UK Colloids 2014:

An International Colloid and Interface Science Symposium

July 6th - 9th 2014 • London • www.ukcolloids.com

CONFERENCE BOOKLET

RSC/SCI Colloids Group

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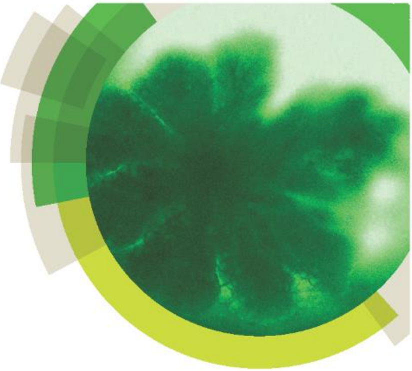

17-19 September 2014, Bristol, UK

Physical Chemistry of Functionalised Biomedical Nanoparticles

Faraday Discussion 175

Themes

Magnetic nanoparticles 1: diagnostics

Magnetic nanoparticles 2: therapeutics

Optical nanoparticles

Other nanoparticles

Speakers

Paul Alivisatos
Lawrence Berkeley National Laboratory

Kerry Chester
UCL Cancer Institute

Peter Dobson
University of Oxford

Mostafa El-Sayed
Georgia Institute of Technology

Hedi Mattoussi
Florida State University

Ivan Parkin
University College London

Oliver Reiser
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http://rsc.li/fd175

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www.colloidsgroup.org.uk

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Photo courtesy of Thanh Nguyen, Department of Physics & Astronomy, University College London

Dear Delegate,

It is my pleasure to welcome you to London for the UK Colloids 2014 Conference. This is the second conference in this series and is being jointly organised by the RSC Colloid and Interface Science Group, the SCI Colloid and Surface Chemistry Group, the Institute of Physics, Polymer Physics Group and the UK Polymer Colloid Forum. Our aim in setting up such meetings is to showcase colloid and interface science performed in the United Kingdom, together with the best cutting-edge science being performed overseas. We hope this meeting will provide an ideal opportunity to meet, present and discuss colloid and interface science with a wide variety of backgrounds. At the last count, we have delegates from 28 different countries and a diverse spread of affiliations and different levels of experience.

The venue we have selected for Colloids 2014 is the Mermaid Theatre. The Mermaid hosted major theatrical productions for over 60 years, before being converted into a conference venue in 2011. Its location, on the North Bank of the Thames is at the crossroads of old and new London, with St. Paul's Cathedral, the Tower of London, the Tate Modern and the Shard only a short distance away. I feel that this is appropriate for colloid and interface science in 2014; the traditional areas of colloid and interface science will be represented at the conference alongside newer areas such as nanoscience and medicine.

The organisation of a large meeting represents a major challenge and throws up many challenges. As chair of the conference I was somewhat surprised to discover that we were also accommodating the Tour de France cycle race on day one of the conference! We have built time into the conference for delegates to view the race. The World Cup is also taking place during the conference. Many of the local bars and pubs will be showing the games (with ample space since England were knocked out so early in the tournament!).

I hope that Colloids 2014 will prove both valuable and inspiring to delegates. My personal advice would be to try and attend some of the sessions which are not directly related to the field you work in. It is such cross-fertilisation which can result in some of the best ideas. Finally, on behalf of the Joint RSC and SCI Colloid Group I hope that you have an enjoyable time in London at Colloids 2014. Our capital is a diverse city, with something to offer for everyone. If there is any way I (or the UK Colloids Team) can help, please do let us know.

Prof. Peter J. Dowding

peter.dowding@infineum.com

Chair UK Colloids 2014 Conference & Chair RSC Colloid & Interface Science Group.

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The Joint RSC/SCI Colloids Group

In 1958 Sir Eric Rideal, a Past President of the SCI, founded the Colloid and Surface Chemistry Group to support the growing importance of colloids and surface chemistry in industry. Subsequently, in 1971 Ron Ottewill, Geoff Parfitt and Dennis Haydon with the support of Sir Eric created the Colloid and Interface Science Group within the Faraday Society, one of the RSC forerunner societies. This was in response to the increasing number of colloid centres being formed in academic institutions.

Since 2002 the two groups have worked jointly forming the "Joint Colloids Group" in order to provide a coherent focus for the UK colloid and interface science community, both in academia and industry. The Colloids Group organises various scientific events ranging from one day meetings to its multiday international meeting, UK Colloids 2014. The group also manages three awards, the McBain Medal, the Thomas Graham Lecture and the Rideal Lecture for early, mid and later career contributions to colloid and interface science.

For further details including our other events please see our website: www.colloidsgroup.org.uk.

Day 1. Monday 7th July, Mermaid Theatre

Conference Opening. 10.00 am							
Plenary 1 Julian Eastoe. 10.15 – 11.15 Auditorium							
Session							
11.30	Keynote #1	**A. Auditorium** **Design: Microfluidics** *Chair: Jerome Bibette* K1. **David Weitz** Harvard University, USA **New Routes to Particle Synthesis: Making particles one by one**	**B. Queenhithe Room Application** *Chair: Wim Thielemans* K2. **Jan Dhont** Forschungszentrum Juelich, Germany **Electric-Field Induced Phases and Dynamical States in Suspensions of Rods : Association and Dissociation of Condensed Ions**		11.30-12.00	Keynote #1	**C. Lower River Room** **Nano** *Chair: Mathias Brust* K3. **Jochen Feldman**, LMU Munich, Germany: **Nanoplasmonics Meets Bio**
12.00	#1	112. **Nicolas Taccoen** Ecole Polytechnique, France **Mechanics of a colloid-armored bubble**	111. **Samuel Eyley** KU Leuven, Belgium **A Simple One-Pot Route to Cationic Cellulose Nanocrystals**		12.00-12.30	Invited #1	I1. **Su Xiao Di**, ASTAR, Singapore: **Studying Protein-DNA Interaction Using Gold Nanoparticles Exploiting Particle Aggregation, Refractive Index Change, Fluorescence Quenching and Enhancement Principles**
12.20	#2	185. **Perrine Colliat-Dangus**, LCMD, CNRS UMR, France. **Millimetric emulsion**	97. **Gregory Smith** Bristol University, UK **Electrophoresis of Polymer Latexes in Nonpolar Solvents**				
LUNCH 12.40 – 13.30 Upper River Room							
13.30	Keynote	**A. Auditorium**	**B. Queenhithe Room**		13.30-	Keynote	**C. Lower River Room**

	#2	Design: Micelle, Microemulsion, and Nanoemulsion *Chair: S. Sajjadi* K4. **Conixta Solans** IQAC-CSIC Spain **Design of nano-emulsions with controlled size by low-energy methods**	Characterisation *Chair: Alison Paul* K5. **Karen Edler**, Bath University **Self-Assembling Colloidal Systems: Structure** **Development from Molecule to Microparticle**		14.00	#2	Nano *Chair: Jochen Feldman* K6. **Mathias Brust**, University of Liverpool: **Cellular uptake of Gold Nanoparticles for Therapy and Imaging**
14.00	#3	121. **Jin Woong Kim**, Hanyang University, Republic of Korea **Extremely Stable Nanoemulsions Fabricated by Interfacial Assembly of Amphiphilic Block Copolymers during Phase Inversion**	52. **Richard Campbell**, Institut Laue-Langevin, France **New method to predict the surface tension of** **colloidal polyelectrolyte/surfactant mixtures**		14.00- 14.30	Invited # 2	I2. **Antonios Kanaras**, University of Southampton: **Gold Nanoparticles and Biological Structures**
Short Break							
14.25	#4	151. **David Growney**, University of Sheffield **Effect of block composition on micelle size and steric stabilizer layer thickness: polystyrene-based diblock copolymers**	63. **Grant Webber**, University of Newcastle, Australia **The critical edge: salt effects on polybasic brushes**		14.30- 15.00	Invited # 3	I3. **Larry Yung**, NUS, Singapore: **Plasmonic Nanoparticle Assembly for Biosensing Applications**
14.45	#5	126. **Kaushik Kundu** Indian Statistical Institute, Kolkata, India, **Formation and Characterization of Mixed Cationic Ionic Liquid and Nonionic Polyoxyethylene Type Surfactants Microemulsion Systems**	146. **Stuart Prescott**, UNSW Australia **Hydration of odd-even terminated polyelectrolyte multilayers under confinement**				
Tea Break 15.05 – 15.35 Upper River Room Opportunity to view Tour de France Race							
15.35	Keynote #3	**A. Auditorium** Design *Chair: Christopher Serra* K7. **G. Vladisavljevic** University of Loughborough, **Production of nanoparticles using**	**B. Queenhithe Room** Characterisation *Chair: Rico Tabor* K8. **Terence Cosgrove**, University of Bristol **Dynamics of Nanoparticles in melts,**		15.35- 16.05	Keynote #3	**C. Lower River Room** Nano *Chair Xiao Di Su* K9. **Federico Rosei**, INRD, Canada: **The role of surfaces and interfaces in multifunctional materials**

		membrane contactors and microfluidic devices	solutions and at surfaces as studied by NMR				
16.05	#6	234. Erika Eiser, University of Cambridge, Designing Disorder Using DNA-Functionalized Colloids	2. Grace Cookey, University of Bristol Is CMC of surfactant mixtures an ill-defined parameter?		16.05-16.25	#1	47. Peter Griffiths, University of Greenwich: Understanding the structure-function relationships of colloidal drug delivery vehicles with neutron scattering and spin resonance
16.25	#7	109. Christine Dalmazzone, IFPEN &, Université de Bordeaux I, France Study of the water/crude oil interfacial properties by microfluidic	170. Martin Greenall, Aberystwyth University Size selection in self-assembly: a theoretical study		16.25 - 16.45	#2	116. Marina Resmini, Queen Mary University of London: Switchable fluorescent PEG-b-PPS micelles for non-invasive transdermal drug delivery
Short Break							
16.50	#8	182. Dimitris Josephides, Kings College London, UK. Stabilising the dripping regime of viscous droplet production via core-shell templating	102. Shirin Alexander, University of Bristol The Aggregation Behaviour of Polyisoprene–Pluronic Graft Copolymers in Selective Solvents		16.50-17.10	#3	69. Maria Wuithschick, Humboldt Uni of Berlin, Germany Turkevich in new robes: key questions answered for the most common gold nanoparticle synthesis
17.10	#9	174. Wei Wang Sichuan University (China) & Harvard University (USA) Hole-Shell Microparticles from Controllably Evolved Double Emulsions	74. Jamie Hurcom, Cardiff University The interfacial structure of polymeric surfactant stabilised air-in-water foams investigated in-situ by small-angle neutron scattering.		17.10-17.20	#4	71. Minh Chau Pham, Uni. Paris Diderot Sorbone, France Direct Electrochemical Detection of micro RNAs using composites Conducting Polymer/Carbon Nanotubes or Reduced Graphene Oxide
Break							
Thomas Graham Lecture. Steve Armes 17.30 – 18.30 Auditorium							
Poster/ Drinks. 18.30– 20.00 Upper River Room							

Day 2. Tuesday 8th July

Plenary 2. Kenneth Dawson 09.00 – 10.00 Auditorium								
Session								
10.15	Keynote #4	A. Auditorium Design: Emulsions *Chair: David Weitz* K10. Jerome Bibette, Laboratoire Colloides et Matériaux divisés, France Microorganism Growth Variability in Droplets	B. Queenhithe Room PCF *Chair: Alex Routh* K11. Dirk Aarts University of Oxford, Contact Line – Quo Vadis?	D. Bishopsgate Room Application *Chair: Jan Dhont* K12. Limin Wu Fudan University, China Fabrication and Assembly of Polymeric/Inorganic Nanocomposite Colloidal Hybrid Hollow Spheres		10.15-10.45	Keynote #4	C. Lower River Room Nano *Chair: Etienne Duguet* K13. Jesus Martinez de la Fuente, University of Zaragona, Spain: DNA as Molecular Local Thermal Probe for Magnetic Hyperthermia Analysis
10.45	#10	90. Neda Sanatkaran Cape Peninsula University of Technology, Republic of South Africa Stability of highly concentrated W/O emulsions with super-cooled dispersed phase: Effect of Surfactant Structure	42. Victoria Cunningham University of Sheffield, Thermo-responsive Diblock Copolymer Worm Gels with Tunable Critical Gelation Temperature	73. Dmitry Shchukin Liverpool University, UK Nanocapsule-based Active Coatings		10.45-11.05	Invited # 4	I4. Galina Galoverda, Xavier Uni, USA: Development of Non-Polymeric Amphiphilic Coating for Metal Oxide Nanoparticles to be used as Delivery and Imaging Agents
Coffee Break 11.05 – 11.25 Upper River Room								
11.25	Keynote #5	A. Auditorium Design: Pickering Emulsions *Chair: Conxita Solans* K14. Bernie Binks University of Hull, UK Particle-stabilised novel materials	B. Queenhithe Room PCF *Chair: Stefan Bon* K15. Joseph Keddie University of Surrey, Harnessing Capillary Pressure in the Assembly	D. Bishopsgate Room Application *Chair: Markus Retsch* K16. Vesselin Paunov, University of Hull Colloidal Cell Imprints for Biosensor and		11.25-11.55	Keynote #5	C. Lower River Room Nano *Chair Etienne Duguet* K17. Claire Billotey, University of Lyon, France: Knowledge and take off of Clinical constraints: a

			of Colloidal Particles in Nanocomposites	**Antimicrobial Applications**				**security to reach Nanomedicine !**
11.55	#11	123. **Erica Wanless**, University of Newcastle, Australia **Arrested Coalescence Behavior of Giant Pickering Droplets and Colloidosomes stabilized by Poly(*tert*-butylaminoethyl methacrylate) Latexes**	115. **Muriel Lansalot**, University of Lyon, France, **Cationic polymer latexes prepared by RAFT-mediated surfactant-free emulsion polymerization for the modification of cellulose surfaces**	138. **Kirsi Yliniemi**, Aalto University, Finland **Towards Smart Drug Carriers: Formation of pH-Responsive Polyelectrolyte Shell around Magnetic Core**		11.55-12.25	Invited # 5	I5. **Sylvie Begin**, University of Strasbourg, France, **Dendronized magnetic core-shell and cubic shaped nanoparticles designed for targeting, MRI and hyperthermia**
Short Break								
12.20	#12	**Design** 28. **Frederic Hapiot**, Université d'Artois, France. **Aqueous Organometallic Catalysis: Contribution of CD-Based Hydrogels and CD-Substituted Polymers**	**Characterisation** 113. **Pavel Metejicek**, Charles University of Prague, Czech Republic **Metallacarboranes as a New Class of Surfactants: Aggregation in Water and Interaction with Polymers**	**Application** 191. **Priyank Mohan**, Japan Advanced Institute of Science and Technology, Japan **FePtAu Nanoparticles as Novel Magnetic Bioprobes**		12.25-12.55	Invited #6	**Nano** I6. **Florence Gazeau**, University of Paris Diderot: **Controlling biodegradation and fate of magnetic particles for medical applications**
12.40	#13	178. **Olivier Cayre**, University of Leeds **Complex Colloidal Polymer Particles *via* Radical Dispersion Polymerization in Non-Polar Solvent for Electrophoretic Display Applications**	89. **Gavin Hazell**, University of Bath, **Polymer Stabilised Nanodiscs adsorbed at the Silicon-Water Interface**	130. **Mehriban Akin Ulusoy**, University of Hannover, Germany **Aqueous Synthesis of Red-Emitting CdTe/CdS/ZnS Quantum Dots and Their Interactions with Cells**				
LUNCH 13.00 – 14.00 Upper River Room								

