) 827) showed the role of an outward capillary flow in their formation. Consequently it is possible that these flows can be harnessed to enhance the association of two different dispersed components in a drying drop. In the case of plant protection products sprayed onto crops this can be applied to modify the association between active ingredient particles and an uptake enhancing adjuvant in the form of an oil in water emulsion, resulting in formulations that are "self organising" once applied.

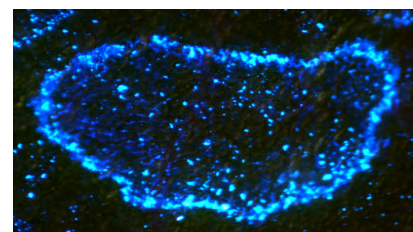
Deposits formed from drying drops containing fluorescent particles and emulsion droplets were imaged with fluorescence microscopy and showed surprisingly unexpected forms depending on surfactant concentration. At high concentrations annulus deposits were observed where both the particles and oil were combined in the annulus. However, low surfactant concentrations resulted in a particle rich annulus with a separate, unassociated oil rich central deposit. The transition between these different behaviours corresponded to the surfactant cmc and the central oil deposit could be attributed to the presence of an inward Marangoni stress at the air:water interface that carried the buoyant oil droplets to the centre.¹ The opposing outward flow and inward Marangoni stress could be utilised for transport by adjusting the relative densities between the various dispersed and continuous phases to produce deposits with different microstructures. Adjustments to the drop rheology to inhibit these flows were also studied to produce additional deposit microstructures. The resulting penetration enhancement for these different microstructures was determined by leaf cuticle membrane penetration studies and showed that the penetration is dependent on the distribution within the deposit and the degree of association between the two components. Consequently, by utilising these techniques to manipulate the transport it is possible to engineer "smart" formulations that produce specific deposits with enhanced performance.



Time lapse image (4s) of particle flow during drying illustrating formation of annulus.



Suspo-emulsion deposit where Marangoni flows have separated the emulsion (centre) and particles (annulus), resulting in low penetration.



Suspo-emulsion deposit where emulsion and particles are combined in the annulus, resulting in enhanced penetration and biodelivery.

¹ M.A. Faers & R. Pontzen, Factors influencing the association between active ingredient and adjuvant in the leaf deposit of adjuvant containing suspo-emulsion formulations, Pest Management Science **64** (2008) 820-833.

Microfluidic evaporation for nanoparticles assembly

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We study gold nanoparticle (NPs) superlattices formation using an original microfluidic technique: microevaporation [1]. Our goal is to form NPs superlattices working as metamaterials in the visible range and to understand mechanisms of their formation knowing NPs interactions.

Microevaporation techniques allow the concentration of any solute in a microfluidic device. The device is made of a microchannel molded in an elastomer (PDMS) in contact with a thin PDMS membrane permeable to water. As the solvent evaporates, solutes are continuously concentrated up to form superlattices [2].

Here, we aim at forming gold NPs superlattices starting from dilute solutions. Stable gold NPs in a volatile solvent are required. We synthesize spherical NPs in water (15 ± 2 nm), with thiol-PEG ligand as steric stabilizing agent [3].

Within the microevaporation device, we follow in space and time the evolution of the concentration of NPs using colorimetry (figure A) and X-ray scattering (figure B).

Upon concentration, the red color (NPs plasmon) gets more and more pronounced until a dense dark state grows along the microevaporator. From the measured growth velocity, we estimate the volume fraction of this dense state at about 40%.

We also performed in-situ microfocused small angle X-ray scattering during microevaporation (ID13, ESRF, France). A typical diffraction pattern is shown in figure 1B and suggest that ordered structures are present in the dense state. While we are still analyzing these results, they seem to open a promising route for the formation of three-dimensional superlattices.

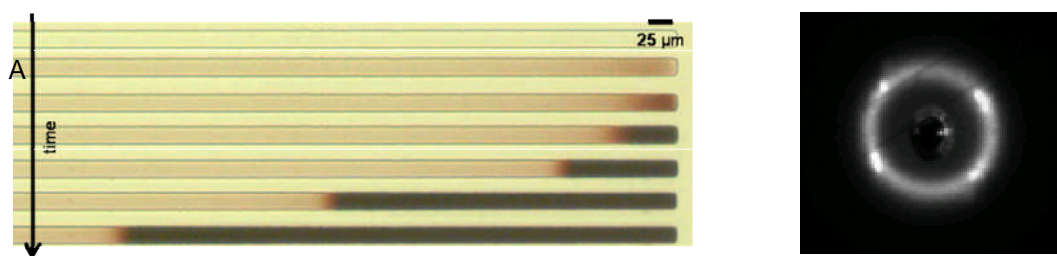


Figure A) Evolution of the solution color in the microevaporator. The reservoir is on the left, the tip of the channel on the right. **B)** SAXS diffraction pattern observed during gold NPs concentration process.

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Colloids crossing mucosal barrier: non-invasive delivery of biological

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Delivery of biotherapeutics (peptides, proteins, antibodies, nucleic acids, siRNA) *via* the mucosal surfaces to produce systemic therapeutic effect is a highly attractive option towards achieving an 'injection free' therapy. However, epithelial cells at the mucosal surfaces present a formidable biological barrier to the transport of biotherapeutics. Our work is focused on answering the following questions: Can colloids enable big and/or hydrophilic molecules to cross a mucosal barrier to achieve systemic therapy? Which transport pathways can be exploited by the colloidal particles to enhance the mucosal transport of biotherapeutics?

We are investigating the use of colloidal particles with specific surface modifications to trigger their active transport across the mucosal surfaces. Using the cell layers of an airway epithelial cell line (Calu-3) as a representative mucosal surface, we studied the potential of the natural transcytotic pathways of vitamin B₁₂ and immunoglobulin IgG, in addition to the folate receptor uptake pathway, to transport colloidal particles across mucosal surface. Sub-200 nm colloids were surface modified with these ligands and their cellular uptake and transport across the cell layers assessed. Expression of relevant cellular receptors (cubilin, neonatal Fc and folate receptors) by the cell layers was demonstrated by immunofluorescence assays.

Confocal microscopy examinations illustrate ligand-receptor dependent cellular internalisation and transport in the apical-to-basolateral direction of the modified colloids, whereby studies on the uptake pathways using specific inhibitors illustrate the complexity of the intracellular trafficking of the colloids. Interestingly, for vitamin B₁₂ modified colloids the tracking studies revealed that, unlike vitamin B₁₂ ligand *per se*, the B₁₂ modified colloids circumnavigate lysosomal compartments and translocate across the cell to a significant degree. Surprisingly, the folate modified colloids also demonstrate the ligand-receptor dependent apical-to-basolateral transport in the cell layers, the event that has not been demonstrated previously.

Our work therefore demonstrates the possibility of promoting transmucosal delivery of colloidal particles across mucosal surfaces by exploiting natural transport pathways and suggests that such systems could act as carriers of biotherapeutics.

The kinetics of colloidal aggregation – Effect of bimodal Hamaker constant distribution and Brownian forces.

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The kinetics of self-assembly of colloidal particles was studied using a Discrete Element Method, or molecular dynamic, computer simulation. In particular, the effect of changing the Hamaker constant on the rate of particle aggregation was considered. The simulation methodology is similar to that of Moreno-Atanasio et al. [1]. The long range van der Waals interactions were modelled using the Hamaker equation [2]. Long range electrostatic forces were excluded from this study while the forces experienced by particles during elastic contact were given by Hertz' law. The effect of Brownian forces was also considered.

The test sample consisted of 1000 spherical silica particles with density 2200 kg/m^3 and $R_1=R_2=50 \text{ nm}$. Eight cases with a bimodal Hamaker constant distribution were considered, half with Brownian forces acting on the particles and half without. In each case the first species of 500 particles were assigned a Hamaker constant of $H_1=9 \times 10^{-20} \text{ J}$, a typical value for silica particles, while the remaining 500 had $H_2=\{0, 1, 5, \text{ or } 9\} \times 10^{-20} \text{ J}$. The kinetics of self-assembly were analysed using the number of contacts, the number of small clusters (single particles, pairs and triplets) and the size of the largest cluster.

The characteristic aggregation time for every self-assembly, as determined from the evolution of the inter-particle contacts, follows a non-linear relationship with the potential energy pre-existing in the suspension before the aggregation process. The aggregation time increases as the Hamaker constant decreases, and Brownian forces increase the self-assembly rate.

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Spontaneous formation of non-spherical O/W emulsion droplets in particle stabilised systems

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Recently, Studart et al.¹ reported the formation of non-spherical emulsion droplets in silica stabilised monodispersed emulsions formed in a micro-fluidics device. This paper reports on similar effects seen in a Pickering O/W emulsion stabilised by a surface modified kaolinite. At sufficiently high concentrations the emulsion droplets, although flocculated to some degree, showed good stability towards coalescence and were normal spherical droplets. However, at low concentrations, the droplets showed greater flocculation, and at the lowest concentrations the droplets were seen to coalesce into non-spherical geometries over time. This was due to a combination of the irreversible nature of the particle adsorption at the interface and an initial effective fractional surface coverage by the kaolin of less than 1.