14.00	#14	A. Auditorium Design: Pickering Emulsions *Chair: Bernie Binks* 117. Catherine Whitby, University of South Australia, Australia Destabilising Pickering Emulsions	B. Queenhithe Room Characterisation *Chair: Alex Routh* 62. Rico Tabor, Monash University, Australia Measuring the hydrophobic force in a soft matter system	D. Bishopsgate Room Application *Chair: Shannon Notley* 44. Rui Xie Sichuan University, China Bio-Inspired Mini-Eggs with pH-Responsive Membrane for Enzyme Immobilization		14.00-14.30	Invited talk # 7	C. Lower River Room Nano *Chair Sylvie Begin* 18. Etienne Duguet, University of Bordeaux, France: About the opportunity to include inorganic components in nanoscaled drug delivery systems
14.20	#15	147. Valerie Ravaine, Université de Bordeaux, France Pickering emulsions stabilized by soft microgels	150. Martin Sweatman, University of Edinburgh Cluster formation in fluids with competing short-range and long-range interactions	162. Fanny Yuen University of Cambridge, UK Life in Extreme Environments: The Role of Intrinsically Disordered Proteins under Conditions of Abiotic Stress		14.30-15.00	Invited talk # 8	17. Laurence Motte, University of Paris 13, France: Synthesis and functionalisation of nanoparticles and some biological applications
14.40	#16	183. Jennier Krings, Westfälische Wilhelms-Universität Münster, Germany Photoresponsive Aggregation of β-Cyclodextrin Capped Nanoparticles	4. Malcolm Povey, University of Leeds Crystal nucleation kinetics in colloids	190. Claudia Pigliacelli Politecnico di Milano, Italy Development of Fluorinated Colloidal Gold Nanoparticles as Theranostic Drug Delivery Systems				
15.00	#17	169. Ibrahim Salama, Cardiff University, Stabilisation of Fluorinated Oil-in-Water Emulsions using Fluoroalkyl-Functionalized Silica	39. Sean Breann Ó Conchúir, University of Cambridge The breakup mechanism of biomolecular and colloidal aggregates in a shear flow	1. Etienne Duguet, University of Bordeaux, France: Multipod-like Polystyrene/Silica Clusters Designed by Seeded-growth Emulsion		15.00-15.30	Invited talk #9	19. Carla Cannas, University of Cagliary, Italy: Hydrophobic nanoparticles: a versatile platform to design colloidal silica-based nanostructures

		Nanoparticles		Polymerization: Towards Colloidal Molecules and Unconventional Inorganic Nanoparticles				
Tea Break 15.20 – 15.40 Upper River Room								
15.40	Keynote #6	A. Auditorium Design: Smart Materials *Chair: Goran Vladisavljevic* K18. **Christopher Serra,** University of Strasbourg, France **Engineering polymer micro and nanoparticles with controlled size, composition and morphology by microfluidics-assisted emulsification**	B. Queenhithe Room Characterisation *Chair: Peter Griffiths* K19. **Victor Starov,** Loughborough University **Superspreading vs surfactant enhanced spreading: the role of adsorption on water/air interface**	D. Bishopsgate Room Application *Chair: Vesselin Paunov* K20. **Harry Frampton** BP Upstream Technology, UK **Colloid Uses and Use of a Colloid in Enhanced Oil Recovery**		15.40-16.10	Keynote #6	C. Lower River Room Nano *Chair: Marina Resmini* K21. **Shinya Maenosono,** JAIST, Japan : **Core@shell heterostructured nanoparticles for next-generation SERS applications**
16.10	#18	153. **Xiao-Jie Ju** Sichuan University, China. **Multi-Stimuli-Responsive Microcapsules for Adjustable Controlled-Release**	38. **Adam Eales,** University of Cambridge **Achieving a 'flatter' film profile for application s in P-OLED displays: a numerical and experimental investigation of mixed solvent inks and their influence on film shape**	58. **Merlin Etzold** University of Cambridge, UK **Model Sheet Structure for Cement**		16.10-16.30	#7	133. **Jean-Paul Lellouche,** Institute of Nanotechnology, France: **Ultra-Small Functional α-Maghemite Nanoparticles: Surface Engineering for Effective siRNA/microRNA-Mediated Delivery/Gene Silencing Applications**
16.30	#19	141. **Zhenzhong Yang,** Chinese Academy of Sciences, China **Janus Materials**	100. **Michael Neeson,** University of Melbourne, Australia **The evaporation of a capillary bridge between**	204. **Vincent Poulichet** Imperial College, London, UK **Microparticle Disassembly from Fluid Interfaces:**		16.30-16.50	#8	160. **Jean-Daniel Marty,** University Paul Sabatier, France, **Stimuli responsive hybrid nanomaterials**

			a particle and a substrate	Remotely Triggered Particle Delivery				from synthesis to applications in nanomedecine
Short Break								
17.00	#20	168. Tiffany Wood University of Edinburgh, UK Liquid Crystal Gels	96. Steve King ISIS Facility, UK On the Fate of Silver Nanoparticles in Simulated Primary Wastewater Treatment	144. Alison Tasker University of Leeds, UK The Effect of Stabilizer Choice on Microcapsule Morphology		17.00-17.20	#9	19. Felix Schacher, FSU Jena, Germany: Patchy+Smart = Efficient?- Design of Advanced Micellar Carriers with Tunable Charge and Composition
17.20	#21	70. Clare Mayes Imperial College London, Colloidal Suspensions of Pharmaceutical Solids in Non-aqueous Systems	61. Vladimir Kolesnichenko, Xavier University, USA NMR Relaxivity Studies on Surfactant-free Superparamagnetic Iron Oxide Nanoparticles: the Effect of Particle Size, Magnetization and an Iron Oxidation State	158. Joseph Keddie, University of Surrey, UK Large-area Patterning of the Tackiness of a Colloidal Nanocomposite Adhesive by Sintering of Nanoparticles under IR Radiation		17.20-17.40	#10	80. Ang Shan, NUS, Singapore: Probing the True Near-Field Interaction between Metallic Nanoparticle and Fluorophore in Bulk Colloidal Solution Using Toehold-Mediated Internal Control
Break								
Conference Dinner: Park Plaza Riverbank: 19.00								

Day 3. Wednesday 9th July

Plenary 3. Ray Dagastine 09.00 – 10.00 Auditorium							
Session							
10.15	Keynote #7	A. Auditorium Characterisation *Chair: Peter Wiright* K22. Stefano Capelli, Eindhoven University of Technology, The Netherlands. Interaction of particles with fluid-fluid interfaces quantified using magnetic tweezers	B. Queenhithe Room Application *Chair: Stuart Prescott* K23. Markus Retsch Bayreuth University, Germany The Versatile Properties of Hollow Spheres		10.15-10.45	Keynote # 7	C. Lower River Room Nano *Chair: Lanry Yung* K34. Quentin Pankhurst, UCL IBME
10.45	#22	6. Alberto Striolo, University College London, UK Understanding Pickering Emulsions Using Mesoscale Simulations	35. Kate Thompson University of Sheffield, Can Polymersomes form Colloidosomes?		10.45-11.15	Invited talk #10	19. Nguyen T.K. Thanh UCL, UK: Next Generation of Magnetic Nanoparticles
Coffee Break. 11.05 – 11.25 Upper River Room							
11.25	Keynote #8	A. Auditorium Design: Smart Materials *Chair: Goran Vladisavljevic* K25. Stefan Bon, University of Warwick, Chemotaxis of catalytic silica-manganese oxide "matchstick" particles	B. Queenhithe Room Colloid Physics *Chair: Cécile Dreiss* K26. Paul Clegg, University of Edinburgh Using demixing, remixing & wetting to organize colloidal particles				C. Lower River Room PCF *Chair: Steve Armes* K27. Paul Bartlett, University of Bristol, Colloid electrostatics at very low ionic strengths
11.55	#23	118. Mihail Popescu, Max Planck Institute, Germany Self-Diffusiophoresis of Chemically Active Colloids	157. Joseph Keddie, University of Surrey Assembly of colloidal particles in vertical and lateral directions in thick films				195. Imre Varga, Eotvos Lorand University, Hungary, Preparation of Soft, Responsive Nanogel Particles with Controlled Internal Structure
Short Break							
12.20	#24	188. Alan Luna University of Bordeaux 1 Pessac, France.	22. Richard Buscall Exeter, UK				49. Sarah Canning, University of Sheffield,

		Formulation of electrostrictive materials for energy harvesting devices	**How do important state variables like particle concentration and strength of attraction affect the rheology of cohesive colloidal suspensions?**	**Self-Assembly of Poly(Methacrylate-co-Acrylic Acid) Copolymers of Varying Architecture Synthesised by RAFT Polymerisation**
12.40	#25	187. **Ankur Chaurasia** King's College London, **Controlling Shell Thickness of Large Core-Shell Drops in Non-Confined Microfluidics**	193. **Joerg Polte**, Humboldt-Universität zu Berlin, Germany **Taking a look into the black box – new perspectives of nanoparticle formation**	180. **A. Chebil**, LCPM, France, **Elaboration of polysaccharide-covered polyester nanoparticles for the encapsulation of polyphenolic molecules.**
LUNCH. 13.00 – 14.00 Upper River Room				
14.00	**Keynote #9**	**A. Auditorium** Characterisation *Chair: Alberto Striolo* K28. **Eric Buhler**, University Paris, France **Control over the Self-assembly of Nanoparticle Semiflexible Biopolyelectrolyte Complexes**	**B. Queenhithe Room** Colloid Physics *Chair: Paul Clegg* K29. **Yujun Feng** Sichuan University, China **CO_2-switchable wormlike micelles**	**C. Lower River Room** Application *Chair: Harry Frampton* K30. **Ravi Sharma** Cabot Corporation, USA **Use of Particle Technology in Development of Advanced Functional Materials**
14.30	#26	155. **Jan Forsman**, Lund Unversity, Sweden **Many-body depletion interactions**	5. **Steve Ebbens**, University of Sheffield **Realising autonomous transport applications for Janus particle catalytic swimming devices**	32. **Satoshi Watanabe** Tokyo University of Science, Japan **Micromolding in Capillaries for Nanopatterning of Rare-Earth-Ion-Doped Nanoparticle Films on Plastic Sheets**
14.50	#27	106. **Alan Parker** Firmenich SA, Geneva, Switzerland **Ostwald ripening of emulsions stabilized by a complex proteoglycan - gum Arabic**	181. **Huanhuan Feng** University of Wageningen, The Netherlands **Switching between two modes of coalescence in dense thermo-responsive emulsions**	206. **Nikolaos Dimitratos**, Cardiff University, **Designing Bimetallic Nanoparticles for High Catalytic Performance**
15.10	#28	84. **Beatrice Cattoz**, University of Greenwich **Probing nanoparticle interactions with biological system for drug delivery applications**	**J. Mattsson**, University of Leeds **Dynamic arrest in soft colloidal matter**	131. **Pedro Rodríguez-Dafonte** University of Santiago de Compostela, Spain **Catalyzed H-D Exchange Media in Micelles of Ionic Liquids**

Short Break				
15.40	Keynote #10	A. Auditorium Characterisation *Chair: Keith Bean* K31. Timothy Hunter, University of Leeds Characterization of suspension separation in thickeners, by an acoustic backscatter system	B. Queenhithe Room Application *Chair: Limin Wu* K32. Shannon Notley, Swinburne University of Technology, Australia Exfoliation of layered materials for energy, water and biomedical applications	C. Lower River Room PCF *Chair: Joe Keddie* K33. Brian Saunders, University of Manchester, High-performance doubly crosslinked microgels for biomaterial applications
16.10	#29	95. Dave Fairhurst, XiGo Nanotools Inc, USA Characterization of Graphene, Graphene Oxide and Nanographite Dispersions using NMR Solvent Relaxation	107. Mahoulo Ahouansou, University of Leeds, Influence of particle shape and concentration on the pattern of dried colloidal droplets	40. Jun Bae Lee, COSMAX R&I, Republic of Korea, Liquid Crystal Emulsions for Efficacy
16.30	#30	175. Alison Sham Australian National University, Canberra Functional Graphene-Polyelectrolyte Thin Films Formed By Hydrogen Bonding	173. Manish Tiwari University College London Carbon nanoparticle colloids for facile and multifunctional superhydrophobic surfaces	82. Alessandro Patti, University of Manchester Heterogeneous Dynamics of Polymer Chains and Spherical Nanoparticles in Nanocomposites
16.50. Closing Ceremony/ Presentation of Awards Auditorium				

Abstracts for Oral Presentations

Plenary 1: Surfactants for non-aqueous solvents

Professor Julian Eastoe, University of Bristol

For common surfactants in aqueous solutions the concepts of hydrophilicity and hydrophobicty are well established. Textbooks explain the properties of dilute aqueous phases of surfactants in terms of the hydrophobic effect and the Israelachvili-Ninham packing parameter. However, these approaches do not apply so well in solvents other than water.

The talk will explore the generality of solvopilicity and solvophobicity, as well as the importance of chemical structure and architecture of surfactants designed for non-aqueous solvents including supercritical CO_2.

Effect of solvent quality on aggregate structures of common surfactants
Langmuir 2008, 24, 12235-12240.

Controlling aggregation of non-ionic surfactants using mixed glycol media
Langmuir, 2007, 23, 4199-4202.

Universal surfactant for water, oils and CO_2
Langmuir, 2010, 26, 13861–13866.

Design principles for supercritical CO_2 viscosifiers
Soft Matter, 2012, 8, 7044 – 7055.

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K1. New Routes to Particle Synthesis: Making particles one by one

David Weitz, University of Harvard, USA

This talk will describe several new methods to create particles of controlled size and properties, using a variety of templating strategies and taking advantage of the control offered by microfluidic assembly. In addition, possible routes to scale up will be discussed.

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112. Mechanics of a colloid-armoured bubble

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We investigate the dissolution of a single air-in-water bubble whose surface is coated with solid particles, as an elementary model of an aging particle-stabilized foam. A microfluidic setup is used to produce a single bubble on demand, force the adsorption of particles to its interface, and hold it stationary for long-term observation. When the gas dissolves in the surrounding liquid, the particles on the interface eventually jam, thus forming a rigid shell that encloses the bubble. We finely tune the stress bearing on that shell only by shifting the thermodynamic state of the bubble out of equilibrium. This is done by precisely controlling the pressure and temperature inside the observation chamber.

We experimentally demonstrate the existence of a threshold pressure below which the shell is able to arrest the dissolution of the gas. In that case, the lifespan of the dissolving bubble is increased from minutes to hours. Above this pressure value, the armor cannot withstand the compressive stress due to dissolution. It then buckles, which leads to the complete disappearance of the bubble.

These experiments yield a quantitative measure of the mechanical resistance of a colloidal shell against ripening. We show that the strength of the armor depends on the geometry of its constitutive particles for a given surface chemistry. This is an important result when optimizing the stabilization of a foam solely with particles. It opens the possibility to study the behavior of more complex armors, by varying the size distribution, the shape and the chemistry of the particles.

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185. Millimetric emulsion

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The stabilisation of emulsion droplets having a millimetre size is extremely difficult to achieve. This observation principally results from a large contact area between drops that favours coalescence. Moreover, creaming or sedimentation of droplets under gravity is enhanced. In collaboration with the company Capsum, we developed a fabrication process of such emulsions by stabilising the interfaces with a thin layer of polymers.

Designed by millifluidic, a calibrated emulsion of oil in water is obtained. Their size is uniform and can range from 0.5 to 2 millimetres. The process is an online formation; the droplets are made one by one. It prevents any contact between them during the formation of the polymer membrane, thus there is no coalescence during the fabrication.

In the laboratory, we investigate the stability properties of this emulsion towards deformation and breakup of the polymer shell, depending on the physico-chemical conditions. The variations of pH and ionic strength of the continuous phase have an impact on the mechanical properties of the membrane.

We examine the behaviour of a collection of droplets when undergoing compression. First, we study the equation of state of an emulsion column under a gravitational field, in order to determine its elastic modulus.Then, larger pressures can be reached by the mean of centrifugation. It allows us to estimate the critical breakup threshold of the membrane, leading to phase separation.

The mechanical properties of the polymer membrane at the level of a single droplet are also explored. Flow of droplets in a channel is realised and we observe their deformation. The analysis of their shape gives us information about the interfacial properties of the membrane.

The investigation is also carried out for oil droplets without any membrane (free interface), or stabilised with classical surfactants (small amphiphile molecules).

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K2. Electric-Field Induced Phases and Dynamical States in Suspensions of Rods:

Association and dissociation of condensed ions

Jan K.G. Dhont *and Kyongok Forschungszentrum Juelich, Kang,Institute of Complex Systems (ICS) Soft Condensed Matter (ICS-3), Juelich, Germany*

Concentrated suspensions of long and thin, stiff rods (fd-virus particles) at low ionic strengths are found to exhibit various phases and dynamical states under external electric fields, depending on the field amplitude and frequency. A non-chiral nematic, a chiral nematic and a homeotropically aligned homogeneous phase are observed, and a dynamical state where nematic domains melt and form.
The transition from a non-chiral to a chiral nematic and the existence of the dynamical state are explained in terms a cyclic field-induced dissociation and association of condensed ions. A theory will be presented, with a semi-empirical model for the field-induced dissociation/association of condensed ions, that reproduces the experimentally found location of transition lines in the field-amplitude versus frequency plane, as well as the time scales on which melting and forming of nematic domains occurs. The homeotropic uniform phase at relatively high frequencies will be argued to be the result of hydrodynamic interactions through field-induced electro-osmotic flow.

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111. A simple one-pot route to cationic cellulose nanocrystals

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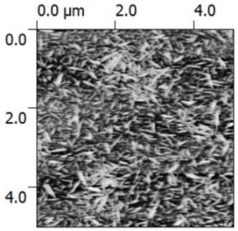
Cellulose nanocrystals (CNCs), produced by acid-hydrolysis of native cellulose (AFM image, right), have attracted substantial attention owing to their mechanical properties and also particularly due to their potential application as a reinforcing agent in nanocomposite materials. Applications of CNCs can be extended through the modification of their surface hydroxyl groups which has the potential to impart virtually any desired functionality such as hydrophobicity, cationic or anionic charge, or fluorescence which in turn opens up many more potential applications than may be achievable with unmodified cellulose. Various modifications of CNCs have been reported, with the majority of work being dedicated to making CNCs hydrophobic, particularly to improve compatibility with polymer matrices.



Cationization of cellulose nanocrystals has been reported several times in the literature so far. The highest reported modification was DS 0.35 with glycidyltrimethylammonium chloride and pre-treatment of cellulose nanocrystals with sodium hydroxide. Despite the aggressive alkali treatment, and high extent of modification, the crystallinity of the product was not reported.

Described herein is a methodology for one-pot grafting of pyridinium cations onto the surface of cellulose nanocrystals using an esterification technique not used previously with nanocrystalline cellulose. The resulting cellulose nanocrystals have a surface degree of substitution of up to 1.1 for α-methylbenzylpyridinium bromide and 0.45 for benzylpyridininium bromide and fully retain their crystal structure after modification. Explanation for the large variation in modification despite little change in structure is provided.

The pyridinium grafted cellulose nanocrystals synthesized via this methodology have a high surface charge density and were able to form stable suspensions that show birefringence even after being fully dried (polarized photomicrograph, left). Future applications of these nanocrystals will also be discussed.

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97. Electrophoresis of polymer latexes in nonpolar solvents

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In recent years, the number of published studies reporting charged colloids in nonpolar, low-dielectric solvents has increased markedly.1 This has primarily been motivated by the many applications of charged species in industries such as petrochemicals, printing toners, and, recently, electrophoretic displays.2 A common motif used to produce charged colloids in nonpolar solvents is Aerosol OT (AOT) surfactant as charging agent with poly(methyl methacrylate) (PMMA) latexes in aliphatic solvent.3 Although the particle charge originates from interactions on the surface, either adsorption of charged species or dissolution of species into surfactant inverse micelles, there have been few attempts to determine the structure of the charging agents that interact with the colloids.

The use of small-angle scattering techniques to measure the solution and surface structure of charged colloidal particles will be discussed. Small-angle neutron scattering (SANS), in particular, is powerful in predominantly organic systems, as hydrogen/deuterium isotopic labeling leads to high contrast. Contrast-variation SANS experiments have been performed using deuterium-labeled AOT-D34 PMMA latexes in particle contrast-matched dodecane. The scattering profiles of AOT-D34 when PMMA latexes are contrast matched can be described with a model consistent with AOT surfactant penetrating throughout the entire latex, rather than being localized in the stabilizer shell.

These experiments have yielded insight into the surface interactions between surfactants and latees, and the consequences of the structures on the charge of colloids will be discussed. More generally, the results shed new insight on the industrially significant phenomenon of charge stabilization of polymeric colloids in nonpolar solvents and are expected to contribute to design and optimization of charge control additives for these technologically relevant systems.

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K3. Nanoplasmonics Meets Bio

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I will report on our recent efforts to utilize some of the unique plasmonic properties of noble metal nanoparticles for sensing and controlling nano- and microscale processes in aqueous solution. The use of optical forces and of local optothermal heating is in the focus of our investigations. Examples range from controlled laser printing with nanoscale precision via the study of DNA-binding events to the direct optical monitoring of flow generated by bacterial flagellar rotation.

Optically trapped gold nanoparticle enables listening at the microscale

A. Ohlinger et al., Phys. Rev. Lett. 108, 018101 (2012)

Tuning DNA Binding Kinetics in an Optical Trap by Plasmonic Nanoparticle Heating
L. Osinkina et al., Nano Lett. 13, 3140 (2013)

Two-Color Laser Printing of Individual Gold Nanorods
J. Do et al., Nano Lett. 13, 4164 (2013)

Direct optical monitoring of flow generated by bacterial flagellar rotation
S. Kirchner et al., Appl. Phys. Lett. 104, 9 (2014)

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I1. Studying Protein-DNA Interaction using Gold Nanoparticles Exploiting Particle Aggregation, Refractive Index Change, Fluorescence Quenching and Enhancement Principles

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Gold nanoparticles (AuNPs) have a unique optical phenomena termed localized surface plasmon resonance (LSPR) that is determined by particle shape, size, inter-particle distance (or aggregation status), and local refractive index. AuNPs also can modulate fluorescence emission of proximal fluorophores under the Förster resonance energy transfer (FRET) and/or nanoparticle surface energy transfer (NSET) mechanisms. In this study we use AuNPs (13 and 100 nm in diameter) as sensing elements to study sequence dependent protein-DNA interactions by exploring all possible principles, namely (1) particle aggregation based colorimetric sensing, (2) refractive index sensing, and (3) fluorescence quenching/enhancement based fluorimetric sensing, exemplified by transcription factors, i.e. FoxA1 (Forkhead box A1) and AP-2γ (activating enhancer binding protein 2 gamma), and their respective DNAs. We conclude that the first principle, i.e. particle aggregation based colorimetric assay that measures preformed complex by exploring complex protection of AuNPs from salt induced aggregation, is simple to use. However, its performance is protein specific. For second and third principles that measure on-particle complex formation, we prove that the fluorescence quenching/enhancement assays supported by AuNPs are more sensitive than that exploits analyte-binding induced refractive index principle. This study provides a comprehensive assessment of the versatility of AuNPs as sensing probes for studying bioaffinity interactions especially protein-DNA complexes. The discovery of the DNA binding properties of FoxA1 and AP-2γ is important in revealing their roles in gene regulation.

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K4. Design of nano-emulsions with controlled size by low-energy methods

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Condensation or low-energy emulsification methods are focusing an increasing attention from fundamental and applied viewpoints [1]. These methods use the internal chemical energy of the components, which is released during the emulsification process, and allow producing emulsions with nanosized droplets, low polydispersity and high kinetic stability. They can be classified as phase inversion and direct or self-emulsification methods. The so-called phase inversion methods make use of the chemical energy released during the emulsification process as a consequence of a change in the spontaneous curvature of surfactant molecules, from negative to positive (obtaining oil-in-water, O/W, nano-emulsions) or from positive to negative (obtaining water-in-oil, W/O, nano-emulsions). This change of the surfactant curvature can be achieved by a change in composition keeping the temperature constant (Phase Inversion Composition method, PIC) [2, 3], or by changing the temperature with no variation in composition (Phase Inversion Temperature method, PIT) [4, 5]. It has been shown that low interfacial tension, ɣow, values and the presence of surfactant molecular assemblies with zero average curvature such as lamellar liquid crystals or bicontinuous microemulsions during the emulsification process play a decisive role in the formation of emulsions with minimum droplet size by phase inversion methods [1]. This presentation will deal with the design of nano-emulsions with minimum droplet size by low-energy emulsification methods, with special emphasis on those based on phase inversion. In particular, the main factors allowing to control droplet size in systems using conventional surfactants (non-ionic or ionic) and nonpolar or semipolar oils as well as in systems with a polymer dissolved in a polar solvent as oil component will be discussed.

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121. Extremely Stable Nanoemulsions Fabricated by Interfacial Assembly of Amphiphilic Block Copolymers during Phase Inversion

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Recently, there have been intense interests in incorporation of amphiphilic block copolymers to develop stable emulsion systems, since they have abilities not only to reduce interfacial tensions at the oil-water interface, but also to form a mechanically stable polymer membrane at the interface. These unique behaviors of amphiphilic block copolymers make themselves useful for exploring a variety of applications as polymeric surfactants. The objective of this talk is to demonstrate that extremely stable nanoemulsions can be produced by effective assembly of amphiphilic block copolymers during phase inversion. The amphiphilic block copolymer we use is poly(ethylene oxide)-b-poly(ε-caprolactone) block copolymer (PEO-b-PCL). The phase inversion emulsification process is established by characterizing emulsion phases as well as by confirming remarkably improved emulsion stability. In our study, right after the phase inversion, the O/W embryo emulsion is obtained in a few micrometers. To decrease the drop sizes in nanometer scales, strong mechanical stress, sonication, is applied to the embryo emulsion. This enables production of emulsions whose size ranges in 100-200nm. Usually, the repeated freeze-thawing completely destroys the interface of emulsions and leads to the phase separation. In our nanoemulsion system, however, no separation of oil from the system can be observed. Moreover, the emulsion size stays constant. It appears that well-assembly of PEO-b-PCL at the oil-water interface generates a mechanically flexible but tough polymer thin film, thus remarkably improving the emulsion stability. We expect that our emulsification method has great potentials for developing a variety of emulsion-based complex formulations that can not only encapsulate active materials, but also show tolerance to environmental factors, such as pH, salts, and heat.

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151. Effect of block composition on micelle size and steric stabilizer layer thickness: polystyrene-based diblock copolymers are effective dispersants for carbon black particles in n-dodecane

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Three commercial polystyrene-based diblock copolymers are evaluated as dispersants for carbon black particles in n-dodecane. Each diblock copolymer forms polystyrene-core micelles in this solvent as judged by variable temperature ^{1}H NMR spectroscopy, DLS, TEM and SAXS. According to a UV spectroscopy supernatant depletion assay, these diblock copolymer micelles adsorb onto the carbon black particles to form a relatively thick stabilizer layer. Consequently, the effective density of the sterically-stabilized carbon black particles is substantially lower than that of the pristine carbon black particles (1.89 g cm^{-3} as judged by helium pyconometry). In each case, the effective particle density can be determined by determining the particle velocity in both n-dodecane and d$_{26}$-n-dodecane via analytical centrifugation. Using this corrected particle density enables the true particle size distributions of these carbon black dispersions to be assessed and the thickness of the steric stabilizer layer can be estimated. It is found that the mean particle diameter of the carbon black is close to its primary grain size of 74 nm (as judged by BET nitrogen adsorption studies), which suggests a relatively high degree of dispersion for this model colloidal substrate.