The droplets are thought to undergo arrested coalescence¹, in which the fusing together of two droplets reduces their total interfacial area so that the effective surface coverage by the particles increases. However, because the particles tend not to desorb from the interface, the droplets are forced to adopt non-spherical shapes to accommodate the particles when the area occupied by the particles is greater than that of the sphere of equal volume to that of the two particles combined. Analysis shows that this occurs in a relatively narrow range of surface coverage. A wide range of droplet shapes have been observed, ranging from dumb-bells to droplets with horn-like protrusions. Below a critical surface coverage, dependent on the size ratio of the droplets, the droplets form spherical droplets after coalescence.

At an intermediate concentration of clay, the emulsion droplets showed strong flocculation which appeared not to arise from simple droplet- droplet attraction. Freeze fracture SEM suggested that adjacent flocculated droplets share adsorbed particles, as suggested by Horozov and Binks².

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Interactions between biosurfactants and particles as colloid stabilizing agents

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Most foods and certainly most processed foods can be described as being colloidal in nature, i.e., they consist of small volumes of solid, liquid or gaseous matter dispersed or aggregated in continuous fluid phase. A major biosurfactant influencing colloidal stability is protein, since proteins adsorb to almost all surfaces and often form films with particularly high interfacial strength. Solid particles of the correct size and wetting characteristics possess certain advantages as stabilizers of foams and emulsions, but relatively little is known about what happens when both surface active particles, proteins and other biologically relevant surfactants are present together. Crystals of saturated fat are the only commonly occurring biosurfactant solid particles present in foods, but saturated fat is possibly not an ingredient to promote because of the perceived link with heart disease. Here we show how useful alternative surface active particles can be created from other food ingredients, such as cellulose and starch granules. Benign inorganic particles modified by adsorption of appropriate biosurfactants can also be used, such as silica particles with adsorbed surfactants. Various insoluble organic crystals of flavonoid compounds can also act as stabilizers of Pickering emulsions. Effects on colloidal stability were investigated via measurements of adsorbed film strength; air bubble coalescence and disproportionation; coalescence and creaming of oil-in-water emulsions. In general, it is shown that the surface active particles on their own often exhibit lower surface activity, film strength and stabilizing properties than proteins, but combinations of particles + proteins (or other surfactants) show enhanced the film strength, with concomitant increases in bubble and emulsion droplet stability. In effect, particles appear to act as reinforcing filler particles in the adsorbed films. This has implications for food colloid stability, the encapsulation and delivery of various insoluble dietary components and the oral delivery of pharmaceuticals.

Competitive adsorption of surfactants with non aqueous colloidal particles used in lubricant additives

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Additives are used in lubricants to minimise destructive processes in the engine (*e.g.* wear and corrosion) and to confer beneficial properties (*e.g.* improved fuel economy). Overbased detergents are an integral element of such systems, and consist of surfactant stabilised inorganic nanoparticles (comprising calcium carbonate). Such additives represent “model” hard-sphere systems with narrow polydispersity and mean core radius $\sim 2 - 5$ nm. Overbased detergents are used in lubrications to provide protection against corrosion, ensure piston cleanliness and prevent sludge formation. In addition to surfactants used to stabilise detergents, other surface active species are present in lubricant additive formulations (*e.g.* to prevent agglomeration of soot and to reduce the coefficient of friction and hence improve fuel economy). Interactions/ competition between such additive species can result in modification of stability/ properties. The kinetics of surfactant exchange has been extensively studied for (liquid) microemulsion droplets in non aqueous media. However, competitive adsorption behaviour of surfactants at the solid/ (non-aqueous) liquid interface has received relatively little study to-date. This talk will highlight recent mechanistic studies of interaction of surfactant stabilised overbased detergent particles with other surface active species found in the engine.

A convenient method for studying the kinetics of interaction in such systems involves the use of partially deuterated aromatic surfactants produced by an H – D exchange reaction which comprised a d-head group, d-aromatic ring and an h-tail (of C18) in time-resolved stopped flow measurements using small angle neutron scattering (using D22 at the ILL, Grenoble). In addition, NMR diffusion (utilising Pulsed Field Gradient NMR) has been utilised to elucidate further mechanistic information regarding interactions.

Solution Conformation of Polymer-Drug Conjugates: Contrast-variation SANS as a tool to elucidate the microstructure of uni-molecular aggregates.

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Polymer-drug conjugates (PDCs) are advanced drug delivery systems that make it possible to target drugs to sites of disease and can enable the controlled release of drugs into the body [1]. There is particular interest in their potential as anti-tumoral therapeutics, where the use of a biocompatible, water-soluble polymer carrier linked to a powerful chemotherapeutic molecule affords increased solubility of a hydrophobic drug, enhanced circulation times in the body and concentration of the active molecule to tumour sites where it is selectively released, thereby reducing toxicity and side-effects.