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126. Formation and Characterization of Mixed Cationic Ionic Liquid and Nonionic Polyoxyethylene Type Surfactants Microemulsion Systems

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Physicochemical, thermodynamic and microenvironmental properties of mixed cationic 1-hexadecyl-3-methylimidazolium chloride (C16mimCl) and nonionic polyoxyethylene (20) cetyl ether (Brij-58) microemulsions (at equimolar composition) stabilized by 1-pentanol (Pn) and n-heptane (Hp) have been investigated by phase behavior study, electrical conductance, dynamic light scattering (DLS), steady-state fluorescence and Fourier transform infrared (FTIR) spectroscopy measurements in absence and presence of 1-butyl-3-methylimidazolium tetrafluroborate (C4mimBF4) or 1-butyl-3-methylimidazolium chloride (C4mimCl). Interfacial composition and spontaneity of Pn transfer process from Hp to the interface have been estimated by the dilution method. Addition of Brij-58 to C16mimCl microemulsion exhibits larger single phase microemulsion zone. The spontaneity of Pn transfer process is larger for mixed composition compared to single C16mimCl microemulsion. Formation of mixed ionic liquid (IL)/nonionic surfactant microemulsions are found to be exothermic with negative entropy change (less disordered or organized). All these systems exhibit volume-induced percolation in conductance. Droplet size increases with increase in water content (ω) whereas it decreases with increase in temperature. Addition of C4mimBF4 or C4mimCl produce smaller droplets compared to aqueous system. The physicochemical changes in the microenvironment of the mixed systems as a function of ω and [C4mimBF4] have been delineated from the measurements of the micro-polarity around fluoroprobe (1,8-anilinonaphthalenesulfonic acid, ANS). It reveals from vibration spectroscopy measurements that addition of Brij-58 to C16mimCl microemulsion increases the relative proportion of bulk water at a fixed ω. With increase in ω, bulk water and bound water have been

found to be gradually increases and decreases, respectively for mixed microemulsions. Further, antibacterial activity of these systems against the strains gram-positive - Bacillus subtilis and gram-negative - Escherichia coli bacteria have been examined at different compositions, by measuring the diameter of the inhibition zone (“diz”) at 303K. Correlations of the results in terms of the evaluated physicochemical parameters have been presented.

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K5. Self-Assembling Colloidal Systems: Structure Development from Molecule to Microparticle

Karen J Edler[1], *Matthew Wasbrough*[1], *Daniel Bowron*[2], *Rowan Hargreaves*[2], *Gareth Price*[1]

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Our research studies primarily the use of self-assembled amphiphiles to template nanostructures in other materials and to understand hierarchical structure formation as nanostructure particles themselves form microparticles or films. This talk will present our work using neutron and X-ray scattering to characterise self-organised systems based on surfactant self-assembly across a wide range of length scales. Wide angle scattering has been used to gain information on the molecular scale, to probe the distribution of water and counterions around micelles, which may influence the initial binding of species to these structures. Small angle neutron scattering (SANS) and grazing incidence X-ray small angle scattering (GISAXS) provide details on the processes of mesophase construction, while ultra-small angle neutron scattering (USANS) and spin echo small angle scattering (SESANS) allow us to follow particle growth up to micron length scales. Characterisation using these techniques will be discussed using examples from surfactant-silica and surfactant-polyelectrolyte systems which develop hierarchical ordering.

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52. New method to predict the surface tension of colloidal polyelectrolyte/surfactant mixtures

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While the surface tension of complex mixtures determines the fate of important natural processes like the stability of aerosol droplets in clouds and the biological function of lung surfactants, the property is notoriously difficult to interpret and model. For example, it was established over a decade ago that some strongly interacting colloidal polyelectrolyte/surfactant (P/S) mixtures exhibit a peak in their surface tension isotherms [1]. Recently we have systematically linked the peak of a strongly interacting P/S mixture to slow dynamic changes in its bulk phase behavior [2], and we went on to demonstrate the non-equilibrium nature of the system [3]. Here we present a new approach that successfully predicts the surface tension of two synthetic mixtures (Pdadmac/SDS and NaPSS/DTAB) and one biologically-relevant mixture (DNA/DTAB). The approach is based on the non-equilibrium framework of comprehensive precipitation of kinetically-trapped aggregates followed by their transport under gravity away from the probed interface. Importantly our approach does not need any measurements of the surface properties of the mixtures; only the surface tension isotherm of the pure surfactant and some bulk measurements of the mixtures are required. This simplification in our understanding of the surface properties of strongly interacting mixtures may lead to the optimization of applications involving commercial synthetic polymers, DNA and proteins at surfaces, such as in common household formulations as well as drug and gene delivery applications.

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63. The critical edge: salt effects on polybasic brushes

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In situ ellipsometry was used in a constant flow regime to elucidate intrinsic behaviour of a polymer brush in reaction to changes in solution pH and ionic strength. Brushes of poly(2-(diethylamino)ethyl methacrylate) (PDEA) were synthesised using the ARGET ATRP methodology from covalently surface-bound silane-based initiator moieties. Brushes initially at pH 9 (10 mM added electrolyte) swell when the pH is reduced below the brush pK_a. Equilibrium measurements show the pH-induced transitions are hysteretic in nature; brushes swell incrementally as pH is reduced but collapse over a narrow pH range when returned above the pK_a. Kinetic measurements as pH is cycled between 9 and 4 demonstrate proton and solvent ingress during brush swelling is much faster than neutralisation and solvent egress during collapse. These differences are attributed to the formation of a hydrophobic ‘skin’ in the outer extremity of the brush, retarding the movement of protons and solvent from the brush. When pH is maintained below the pK_a the brushes exhibit complex behaviour dependent on the type and concentration of added electrolyte. The brushes remain swollen at intermediate salt concentration (~1 – 50 mM), with thickness dependent on salt type: $KCH_2O_2 > KNO_3 > KSCN$. The brushes collapse gradually as the concentration increases further. The concentration dependence in this salted-brush regime is weaker than predicted by common polyelectrolyte theory. Interestingly, as the salt concentration is reduced into the osmotic-brush regime the brushes exhibit a ‘critical edge’; the brushes entirely swell and collapse over a narrow range of electrolyte concentration. This transition is reversible, and the precise range is a function of the added electrolyte. This behaviour is in stark contrast to theory, which predicts a gradual reduction in brush thickness. The response of the brush is discussed in terms of the chaotropic or kosmotropic nature of the salt.

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146. Hydration of odd-even terminated polyelectrolyte multilayers under confinement

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Using a combination of neutron reflectivity and a surface force type apparatus, the hydration of polyelectrolyte multilayers, PEMs, is investigated whilst under a confining pressure. PEMs were fabricated from poly(styrenesulfonic acid), PSS and poly(allylamine hydrochloride), PAH, by spin coating on a silicon substrate. The polyelectrolyte used as the terminating layer of the PEM was varied. By selectively deuterating some layers, a low resolution distribution of the water volume fraction within the PEM can be determined. When swollen with water and unconfined, PSS-terminated samples are approximately 26% v/v water and this decreases to 15% when a confining pressure of 5 bar is applied. By comparison, PAH terminated samples are 20% water when unconfined and dehydrate to 10% water at 5 bar. The water is generally uniformly distributed within the bulk of the sample, though bi-layers nearest to the final adsorbed layer of a PAH-terminated sample are found to have a significant increase in their hydration. Also considered is an experiment where the inherent charge of the final adsorbed layer of a PEM is neutralised by compressing it with an oppositely terminated PEM, adsorbed onto the flexible membrane of the apparatus. This allows the level of hydration expected for an uncharged PEM to be assessed and demonstrates that the influence of the excess charge in the final adsorbed layer only acts as a perturbation to the internal hydration of the sample. A detailed scheme will be discussed whereby the amount of internal charge is directly responsible for the hydration of a PEM.

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K6. Cellular uptake of Gold Nanoparticles for Therapy and Imaging

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Gold nanoparticles inside cells can have many applications ranging from cell tracking tools to externally addressable agents for photothermal and/or photodynamic cancer therapy. While it is usually possible to obtain nanoparticles with the correct chemical and optical properties required for any application envisaged, it is far more difficult to control cellular uptake and intracellular fate of the particles sufficiently well to ensure the success of the application. In this lecture, I will present our experience of cellular uptake studies with both spherical, and rod-shaped gold nanoparticles, with special emphasis on the use of the cell penetrating peptide TAT, that appears to have a major influence on this process. Two subsequent applications of intracellular gold nanoparticles will be discussed in detail, (i) the photodynamic damaging and/or killing of human cancer cells in culture, and (ii) the photoacoustic tracking of stem cells labelled with gold nanorods. It will be demonstrated how subtle changes in the chemistry of the ligand shell of the particles can have quite significant consequences for the uptake mechanism and hence will also influence the intracellular fate of the particles. I will attempt to define the most important design factors in order to obtain the most suitable type of nanoparticle for each purpose and I will also briefly discuss a simple physico-chemical model that than can to some extent predict the interactions of nanoparticles with a biomembrane.

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I2. Gold Nanoparticles and Biological Structures

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Understanding the interactions of nanoparticles with skin is of high importance for the development of new ways to deliver drugs efficiently but also in order to realize potential toxicity risks. Certainly, the study of the penetration of skin with nanoparticles is a complex research task because it involves a number of parameters that cannot be easily controlled related to the complexity of the skin and the type of nanoparticles.

In this presentation we take a thorough analytical approach to answer key questions concerning these interactions. We will particularly focus on how the charge, shape and function of nanoparticles influence the penetration through skin. For our studies we chose to work with gold nanoparticles due to the ease of their surface modification.

To gain a good understanding, we employ a number of techniques such as ICP-OES to quantitatively measure the penetration of nanoparticles, as well as two-photon photoluminescence microscopy and tem cross sectioning to analytically detect the particles in the skin. Moreover we will hypothesize potential mechanisms of penetration.

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I3. Plasmonic Nanoparticle Assembly for Biosensing Applications

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Gold and silver nanoparticles are known to the plasmonic nanoparticles that exhibit strong localized surface plasmon resonance (LSPR). In particular, the controllable synthesis and surface chemistry as well as uniform size population properties of gold nanoparticles (AuNPs) have made AuNPs a promising candidate as signal readouts for molecular sensing. By controlling the number of ssDNA molecules conjugated on each AuNP, we are able to make controllable and defined nanoparticle assembly and use the distinct signatures of the assembly for biosensing studies. For example, the dimeric AuNP assembly exhibits a different electrophoretic mobility and has allowed us to use gel electrophoresis for gene detection. The AuNP assembly also exhibit a distinct plasmonic scattering signature from that of single AuNP, and this has led us to monitor the presence of target gene/DNA molecules through in situ change of the plasmonic signature. Furthermore, the strong plasmonic scattering properties of these nanoparticles have made them detectable at very low concentration using the standard light scattering instrument. This further opens opportunities to investigate the assembling process of AuNP dimer, trimer, and higher order multi-mer using standard lab equipment. In this talk, I will provide our recent studies in exploiting the plasmonic properties of AuNP assemblies for different biosensing applications.

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K7. Production of nanoparticles using membrane contactors and microfluidic devices

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We have produced size-tunable nanoparticles with narrow particle size distribution by micromixing combined with nanoprecipitation using two different microfluidic devices: (i) membrane contactors consisted of a nickel microengineered membrane with a pore diameter between 5 and 20 μm and pore spacing of 80 or 200 μm fabricated by UV-LIGA process[1] and (ii) co-flow glass capillary devices consisted of coaxial assembly of round and square glass capillaries placed on a microscope slide[2]. A variety of different nanoparticles have been produced, including gold nanoparticles, polycaprolactone nanoparticles loaded with nanoclay nanopowder, biodegradable micelles from poly(ε-caprolactone)/poly(ethylene glycol) diblock copolymers and liposomes. Typically, the organic phase containing particle-forming material and hydrophobic active was injected through the membrane pores into the aqueous phase and the particles were formed as a result of controlled interpenetration of two miscible solvents. A shear rate at the membrane/aqueous phase interface was controlled by stirring, cross flow or membrane oscillations. Alternatively, the organic phase was injected through a tapered inner capillary into a co-flowing aqueous phase in the outer square capillary. Gold nanoparticles were formed by reduction of tetrachloroaurate (III) with ascorbic acid and the reactants were delivered with two coaxial aqueous phase streams generated in glass capillary devices.

The size of nanoparticles produced in membrane contactors was precisely tuned by controlling the membrane pore size, the shear rate on the membrane surface and the aqueous to organic phase volume ratio. In glass capillary devices, the particle size was controlled by the flow rates of the two streams and the orifice size of the injection capillary.

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234. Designing Disorder Using DNA-Functionalized Colloids

Lorenzo Di Michele, Francesco Varrato, Giuseppe Foffi, and ***Erika Eiser, University of Cambridge***

Understanding and controlling the properties of amorphous materials is essential in the design of new materials. Among different amorphous structures, colloidal gels play an important role. We use the short-ranged attractive interactions between colloids provided by selective DNA bonding to build ramified amorphous space-spanning structures that can sustain mechanical stress. [1]
The mechanism of aggregation in our system occurs through arrested demixing in binary colloidal mixtures. This leads to the formation of bigels - a new class of materials. We obtain these materials by end-grafting highly specific single-stranded (ss) DNA. As ssDNA can only bind to its complementary counterpart, we can design new colloid-colloid binding rules. Here, we present two types of amorphous gels: Two inter-percolating but independent colloidal gels which we call bigels (Figure), and a single colloidal gel subsequently coated with a single layer of a different type of colloid. Later we call coaxially coated colloidal gels. [2]
I will discuss both the structural analysis and the mechanical properties of such systems. [3]

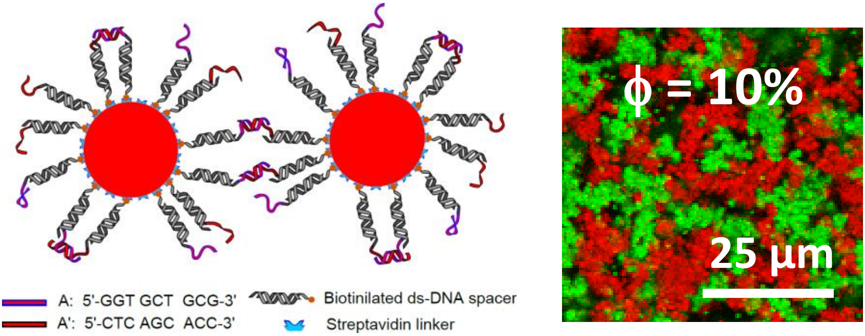

Figure: (Left) Carton of the typical colloid surfaces bound with DNA. The double strands are used a spacers, and the sticky overhangs are designed such that A and A’ cannot bind to B or B’. The polymer strands in between are used to tune strength of the intra-colloidal bonds. (Right) Snapshot from a demixed bigel.[1,2]

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109. Study of the water/crude oil interfacial properties by microfluidic

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In the classical development of oil fields, the average recovery factor defined as the volume produced divided by the initial volume in place is relatively small: around 35%. Several mechanisms contribute to trap the oil in the porous matrix. In the case of water wet rock, capillary trapping contributes to a significant amount. For such fields, the residual oil saturation depends on the capillary number Ca=µU/gamma, where µ is the viscosity, U the fluid velocity and gamma the oil-water interfacial tension. The residual oil decreases strongly with an increase of this number. Consequently, three parameters allow achieving high recovery: the viscosity, the velocity of the injected phase and the interfacial tension between this latter and the crude oil. In practice, the viscosity and the velocity cannot be increased largely but surfactants can be injected to reach ultra-low interfacial tension with the crude oil; this process is called chemical EOR (Enhanced Oil Recovery). Typically, interfacial tension lower than 10-2 mN/m can be achieved in conditions of Winsor III. The dependence of Winsor III with the salinity in presence of ionic surfactants is well-known at atmospheric pressure and ambient temperature. Nevertheless, these conditions are very far from the ones in reservoir (ie. high pressure and high temperature). Consequently, it is legitimate to study the influence of temperature and pressure on interfacial properties between crude oil and EOR formulations.

In this paper, we try to assess this question thanks to an experimental set-up and a method that we are currently developing in our lab. This set-up is a high-throughput microfluidic tensiometer based on the Rayleigh-Plateau instability1. In fact, in coaxial flows, the transition between a droplet and a jetting regime depends on the velocities of each phase, the viscosity ratio, the confinement and the interfacial tension1. As the three first parameters are known, we can calculate the dynamic interfacial tension.

1 P. Guillot et al. Stability of a jet in confined pressure-driven biphasic flows at low Reynolds number, PRL 99, 104502 (2007)

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182. Stabilising the dripping regime of viscous droplet production via core-shell templating

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Many methods to create highly monodisperse emulsions of a wide range of sizes rely on the use of micro engineered devices such as membranes or microchannels. This high uniformity is a result of droplets being produced on a drop by drop basis and in almost all cases the dispersed phase must be in the dripping regime. Creating highly monodisperse emulsions where one or both phases have high viscosity is a challenge, as the dripping to jetting transition occurs at much reduced flow rates and can be hard to achieve with conventional pumps. We present a novel method of increasing the range at which dripping occurs and delaying the onset of jetting to much higher flow rates using core-shell templating. In this method, a third, low viscosity inner phase, is introduced in the dispersed phase forcing the dispersed phase to form a shell around each drop and effectively reverts the system from jetting to dripping. Formulations are chosen so that the resulting core-shell droplets are unstable and soon rupture to form highly monodisperse emulsions. The rate of internal droplet production is found to be the governing parameter in the system and must be below a critical frequency. This frequency is found to be well predicted by Plateau–Rayleigh instability theory of jet rupture where the perturbations caused by internal drops are at a wavelength larger than the circumference of the would-be jet. This method is easy to implement in conventional microfluidic designs and equipment and greatly facilitates the ability to produce very uniform emulsions of high viscosity.

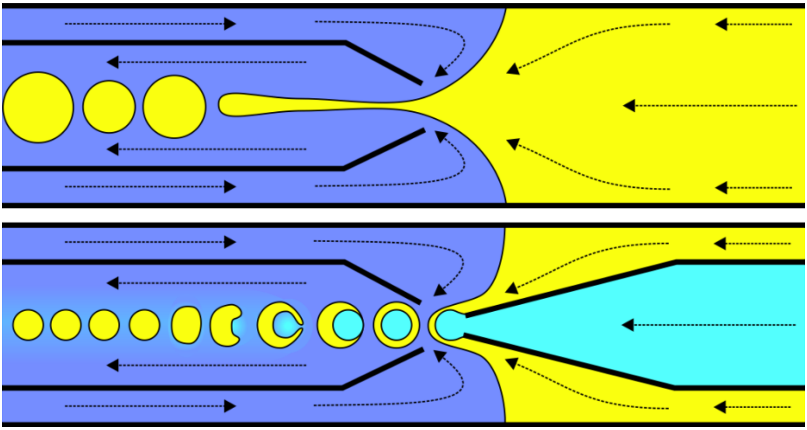

Fig. 1 Schematic of a conventional flow-focused device jetting (top) and the implementation of core-shell templating (bottom)

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174. Hole-Shell Microparticles from Controllably Evolved Double Emulsions

***Wei Wang*[1]**, *Mao-Jie Zhang[1], Rui Xie[1], Xiao-Jie Ju[1], Chao Yang[1], Chuan-Lin Mou[1], David A. Weitz[2] and Liang-Yin Chu[1]*

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In this work, we report a versatile strategy for fabrication of highly controlled hole-shell microparticles with a hollow core and a single, precisely-determined hole in the shell, and with simultaneous, independent control of the properties of the core interface. W/O/W double emulsions from capillary microfluidics are used as initial templates for the microparticles. By controlling the composition of organic middle phase, we vary the adhesion energy between the inner drop and outer phase to control the evolution of the emulsions from initial core-shell to desired acorn-shaped configuration; this produces versatile emulsion templates for controllable fabrication of monodisperse hole-shell microparticles with advanced shapes. Further adjustment of the hole-shell structures can be achieved by changing the size and number of the inner drop via tuning flow rates. Independent control of the interfacial property of the core is achieved by incorporating functional nanoparticles such as thermo-responsive nanogels and gold nanoparticles in the inner drop to coat only the core surface for modification. The hole-shell microparticles enable capture of living cells, size-match capture and size-classification of microspheres, and confined synthesis of functional materials. These microparticles create new opportunities as microcontainers for controlled capture/release, and as microreactors for catalysis and confined reaction. This approach based on controllably evolved double emulsions provides a versatile strategy for preparation of hole-shell microparticles with advanced shapes and specific functions.

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K8. Dynamics of Nanoparticles in melts, solutions and at surfaces as studied by NMR.

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Nanoparticles are used widely in colloidal formulations to deliver enhanced performance capabilities to products, be it reinforcement in composites, stability in emulsions, increased surface area in dispersions etc. However, studying these systems *in situ* is not straightforward as they are often highly concentrated, opaque and multi-component. The physical characterisation of these systems poses challenges; techniques are required which can not only measure the micro- dynamics of their various components but also identify their dispersion and interfacial behaviour. In this talk, I will discuss systems comprised of silica/resin nanoparticles dispersed in polymer solutions and melts as emulsion stabilisers and tethered to the ends of polymer chains. NMR relaxation, diffusion and small-angle scattering have been used as the main experimental tools. Of particular interest is the way that nanoparticles can modify the rheology and stability of these systems in unexpected ways.

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2. Is CMC of surfactant mixtures an ill-defined parameter?

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Micelles were first proposed by McBain in 1913 while studying the electrical properties of sodium palmitate solutions. The surfactant concentration above which micelles form, termed critical micelle concentration (CMC), is an important parameter in surfactant chemistry, as abrupt changes in the solution and performance properties of surfactants and their mixtures occur at CMC.

To adequately evaluate the solution and performance properties of mixed surfactant solutions, the CMCs of the mixtures and component surfactants must be correctly determined. Generally, the CMCs of single surfactants are well-defined and their values do not depend on the technique used; while those of the binary mixtures obtained from different techniques are different.

We have studied several binary mixtures consisting of SDS (an anionic surfactant) and DTAB (a cationic surfactant) with non-ionic surfactants. We will compare their CMCs and those of the individual components obtained from surface tension ($\mathrm{CMC}_{\square}$)□and conductivity measurements ($\mathrm{CMC}_{\square}$). We find that in some mixtures, $\mathrm{CMC}_{\square}$ is up to twenty times higher than ($\mathrm{CMC}_{\square}$)□ for the same mixtures at the same bulk solution compositions. SANS measurements performed in the concentration range bounded by the $\mathrm{CMC}_{\square}$ and $\mathrm{CMC}_{\square}$ show that the micelle size does not remain constant after micellization as predicted by the current thermodynamic models. Rather, it varies with the surfactant concentration for the different compositions we have studied. We thus propose that the CMC of surfactant mixtures is not a well-defined thermodynamic parameter as previously thought.

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170. Size selection in self-assembly: a theoretical study

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Accurate control of the size of the structures formed by the self-assembly of amphiphiles in solution is vital in applications such as drug delivery, as it determines the dosage of chemicals that they can encapsulate and the nature of the microscopic obstacles that they are able to navigate. However, although the radii of micelles may be controlled via the length and architecture of the molecules, this is difficult to achieve for larger structures such as vesicles, which typically have a wide range of sizes.

Using a coarse-grained mean-field model, we investigate two systems in which a direct link can be made between the architecture of the molecules and the radius of a larger self-assembled structure. First, we provide a concrete theoretical demonstration of the basic principle that amphiphile architecture can directly control vesicle size if the membrane symmetry is broken by the use of copolymers with multiple hydrophilic and hydrophobic sections [1]. We present a comprehensive investigation of tetrablock (ABCA) copolymers and suggest how these could be designed to form monodisperse capsules of a required radius.

We then turn our attention to the flat disks (bicelles) formed in mixtures of two species of lipid, and show that the self-consistent field equations in the mixed system have a solution corresponding to disks of a finite radius that is absent when only one type of lipid is present. The system parameters chosen provide a good basic model of a lipid mixture and would also allow our predictions of bicelle radii to be tested in detail in a copolymer/homopolymer blend.

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102. The Aggregation Behaviour of Polyisoprene–Pluronic Graft Copolymers in Selective Solvents

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Novel amphiphilic graft copolymers composed of a polyisoprene (PIP) backbone with Pluronic side chains, polyisoprene-*g*-Pluronic, have been synthesized using a "*graft onto*" technique. Small-angle neutron scattering (SANS) has been used to characterize the conformation of the P123 and P103 Pluronic graft copolymers in selective solvents such as ethanol and hexane and in a non-selective solvent, THF. The results indicated that, in a selective solvent for the side chain Pluronics (e.g. ethanol), "crew-cut" micelles were formed with a large core of ~ 120 Å; data were fitted with a core-shell model. In a good solvent for the backbone (e.g. hexane) "flower-like" micelles were formed with a small inner radius of ~ 64 Å. In the non-selective solvent a swollen polymer coil was found, which was described using the Guinier-Debye model. As THF/ethanol, and THF/hexane can be prepared in any ratio, it was possible to vary the solvent composition gradually in order to study the transition from swollen coil to micelle. When going from 100% THF to 100% ethanol (Figure 1), the transition to micellar behaviour was observed at a ratio of 20:80 (v/v %) THF/ethanol for both grafted copolymers and 40:60 (v/v %) THF/hexane for grafted P123 copolymers.

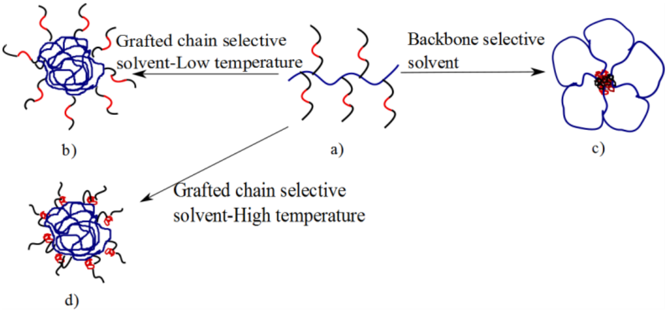

Figure 1. Possible conformations which might be taken on by grafted Pluronics in solution: a) swollen graft copolymer in a non-selective good solvent, b) crew-cut micelle, c) flower micelle, and d) crew-cut micelle with insoluble PPO blocks.

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74. The interfacial structure of polymeric surfactant stabilised air-in-water foams investigated in-situ by small-angle neutron scattering.

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Hydrophilic polyurethane foams find use in a variety of applications; particularly as biomedical materials in the treatment of chronic wounds. The performance of these foams is highly dependent on the behaviour of surfactant at the newly forming air-liquid interface which has consequences for cell window opening and porosity of the final cured solid foam.

In this work the interfacial structure of air-in-water foams stabilised with a series of tri-block polymeric surfactants of the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) ($EO_xPO_yEO_x$) has been probed using small-angle neutron scattering (SANS). A specialised sample environment has been designed, implemented and validated allowing foams to be produced in-situ in the neutron beam. Exemplar data and fitting to a model comprising paracrystalline stacks of adsorbed polymer layers at the air-water interface are presented. A minimum of approximately 5 paracrystalline layers ranging in thickness from 85-160Å interspersed with thicker films (400Å) of continuous aqueous phase were found to best fit the data. An empirical correlation between layer thickness and polymer structure is observed. Correlations to foaming behaviour and interfacial properties are discussed. The insight gained from this study should allow more rational design of polymeric stabilisers for hydrophilic polyurethane foams.

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K9. The role of surfaces and interfaces in multifunctional materials

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The bottom–up approach is considered a potential alternative for low cost manufacturing of nanostructured materials [1]. It is based on the concept of self–assembly of nanostructures on a substrate, and is emerging as an alternative paradigm for traditional top down fabrication used in the semiconductor industry. We demonstrate various strategies to control nanostructure assembly (both organic and inorganic) at the nanoscale. Depending on the specific material system under investigation, we developed various approaches, which include, in particular: (i) control of size and luminescence properties of semiconductor nanostructures, synthesized by reactive laser ablation [2]; (ii) we developed new experimental tools and comparison with simulations are presented to gain atomic scale insight into the surface processes that govern nucleation, growth and assembly [3-7]; (iii) we devised new strategies for synthesizing multifunctional materials for electronics and photovoltaics [8-18]; (iv) we developed a nanoscale surface modification which allows to control cell growth [19], including antibacterial effects [20].

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47. Understanding the structure-function relationships of colloidal drug delivery vehicles with neutron scattering and spin resonance

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Advanced drug delivery systems are increasingly being used to improve the therapeutic profile of conventional therapeutic molecules. Such constructs are designed to confer several clinical advantages over mainstream drugs, including prolonged drug circulation time, reduced toxicity, extended plasma half-life, enhanced water solubility and selective tumour accumulation by the enhanced permeability and retention (EPR) effect. These improvements are introduced through conjugation to polymer or particulate carriers, and a myriad of such supramolecular structures are being explored e.g. Polymer-Unmasked-Masked Protein Therapy (PUMPT), Polymer Enzyme Liposome Therapy (PELT). Of crucial focus, is an environment-triggered response that leads to the release of the active species within its therapeutic profile. To optimise this release, colloid science based analytical tools – neutron scattering, spin resonance - are essential tools to understand how the structure of the polymer based supramolecular vehicle is perturbed in response to changes in the prevailing solution environment i.e. its structure-function profile. This presentation will focus on our recent work in the area of quantifying the solution conformation of polymer-based conjugates, the essential features of surface-decorated nanoparticle formulations and the characterization of their interaction with endogenous proteins, vesicles and glycoproteins.