There is increasing recognition that the conformation adopted by these conjugates during transport and delivery processes can significantly influence therapeutic performance [3][4]. Here we present results from a study using custom synthesised conjugates designed to obtain a better understanding of the dominant factors affecting conjugate conformation. Small-angle neutron scattering (SANS) and Pulsed-Gradient Spin-Echo NMR (PGSE-NMR) have been used to characterise the solution properties of model polymer-drug conjugates based on HPMA copolymers containing Gly-Phe-Leu-Gly peptidyl side-chains as enzyme cleavable polymer-drug linkers[2][3][5]. These experiments have allowed us to investigate the different conformational influence of hydrophobic and steric interactions and interactions between aromatic groups, ultimately allowing for prediction of solution conformation.

The size and shape of unimolecular aggregates has been determined *via*. theoretical modelling of SANS data, revealing a shape change from random coil to a rod-like morphology dependent on the type and amount of hydrophobe attached. Exploiting the isotopic selectivity of SANS experiments, selective deuteration of drug-mimics has facilitated contrast variation SANS experiments to obtain a clearer picture of aggregate microstructure [5].

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Adsorption Kinetics from Polymer/Surfactant Mixtures at an Expanding Liquid Interface

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Mixtures of oppositely charged polymers and surfactants are widely used in industrial applications as detergents, foam stabilisers, wetting agents, emulsifiers, and rheology modifiers. The extent to which polymers and surfactants interact in solution can determine both the bulk and interfacial properties of the system. Our interest is in the dynamics of such systems, rather than their traditionally studied equilibrium properties, as many applications of polymer/surfactant mixtures are employed under conditions far from equilibrium. The sample environment we use for this purpose is the Overflowing Cylinder [OFC], which is an established platform for the study of adsorption dynamics from surfactant solutions. The OFC is based on the creation of a stable continuously expanding air-water interface, which can be studied using different techniques and for long time periods. In this project, a combination of ellipsometry and neutron reflectometry is being employed to study adsorption from polymer/surfactant mixtures at the interface of the OFC.

Different combinations of polymers and surfactants exhibit very different adsorption behaviour on the OFC, even if predictions would have them behave similarly due to their comparable extent of charge. Generally, at low surfactant concentrations, the adsorbed amount at the interface is greater than it would be for either the pure polymer or surfactant in solution. However, at higher surfactant concentrations, the behaviour varies depending on the system. For some systems, a sudden marked decrease in adsorption occurs at concentrations close to the charge equivalence point, generally corresponding to the formation of large aggregates in solution. However, other polymer/surfactant systems show no sudden decrease in adsorption and exhibit very different phase behaviour.

The OFC enables us to examine the influence of bulk phase behaviour on interfacial adsorption, as we can use it to distinguish between the adsorption of soluble species (single molecules and complexes) and bulk phase aggregates. This is due to the fact that only molecules and small complexes can reach the interface on the timescale of surface expansion, due to the lower diffusion rate of macroscopic aggregates. This direct evaluation of the effect of bulk behaviour on surface behaviour is not possible by any other single method.

We are using a combination of ellipsometry and neutron reflectometry to examine the amount and nature of the material adsorbed at the interface from a range of compositions of polymer/surfactant systems. Following this, we aim to combine the data in order to build a model of the variations in adsorption behaviour from polymer/surfactant systems.

BACK

Hydrodynamic stresses in colloidal aggregates under shear flow

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Many colloidal systems consist of particles that are aggregated and dispersed in a liquid. Under stirring conditions, such colloidal aggregates are exposed to hydrodynamic forces, which can cause restructuring or breakup. The quantitative estimation of such behaviour requires a detailed numerical method to deal with the correlation between the flows and aggregates, as the imposed flow is disturbed by the aggregate and the aggregate is restructured by the imposed flow. In this study, we have primarily applied Stokesian dynamics to calculate hydrodynamic forces acting on the primary particles of aggregate. Due to the computational efficiency of this method, we are able to investigate a wider range of aggregate sizes than the finite element method. We have found power-law relationships between the stresses and the number of primary particles for several types of fractal aggregates. The results obtained, in turn, provide a means to estimate the strength of inter-particle bonds by observing the restructuring of colloidal aggregates in experiments. Moreover, it can be shown that the free-draining approximation, which is sometimes used as a first approximation in many studies, fails to predict hydrodynamic forces properly. We also report on the validity of Stokesian dynamics for modelling colloidal aggregates systems, by directly comparing to finite element method simulations. We have obtained insights into the Stokes flows in which colloidal aggregates are dispersed.