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116. Switchable fluorescent PEG-b-PPS micelles for non-invasive transdermal drug delivery

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The application of nanotechnology in medicine has witnessed a significant expansion in the last decade as a result of the development of novel nanomaterials and their unique properties, with drug delivery, in particular, being one of the key areas investigated. Transdermal drug delivery is a challenging area of nanotechnology where successful results have so far been limited to systems considered invasive, such as abrasion and microneedles. Liposomes, transferosomes and solid lipid nanoparticles are among some of the materials extensively investigated, however their limited ability to cross the stratum corneum compared to traditional systems has restricted their applications.

We report the development of a novel non invasive approach to transdermal drug delivery based on the preparation of di-block copolymer micelles (15 nm size) functionalized with a newly synthetized fluorescent probe that is dramatically sensitive to the interaction with our model drug (flufenamic acid). The fluorescence sensor on the micelles allows monitoring not only of drug encapsulation and release, but also micelle penetration in the viable tissues of the skin via topical administration using a new *ex vivo* model. We established that the drug-loaded micelles penetrate very well the epidermis, successfully crossing the *stratum corneum*, as a result of their very small size and physico-chemical properties.

Direct comparison of the flufenamic acid loaded micelles with the commercial cream Mobilisin on ex-vivo human skin provided interesting results. The commercial cream contains a number of different ingredients, some specifically designed to aid and facilitate penetration while the micelles are simply dispersed in water. Yet they provide comparable delivery of the active drug in the lower layers of the skin.

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69. Turkevich in new robes: key questions answered for the most common gold nanoparticle synthesis

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In 1951, J. Turkevich described a synthesis of nanosized gold which is today one of the most commonly used syntheses of colloidal gold nanoparticles.[1] It is based on the chemical reduction of $HAuCl_4$ with sodium citrate in aqueous solution. Since then, many scientific publications provided modifications of Turkevich's method which allow the synthesis of particles with different sizes and properties.[2] However, these recipes were derived from systematic variations of synthesis parameters in a trial and error approach. A comprehensive understanding of the parameter influences on the particle growth mechanism is still missing.

Recently, we were able to deduce a principle growth mechanism of the Turkevich synthesis form time-resolved SAXS experiments.[3] It was shown that particles are formed through a sequence of growth steps comprising fast initial formation of small nuclei, coalescence into bigger seed particles, slow growth of seed particles sustained by ongoing reduction of $Au^{3+,}$ and subsequent fast reduction ending with the complete consumption of the precursor species.

In this contribution, the results of extensive SAXS and UV-vis studies are presented. They reveal a sophisticated correlation between growth mechanism and final particle size distribution by answering the following key questions: How do the different physicochemical processes in the colloidal solution affect the growth mechanism? What determines the final particle size? How can the final size be adjusted precisely?

Therefore, this contribution addresses two main issues of colloidal science: the comprehensive understanding of the most famous gold nanoparticle synthesis and instructions for the deliberate synthesis of gold nanoparticles with sizes on demand.

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71. Direct Electrochemical Detection of micro RNAs using composites Conducting Polymer/Carbon Nanotubes or Reduced Graphene Oxide.

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Micro-RNAs (miRNAs) are a class of small, non-coding RNAs which play important role in various regulatory functions and disorders as cancers and heart diseases. Current miRNA analysis methods include real-time RT-qPCR, Northern blotting and miRNA arrays. These approaches although very sensitive and reliable are often expensive and time consuming. That is why a real challenge is to develop devices able to detect and quantify easily and simultaneously different miRNA sequences at sub-picomolar level. Electrochemical biosensors are considered as one of the most appealing techniques in terms of cost, ease of operation and automation. Moreover, nanomaterials combined to electrochemical biosensors are emerging options for miRNA detection including gold nanoparticles, nanostructured platinum electrodes, silicon nanowires, ruthenium oxide nanoparticles, silver nanocluster, carbon nanotubes or graphene.

We have recently designed a label-free and reagentless microRNA sensor based on an interpenetrated network of carbon nanotubes and electroactive polymer , with application to Prostate Cancer Biomarker miR-141 [1] .

Another innovative strategy has been exploited using antibodies directed to RNA/DNA duplexes to design a novel electrochemical immunosensor based on a conducting polymer/reduced graphene oxide - modified electrode to detect miR-29b-1 and miR-141. Square wave voltammetry is used to record the redox signal . Current increases upon hybridization (signal on) with a detection limit as low as 5 fM. The sensor exhibits high selectivity as it distinguishes mismatch. Two specific RNA.DNA antibodies recognizing miRNA.DNA heteroduplexes were used. The results pave the way for easy electrochemical detection of any type of miRNA biomarkers in body fluids. The low limit of detection can be reached without using PCR or enzyme-based amplification process.

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The Thomas Graham Lecture: Novel Pickering Emulsifiers based on Block Copolymer Nano-Objects

Prof. Steve Armes, University of Sheffield

Polymerisation-induced self-assembly (PISA) is a highly versatile, potentially scalable platform technology that allows the efficient, reproducible synthesis of bespoke organic nanoparticles of controlled size, morphology and surface functionality in concentrated solution. More specifically, methacrylic diblock copolymers can be readily prepared via reversible addition-fragmentation chain transfer (RAFT) chemistry at 70oC using an aqueous dispersion polymerization formulation. The first (stabiliser) block is hydrophilic [e.g. poly(glycerol monomethacrylate), or PGMA], whereas the growing second (core-forming) block is hydrophobic [e.g. poly(2-hydroxypropyl methacrylate) or PHPMA]. Growth of the latter water-insoluble block leads to the formation of spherical nanoparticles of 25-100 nm diameter at 10-25% w/v solids. Adjusting the target diblock composition enables the copolymer morphology to be varied systematically from spheres to worms to vesicles. For the latter morphology, addition of a third monomer such as benzyl methacrylate (BzMA) drives microphase separation that is confined within the vesicle membrane, which produces well-defined framboidal vesicles5 Alternatively, addition of ethylene glycol dimethacrylate (EGDMA) leads to extensive crosslinking, which confers enhanced vesicle stability in the presence of ionic surfactants. These block copolymer nano-objects are evaluated as new Pickering emulsifiers for the stabilisation of oil-in-water emulsions. Linear PGMA-PHPMA vesicles do not survive the high shear homogenisation conditions used to generate the oil droplets: instead, vesicles dissociate to form individual diblock copolymer chains, which subsequently stabilise the droplets. Hence a stable emulsion is obtained, but it is not the intended Pickering emulsion. In contrast, the EGDMA-crosslinked vesicles survive emulsification and act as genuine Pickering emulsifiers. However, their adsorption efficiency is relatively low, with a significant fraction of non-adsorbed vesicles remaining in the aqueous phase. Much higher adsorption efficiencies can be achieved using framboidal vesicles, which is attributed to their enhanced surface roughness. In this case crosslinking is not required, because the third PBzMA block is sufficiently hydrophobic to stabilise the vesicular morphology during homogenisation. The worm morphology is particularly interesting in the context of Pickering emulsification, because the specific surface area of worms is only approximately one-third that of the corresponding spherical nanoparticles (for which the mean spherical diameter equals the mean worm width). However, depending on the mean worm length, the mean interfacial adsorption energy for worms is typically 10-100 times higher than that of the related spherical nanoparticles. Thus the worm morphology appears to offer significant advantages over spheres in the context of putative Pickering emulsifiers. Finally, PISA formulations can also be conducted in n-alkanes, instead of water. In this case, the highly hydrophobic diblock copolymer worms that are produced turn out to be highly effective Pickering emulsifiers for water-in-oil emulsions.

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Plenary 2: The Bio-Nano Interface: Current state of Affairs

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Nanotechnology is rapidly becoming an advanced field with applications of novel technologies becoming more prevalent. A long sought goal of nanotechnology is to significantly advance the medical treatment and diagnostics, using novel properties of nanosized carriers and tools to circumvent the issues of existing medicinal approaches. Whilst our understanding of nanoscale phenomenon is ever expanding it is clear that much work is required to elucidate the key factors which control and mediate nano-bio interactions. It is now an established phenomenon that a nanoparticle surface becomes decorated with the components of the surrounding environment.[1] This second identity determines how a nanoparticle with engage with other biological components, be it cells or otherwise.[2] To correctly implement nanotechnology in biomedical applications it now becomes imperative to describe how nanoparticles will interact with the biological systems they are designed to function in. This means a thorough understanding of, at first, the biological identity of these nanoparticles, and subsequently their further interaction with cellular and biological processes.[3] Here we highlight recent advances and developments in understanding how nanoparticles interact with biological systems.

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3 Salvati, A. et al. Transferrin-functionalized nanoparticles lose their targeting capabilities when a biomolecule corona adsorbs on the surface. Nature nanotechnology 8, 137-143
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K10. Microorganism Growth Variability in Droplets

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We have developed new approaches based on water-in-oil droplet and semi permeable capsules, to explore large libraries of confined microorganisms or human cells. We are able to follow the growth of each individual culture (up to millions in parallel) over hours and up to month; each culture is encapsulated and can grow from one individual. From these data we can explore the diversity arising from monoclonal populations and particularly how this diversity varies with a given selection pressure. Some preliminary conclusions about evolving pathways will be discussed. Using semi permeable capsules we are able to explore 3-d growth of tissues or epithelia and open routes to large scale screening of the phenotypic diversity of tissues made out of single cancer human cells.

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K11. Contact Line – Quo Vadis?

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The ongoing miniaturization in science and technology raises new questions about the behaviour of liquids in confinement. One particularly suitable way to study strongly confined liquids is by combining colloid science with soft-lithography techniques. Here, we will focus on contact-line dynamics: as our model system we use a mixture of spherical colloids and non-adsorbing polymers, which allows us to directly study contact-line motion and the accompanying entrainment and pinch-off instabilities at the scale of the thermal interface fluctuations. We interpret our findings within a mesoscopic theoretical framework, where the small separation between fluid and system length scales can be matched to that of the experiments. It turns out that in this regime of lengthscale overlap thermal fluctuations, wettability and gravity all play a crucial role in describing the dynamics.

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42. Thermo-responsive Diblock Copolymer Worm Gels with Tunable Critical Gelation Temperature

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Amphiphilic diblock copolymer nano-objects can be readily prepared using reversible addition-fragmentation chain transfer (RAFT) polymerization. In particular, poly(glycerol monomethacrylate) (PGMA) chain-transfer agents can be chain-extended using 2-hydroxypropyl methacrylate (HPMA) via aqueous dispersion polymerization to form well-defined spheres, worms or vesicles at high solids (≤ 25%). The worm morphology is of particular interest since inter-worm contacts lead to the formation of soft free-standing thermo-responsive gels. However, the critical gelation temperature (CGT) for such gels is rather low (< 20°C) for biomedical applications. Thus a series of diblock copolymers were prepared in which the core-forming block consisted of a statistical mixture of HPMA and di(ethylene glycol) methyl ether methacrylate (DEGMA), which is a more hydrophilic monomer than HPMA. Statistical copolymerizations proceeded to high conversion and low polydispersities were achieved in all cases (Mw/Mn < 1.20). The resulting PGMA-P(HPMA-stat-DEGMA) diblock copolymers undergo polymerization-induced self-assembly at 10% w/v to form free-standing worm gels. SAXS studies indicate that reversible (de)gelation occurs below the CGT due to a worm-to-sphere transition, with further cooling causing molecular dissolution. The CGT can be tuned by varying the mean degree of polymerization and DEGMA content of the core-forming statistical block. For example, a CGT of 31°C was obtained for PGMA59-P(HPMA91-stat-DEGMA39). This is sufficiently close to physiological temperature to suggest that these new copolymer gels may have biomedical applications as readily-sterilizable scaffolds that allow facile cell harvesting after a thermal cycle.

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K12. Fabrication and Assembly of Polymeric/ Inorganic Nanocomposite Colloidal Hybrid Hollow Spheres

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Hollow micro/nanospheres have attracted tremendous interest in the past decades due to their well-defined morphology, low density, large surface area, functional characteristics, and wide range of potential applications, such as nanoscale chemical reactors, catalysts, drug delivery, pigments, photonic crystals, supercapacitors, lithium-ion batteries, gas sensors, pollutant removal, and photodetection.[1]

Generally, there are two kinds of hollow spheres. One is based on inorganic hollow spheres, which are usually fabricated using various templating strategies against (i) polymeric, (ii) inorganic nonmetallic, (iii) metallic particles, and (iv) soft compounds.[2] Another kind of hollow spheres is so-called polymeric hollow spheres, which are usually synthesized by suspension polymerization, emulsion polymerization, core-shell precursors, and self-assembly. However, these strategies involve in many drawbacks, e.g., complex processes (calcination/etching/centrifugation/washing, etc.), or poor morphology and monodispersity of the as-prepared hollow structures.

In this study, we have successfully reported a facile "one-pot" method for fabrication of polymeric/inorganic hybrid colloidal hollow spheres using a mechanism similar to Kirendall effect. Unlike pure inorganic and polymeric colloidal hollow spheres, the as-obtained hollow spheres were shown to have hybrid shells composed of polymeric and inorganic components and so may have the following specific merits: i) excellent comprehensive performances, such as toughness and mechanical strength superior to that of pure inorganic hollow spheres, better morphology and more uniform size than pure polymeric hollow spheres; ii) tunable surface properties; iii) ready miscibility and dispersion in matrices. Furthermore, we have fabricated monolayer or multilayer nanofilm-based devices, using organic/inorganic core-shell composite spheres, inorganic particles, polymer particles as the building blocks.[3-5]

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73. Nanocapsule-based Active Coatings

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Nanocapsules possessing the ability to release encapsulated active materials in a controlled way can be employed to develop a new family of self-repairing multifunctional coatings, which will possess not only passive functionality but also rapid feedback activity in response to changes in local environment. Several approaches to fabricate self-repairing anticorrosion and antifouling coatings on plastic and metal substrates were developed. The release of the active materials occurs only when triggered, which prevents leakage of the active component out of the coating and increases coating durability. This report also covered some principles and recent developments in the fabrication of the nanocapsules with good compatibility with the coating components, the possibility to encapsulate and upkeep active material, and permeability properties of the shell controlled by external stimuli. Depending on the nature of the sensitive components (e.g., weak polyelectrolytes, metal nanoparticles) introduced into the container shell, reversible and irreversible changes of the shell permeability can be induced by various stimuli: variation of the pH, ionic strength, temperature, ultrasonic treatment, alternating magnetic field, electromagnetic irradiation. Different responses can be then observed varying from fine effects like tunable permeability to more drastic ones like total rupture of the container shell. Nanocapsule-based self-healing coatings were demonstrated on industrial scale and their corrosion protection and biocide activity were tested on industrial scale.

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K13. DNA as Molecular Local Thermal Probe for Magnetic Hyperthermia Analysis.

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Magnetic nanoparticles when coupled to an alternating magnetic field are capable of energy absorption and then release it in form of heat.[1] Thus, enabling the heating of the surroundings of the excited nanoparticles which can be used as a tool in many bioapplications.[2,3] The determination of temperature increments around excited nanoparticles represent however an experimental challenge and existing reports tend to show simple and limited assessments.[4,5] We demonstrate experimentally these temperature increments, when 12 nm magnetic nanoparticles are exposed to a radiofrequency radiation. Moreover, by functionalizing the surface of the nanoparticles with DNA molecules and further hybridizing with different length fluorophore-modified DNA an accurate temperature spatial mapping could be determined. Due to the design of these DNAs, different denaturalization temperatures (melting temperature, Tm) could be achieved. The quantification of the denaturalized fluorophore-modified DNA, and by interpolation onto a Boltzmann fitting model, it has been possible to calculate the local temperature increments at different distances, corresponding to the length of each modified DNA, from the surface of the nanoparticles. The local increments achieved were up to 15ºC, and the rigidity conferred by the double strand DNA allowed to evaluate the temperature at distances up to 5.6 nm from the nanoparticle surface.

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I4. Development of Non-Polymeric Amphiphilic Coating for Metal Oxide Nanoparticles to be used as Delivery and Imaging Agents

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Development and study of the magnetic nanoparticles for biological and clinical application remains one of the most challenging research areas in chemistry and materials science. The performance of these particles as, for example, drug delivery, MRI, hyperthermia or cell tracking agents, depends on their magnetic susceptibility. Their ability to form stable aqueous colloids, the mobility, and diffusion properties in biological media, rely on organic coating, which is usually composed of hydrophilic biocompatible polymers such as dextrans or poly(ethylene glycol)s. Some areas of biomedical imaging, labeling and delivery application can benefit from magnetic nanoparticles with higher mobility and penetration, stronger interaction with fluids and tissues, and that can be easily conjugated to biological molecules. The idea of this work was to develop a non-polymeric organic coating of an adjustable size, which might offer a simpler way to obtaining particles with these properties.

Our target capping ligands were based on isophthalic acid core whose two carboxyl groups, being adequately spaced from one another, would strongly bind to the nanoparticle's surface, and assure the adduct's stability in aqueous colloids. The precursor 5-hydroxyisophthalic acid was functionalized via the phenolic hydroxyl group by a nucleophilic oxirane ring opening addition reaction with allyl glycidyl ether. The chain length was varied by changing the stoichiometric ratio of the nucleophile to oxirane monomer, namely 1-1, 1-2 and 1-3 adducts were obtained in pure form. Dihydroxylated derivative of the 1-1 adduct, 5-diglyceroxy isophthalic acid, was synthesized and shown to bind to the surface of 5 nm γ-Fe_2O_3 nanoparticles in reaction with their surfactant-free diethylene glycol colloids. The reported method can be extended to the synthesis of O-substituted derivatives of other hydroxyacids of potential applications in biology and medicine.

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K14. Particle-Stabilised Novel materials

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Colloidal particles may adsorb at a range of fluid-fluid interfaces including air-water, oil-water and air-oil. As a result, they are responsible for the stabilisation of foams (aqueous and non-aqueous) and emulsions (simple and multiple). Such dispersed systems may be stable indefinitely to disproportionation and coalescence due to a close-packed layer of particles around bubbles or drops. The controlled assembly of particles at liquid interfaces also enables the preparation of novel materials, including dry water. The lecture will discuss our recent findings in the following three areas:

(i) Preparation of powdered emulsions using particle mixtures.
(ii) Oil powders and oil gels from Pickering emulsions.
(iii) Oil foams and dry oil stabilised solely by particles of low surface energy.

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123. Arrested Coalescence Behavior of Giant Pickering Droplets and Colloidosomes stabilized by Poly(tert-butylaminoethyl methacrylate) Latexes

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The coalescence of two oil droplets grown at pH 10 in the presence of lightly cross-linked 260 nm diameter charge-stabilized poly(tert-butylamino)ethyl methacrylate (PTBAEMA) latexes was monitored using a high-speed video camera. Three model oils (n-dodecane, isopropyl myristate and sunflower oil) were investigated, each in the absence and presence of an oil-soluble cross-linker (tolylene 2,4-diisocyanate-terminated poly(propylene glycol), PPG-TDI). In the absence of PPG-TDI, rapid coalescence was observed for giant Pickering oil droplets, which exhibited faster coalescence times compared to bare oil droplets. An increase in the damping coefficients for coalescing Pickering droplets (compared to those of bare oil droplets) indicated PTBAEMA latex particle adsorption at pH 10. Addition of PPG-TDI cross-linker to oil droplets in the absence of latex particles led to a reduction in the interfacial tension, confirming the surface-active nature of this reagent. PPG-TDI was added to the oil phase to react with the secondary amine groups on the PTBAEMA latex, producing giant colloidosomes that are stable to coalescence. This stability was not observed for bare oil droplets in the presence of PPG-TDI, confirming that the cross-linked particles at the interface provide the additional stability. Separation of the colloidosomes five minutes after their contact produced a visible neck connecting the droplets. This neck was broken when isopropyl myristate and sunflower oil droplets were separated. In the case of the n-dodecane-based colloidosomes the contact area only stretched upon separation, with no cleavage of the neck being observed, indicating formation of inter-crosslinked colloidosomes containing n-dodecane. Finally, interactions between asymmetric droplets were examined.

The effect of adding oil-soluble cross-linker to only one n-dodecane droplet resulted in “arrested coalescence” in the presence of PTBAEMA latex particles. Here the droplet aging time was found to be critical. Aging times of less than 60 s led to catastrophic droplet coalescence, whereas aging times longer than 60 s indicated cross-linker diffusion from one droplet to the other, which produced inter-crosslinked colloidosomes. Arrested coalescence was only observed for aging times of approximately 60 s.

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28. Aqueous Organometallic Catalysis: Contribution of CD-Based Hydrogels and CD-Substituted Polymers

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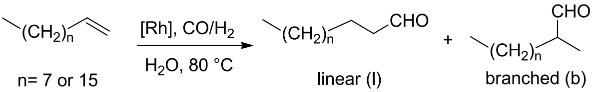
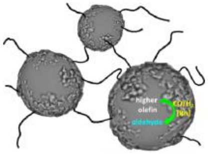
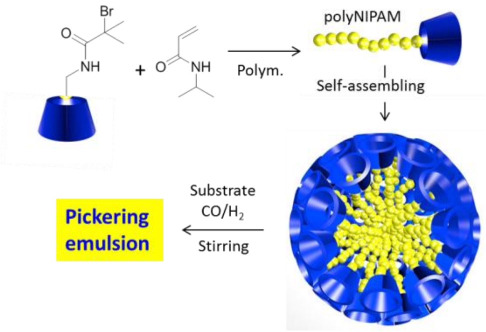
In a green chemistry context, aqueous organometallic catalysis has gained an increasing interest over the past ten years. As such, biphasic systems composed of a substrate-containing organic phase and a catalyst-containing aqueous phase proved to be especially effective to convert terminal alkenes into aldehydes (hydroformylation reaction).1 While modified CDs are appropriate to help converting C10 alkenes, we recently develop novel catalytic systems capable of converting alkenes containing up to 18 carbons in aqueous media.



Herein, two strategies will be especially highlighted.

First, supramolecular hydrogels elaborated from a mixture of native α-cyclodextrin and poly(ethylene glycol)s proved to be appropriate media to favour higher olefins Rh-catalysed hydroformylation. The formation of Pickering emulsions during the catalytic process appeared to be responsible for the catalytic performances.[2]





Second, randomly methylated β-CDs have been grafted to polyNIPAM chains. The resulting amphiphilic molecules self-assembled above 33°C (T>LCST) to form Pickering emulsions that greatly improved the catalytic performances in a higher olefins hydroformylation reaction.

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178. Complex Colloidal Polymer Particles via Radical Dispersion Polymerization in Non-Polar Solvent for Electrophoretic Display Applications

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Developing particles for electrophoretic display (EPD) applications has recently been an area where industrial and academic interest has significantly grown. Current directions are aiming to make EPD devices faster, colored, flexible and generally more reliable. Dispersion polymerization in non-polar solvents is a well-suited technique to prepare latex particles in low dielectric constant, low permittivity medium such as alkanes, a key requirement of EPD particles. We have investigated the possibility of producing a range of latex particles of various core compositions with this technique and will be reporting here our efforts in:

- The use of polydimethylsiloxane-methacrylate as a stabilizer for dispersion polymerization of methyl methacrylate (MMA) and its copolymerization with a range of other monomers such as 4-vinylpyridine and 2-(dimethylamino)ethyl methacrylate in dodecane,
- The influence of varying monomer and stabilizer concentration on the control exerted over the synthesized particle properties,
- A method for introducing a porogen within PMMA particle cores to tune particle density,
- A method for encapsulating pigment particles within PMMA particles, which enables the design of highly reflective inorganic-organic hybrid particles. For this purpose, we will present data obtained from two approaches based on modifying the pigment surface.

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K15. Harnessing Capillary Pressure in the Assembly of Colloidal Particles in Nanocomposites

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Colloidal polymer particles are ideal building blocks for nanocomposite coatings and adhesives, because they allow heterogeneity to be controlled precisely at nanometer length scales. Structure can be built into individual polymer particles, such as via encapsulation of inorganic nanoparticles or via the growth of polymer shells, and these particles can be assembled into hierarchical structures. Alternatively, polymer particles can be blended with inorganic or polymer nanoparticles. In this talk, I will provide examples of both approaches to the design of nanocomposites and outline their advantages. In comparison to the fabrication of polymeric nanocomposites from solutions or the melt phase, the use of waterborne colloids introduces a powerful mechanism to achieve structural control: the capillary (or Laplace) pressure at the meniscus between colloidal particles. We have found that the capillary forces generated during film formation, being on the order of 10-7 N, are sufficiently strong to bend carbon nanotubes (CNTs) (see Jurewicz et al., Langmuir (2012) 28, 8266) and also ex-foliated graphene sheets to create honeycomb-like structures, such as shown in Figure 1. Our recent results on binary particle blends also indicate that the capillary pressure can guide the convective assembly of nanoparticles into precise positions (cf. Norris et al., Adv. Mater. (2004) 16, 1393). Figure 2 shows how Au nanoparticles can be positioned with exquisite control in hexagonal arrays of larger colloidal polymer particles. Rather surprisingly, the type of interstitial void occupied by the Au nanoparticles alternates in a layer-by-layer fashion within the colloidal crystal, in turn influencing the optical properties.

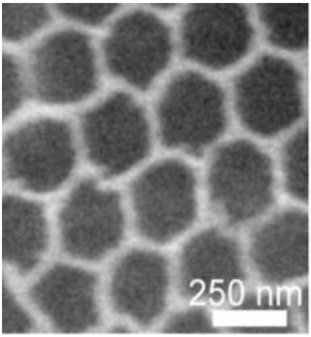

Fig. 1. SEM image of CNTs assembled in a honeycomb structure under the action of capillary forces.

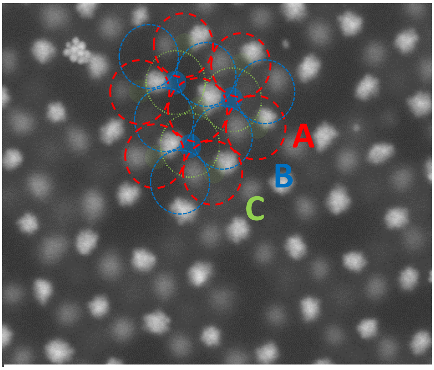

Fig. 2. Au nanoparticles assembled in polymeric colloidal crystal with FCC structure. The Au appears as bright white dots near the surface and as grey dots in the next layer below.

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115. Cationic polymer latexes prepared by RAFT-mediated surfactant-free emulsion polymerization for the modification of cellulose surfaces

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The endeavour to produce new cellulose-based hybrid materials often requires an alteration of the surface properties of this hydrophilic natural material to allow its combination with a non-polar polymer matrix. This paper presents the successful surface modification of a cellulose model surface by the preparation and subsequent physical adsorption of cationic polymer latexes constituted of amphiphilic block copolymers of poly(N,N-dimethylaminoethyl methacrylate-co-methacrylic acid) (P(DMAEMA-co-MAA)) and poly(methyl methacrylate) (PMMA). First, RAFT polymerization of DMAEMA was performed in water at pH = 7. During the polymerization, DMAEMA was hydrolyzed to a small extent, leading to a macroRAFT containing 10% of methacrylic acid units. This P(DMAEMA-co-MAA) macroRAFT was then used for the RAFT-mediated surfactant-free emulsion polymerization of methyl methacrylate (MMA) targeting different molar masses for the hydrophobic PMMA block. During the synthesis, amphiphilic block copolymers formed and self-assembled into spherical cationic latex nanoparticles by polymerization-induced self-assembly (PISA). As expected, the size of the particles increased with PMMA molar mass. The cationic latex particles were subsequently adsorbed to cellulose model surfaces in a quartz crystal microbalance with dissipation (QCM-D). The adsorbed amount was found to increase with the size of the particles (i.e. the molar mass of the PMMA block) and the contact angles after adsorption were significantly higher than that of net cellulose. This strategy allows for physical surface modification of cellulose using an aqueous dispersion of particles for which both

the surface chemistry and the surface structure can be altered in a well-defined way.

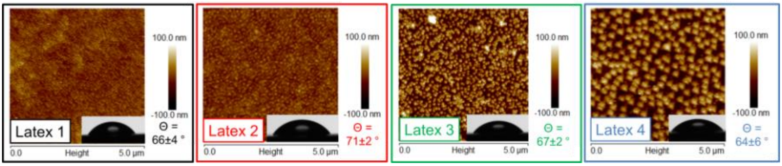

Figure 1. AFM images of PMMA latexes stabilized by cationic P(DMAEMA-*co*-MAA) and adsorbed onto cellulose model surfaces formed on QCM crystals (100 mg L^{-1}). Insert pictures: contact angles.

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113. Metallacarboranes as a New Class of Surfactants: Aggregation in Water and Interaction with Polymers

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Each anion of [3-cobalt(III) bis(1,2-dicarbollide)](-1), CoD-, consists of two carborane nido clusters, surface of which is composed of nine partly hydridic hydrogen atoms that cannot form classical hydrogen bond and two partly positively charged hydrogen atoms attached to carbon atoms. Since the overall negative charge is delocalised, salts of CoD- are fully dissociated in water and counterions are free moving. All these features stand behind peculiar behaviour of metallacarboranes in water: CoD-cluster has a distinct amphiphilic character despite the lack of amphiphilic topology. By a combined experimental study (scattering, microscopy, NMR and calorimetry techniques) of NaCoD aqueous solutions we demonstrated that despite the above-mentioned peculiarities NaCoD behaves like a classical surfactant: It forms micelles with distinct value of CMC. Nevertheless, the micellization is enthalpy driven process due to C-H…H-B interaction. Besides the thorough characterization of NaCoD self-assembly in water, we also studied interaction of CoD- with cationic polyelectrolytes poly(2(4)-vinyl pyridines), P2VP and P4VP, and non-ionic poly(ethylene oxide), PEO. Structure of the precipitants (P2VP/H/CoD, P4VP/H/CoD and PEO/Na/CoD) has been studied by means of WAXS and advanced solid-state NMR techniques. The nanocomposite structure and CoD- dynamics are unique reflecting mutual interactions of polymers with bulky metallacarborane clusters, which can be therefore called as an amphi-dynamic system.

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89. Polymer Stabilised Nanodiscs adsorbed at the Silicon-Water Interface

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Nanodiscs are self-assembled structures that consist of a bilayer of phospholipids controlled in diameter by a protein or polymer stabilising belt. Nanostructured lipid aggregates offer enormous potential as tools for membrane structural biology and biophysics. In particular polymer stabilised nanodiscs (PS-nanodiscs) are easy to assemble and can be used directly in the protein purification step. They have been shown to effectively incorporate membrane proteins in their active form1. Studies of adsorbed layers of nanodiscs containing membrane proteins offer an alternative approach to structural determination by means of x-ray/neutron reflectometry and/or grazing incidence x-ray diffraction. However little work has been completed assessing nanodisc interaction at the solid-liquid interface. An aim of our experiments was to adsorb PS-nanodiscs at the silicon water interface as well as upon two solid supported lipid monolayers containing zwitterionic and cationic lipids. Our studies were completed using neutron reflectometry and a quartz crystal microbalance. Results indicated that PS-nanodiscs composed of mixtures of 1,2-Dimyristoyl-sn-glycero-3-phospho-rac-(1-glycerol) sodium salt (DMPG) and 1,2-Distearoyl-sn-glycero-3-phosphocholine (DMPC) form observable layers on the surface of cationic and zwitterionic lipid monolayers but not directly on the surface of silicon. Packed layers of nanodiscs at the solid-liquid interface may provide an alternative platform for the structural analysis of encapsulated membrane proteins as well as new approaches for drug delivery and bio sensing.

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K16. Colloidal Cell Imprints for Biosensor and Antimicrobial Applications

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We produced a new class of engineered colloids which can recognise the shape and size of targeted microbial cells and selectively bind to their surfaces. These imprinted colloid particles, which we called "colloid antibodies", were recently fabricated by partial fragmentation of silica shells obtained by templating the targeted microbial cells. We demonstrated the shape and size recognition between such colloidal imprints and matching microbial cells. We explored the binding of colloidal imprints to target microbial cells in a binary mixture of cells of different shape and size, which also resulted in high binding selectivity. We probed the role of the electrostatic interactions between the target cells and their colloid imprints by pre-coating both of them with polyelectrolytes. Shape-selective binding occurred predominantly in the case of opposite surface charges of the colloid cell imprint and the targeted cells. Such colloidal cell imprints can be additionally functionalized with surface groups which can enhance their binding efficiency to the microbial cells, deliver a drug payload directly to their surface or allow them to be manipulated using external fields. We fabricated such "colloid antibodies" with photothermal mechanism for shape-selective killing of matching cells. This was achieved by the subsequent deposition of: (i) gold nanoparticles and (ii) silica shell over the microbial cells. We demonstrated that fragments of these composite gold nanoparticle/silica shells act as "colloid antibodies" and can bind to cells of matching shape and deliver gold nanoparticles directly onto their surface. After irradiation with a laser, the localized heating around the gold nanoparticles destroyed only the microbial cells of matching shape. This approach opens a number of avenues for building powerful selective biocides based on combinations of colloid antibodies and other cell killing strategies which can be applied in new selective antimicrobial therapies.

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138. Towards Smart Drug Carriers: Formation of pH Responsive Polyelectrolyte Shell around Magnetic Core

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For the effective activation of drugs and minimisation of side effects the drug has:

1) to be stable until the right target has been found,
2) to cross several biological barriers,
3) to be activated in the right place at the right time.

To fulfill these demands, smart materials – i.e. materials which react to the changes in their environment – have been suggested as drug carriers [1, 2]. The conformation of weak polyelectrolytes is strongly dependent on the degree of ionization which, in turn, can be controlled by pH and thus, nanocontainers covered by weak polyelectrolyte shell are promising candidates for drug carriers: groups of Möhwald and Shchukin [1, 3], for example, have deposited oppositely charged polyelectrolytes on mesoporous SiO_2 or TiO_2 particles by layer-by-layer (LbL) technique and studied the properties of the containers.

In this communication, a rapid method to prepare polyelectrolyte covered Fe_3O_4 particles is presented: this method exploits the magnetic properties of the core and different polyelectrolyte pairs as a pH responsive shell are studied. The shell properties are studied by Dynamic Light Scattering (DLS) while the fundamental studies of polyelectrolyte shell are performed by Isothermal Titration Calorimeter (ITC). DLS measurements demonstrate how the deposition conditions affect the polyelectrolyte shell's response to the pH change while the polyelectrolyte-polyelectrolyte interaction studies by ITC show that the ion pairing between weak anionic and cationic polyelectrolytes is followed by complex coacervation in this colloidal system and such behaviour depends on pH.

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191. FePtAu Nanoparticles as novel magnetic bioprobes

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Magneto-plasmonic hybrid nanoparticles (NPs) have attracted much attention with their demonstration as potential vehicle for simultaneous plasmonic monitoring and magnetic manipulation. These dual functional probes hold great promise as sensing probes for diagnostics and environmental applications such as immunomagnetic/chemo-magnetic separation under plasmonic imaging, dual mode imaging(MRI and plasmonic) and SERS sensing. Much effort has been made in the field of synthesizing mainly core-shell particles such as Fe_3O_4@Au/Ag or FePt@Au/Ag showing their promising ability for biological sensing applications, but there are still several limitations regarding the synthetic techniques and resulting particle characteristics such as inability to uniformly coat magnetic core with the shell material, control over oxidation characteristics of both core and shell, as well as others,. In addition, there is still a large lack in understanding how to truly control the magnetic characteristics of the core material which are suppressed by the addition of shell material or encapsulating ligands. With this in mind, we have developed FePtAu ternary NPs, which are used as a new material for dual functional magnetic/plasmonic applications. Au has traditionally been included in fcc FePt as a dopant to lower the annealing temperature required for the $L1_0$ fct phase transition, however no significant work has been done to fully characterize their potential in magneto-plasmonic applications. In this work, we synthesized FePtAu and heterostructured FePt@Au spherical NPs for dual application of plasmonic imaging and magnetic separation, characterized with the help of TEM-EDS, XRD, ICP-OES, UV-Vis. and SQUID. Preliminary results suggest that the particles can prove to be a better or equivalent promising material as core-shell structures in context to specific use. Our research leads to a deeper understanding of the critical role of physical and chemical properties (precise control of size, shape and composition) and their correlation to the usage of particles in the above mentioned applications.

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130. Aqueous synthesis of red-emitting CdTe/CdS/ZnS quantum dots and their interactions with cells

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Core/shell (CS) semiconductor nanocrystals (so-called quantum dots, QDs) emitting in the near-infrared range are of particular interest owing to deep tissue penetration which is important in biomedical imaging applications. Therefore, recent studies mostly focused on developing new strategies which will allow simple manufacturing of QDs with large spectral shifts. [1] By using the lattice strain between a small soft core (CdTe) and a thick compressive shell (ZnS, CdS), Nie and coworkers (2009) [2] presented a new class of CS QDs (magic-core/thick shell) exhibiting type-II behavior with greater photostability and giant spectral shifts in comparison to traditional CS QDs. Furthermore, growth of an external shell with a wide bandgap serving as an outer protection layer, resulting in a core/shell/shell (CSS) system, can even create more qualified and stabile QDs while maintaining the lattice strain induced spectral tuning properties.

Herein, a simple strategy was developed for aqueous one-pot synthesis of magic-core/thick shell CdTe/CdS QDs and further overgrowth of ZnS shell around CdTe/CdS QDs. Zinc sulfide was chosen as outer shell material due to its chemical inertness, wide bandgap energy and negligible toxicity which gains specific interest in biomedical applications. Moreover, it assures effective passivation of surface trap states giving rise to enhanced fluorescence quantum yields. [3] The optical and structural properties of QDs have been investigated through the measurements of quantum yield, photostability, XRD and DLS size analysis. The effect of a protective ZnS shell around CdTe/CdS QDs has been evaluated in terms of fluorescence efficiency and biocompatibility. Their size and composition dependent cellular interactions were examined by means of *in vitro* cytotoxicity assays. Furthermore, aptamers directed to cancer cell surface-specific receptors were conjugated to QDs and utilized as targeting moiety in cell labeling studies.

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K17. Knowledge and take off of Clinical constraints: a security to reach Nanomedicine!

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Despite the numerous nanoprobe developments since 15 years and the research fundings devoted to the nanotechnology, only some (around thirty in France) have obtained the medicine status. These medicines are principally drug vectorization probes, and some are nanoparticles used as contrast MRI agents. The advantage that brings the nanovector is the protection against the degradation accelerated by the active principle and an enhance the , the small size and the chemical composition of the nanovector allowing a passage of the various biological barriers. This nanovectorisation allows to administer more low doses of medicine and thus to reduce the side effects, or to equivalent doses, to increase the efficiency of the drugs.

It commonly accepted that the development of a new medicine is a very long (15-20 years) and very expensive process, and in fact is a very uncertain course with multiple obstacles, by resulting only 1 over roughly 10,000 screened molecules reached the medicine status.

For medicine based on nanotechnology, this course is more complex, especially due to safety parameter, with specific toxicity and the absence of optimal tools to evaluate it. Considering the history of recent failure of nanomedicine development at end clinical stages, the taking into account of biodistribution and pharmacokinetic datas and the real clinical needs at a very early stage of nanoprobe developments appear as an essential tool to optimize this evaluation an enhance the success of this course. But the studies of pharmacokinetics realized to the animal can enough not take into account the human clinical reality and raise the problem of the adequacy of the animal model. So, despite no toxicity revealed by regulatory toxicology tests, hard adverse effects would be revealed during the II or III clinical trials, with a resulting rough arrest of the clinical trial.

The knowledge of clinical reality and existent medicines should be also taking into account, a new medicine should be demonstrated to give a true medical advantage. So the orphan diseases, especially poor prognosis cancer without efficient therapy were frequently selected by pharmaceutical industry to perform the clinical proof of concept. But, the economic reality will imply to enhance the clinical scope and market to make profitable the very important fundings.

The ethical patterns should not be underestimated.

In conclusion, as for any medicine, the passage of the clinical stage is a long and uncertain course, with multiple obstacles, but among which some are more complex to cross for nanomedicine, as for the evaluation of the safety because of still not optimal tools of study. The studies of biodistribution and pharmacokinetics appear as an essential tool to optimize this evaluation.

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I5. Dendronized magnetic core-shell and cubic shaped nanoparticles designed for targeting, MRI and hyperthermia

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Some of the significant and most promising applications for inorganic nanoparticles (NPs) lie in the fields of biology and biomedicine. Due to their magnetic properties tuned by their shape and/or composition, superparamagnetic iron oxide NPs (SPIO) with appropriate surface chemistry can be used in numerous in vivo applications such as MRI contrast enhancement, hyperthermia treatment, cell sorting, drug delivery...

In that context, we will present the main synthesis ways of iron oxide NPs and their functionalization and we will propose a concept combining a dendritic coating of magnetic oxide nanoparticles with phosphonate anchors. Indeed, phosphonates ensure a strong anchoring at the NPs surface while preserving their magnetic properties, and dendritic shells, in addition to their small and easily controllable size (as a function of their generation), are promising building blocks simultaneously solving the problems of biocompatibility, large in vivo stability and specificity. Dendronized iron oxide nanoparticles were demonstrated to induce any cytotoxicity. In vivo and in vitro MRI measurements showed that the contrast enhancement properties of the dendronized NPs were higher than those obtained with commercial polymer-coated NPs. Moreover, both types of dendronized NPs were eliminated by urinary and hepatobiliary pathways without unspecific uptake especially in the RES organs and in the lungs. The design of dendronized NPs was further improved to obtain theranostic nano-objects (which can both identify disease states and simultaneously deliver therapy) by adjusting the morphology and the composition of the inorganic magnetic core and by designing multifonctionalized dendrons. These NPs were found suitable to combine imaging and therapy by hyperthermia. Finally these dendronized NPs bearing melanin vectors were demonstrated very suitable to specifically target in vivo tumoral cells.

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I6. Controlling biodegradation and fate of magnetic particles for medical applications

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Many research efforts are presently focused on the life cycle and toxicity of nano-sized materials. While most toxicology studies warn about the effects of nanomaterials on biological functions (cytotoxicity, immunogenicity, genotoxicity…), the physical transformations of nano-objects in living environment are mostly unknown. Yet the mechanisms of biological transformations – aggregation, protein adsorption, degradation and elimination - determine the long term fate of nanoparticles in the body, their safety as well as their therapeutic outcome.

Here we propose a multiscale methodology to examine the influence of intracellular lysosomal confinement on the structure and physical properties of magnetic nanoparticles that show outstanding properties for magnetothermal therapy and MRI detection.

Our material science approach – combining nanoscale TEM observations of nanoparticle structure with the follow-up of magnetic properties in biological environment - opens up a new way to evaluate the life cycle of nanoparticles in the body and identify their biodegradation products. We will present several examples of magnetic nanostructures – iron oxide nanospheres, nanocubes, cooperative nanoflowers and iron oxide/gold dimers with different coating – and examine how cell-induced morphological degradation critically alters their magnetic properties, heating power and Magnetic Resonance relaxivity over time. Hence maintaining nanoparticles in the extracellular matrix of the tumor environment might be more advantageous for thermal therapy than favoring uptake by tumor cells. By contrast, specific internalization by the monocyte/macrophage system warrants the long term metabolization of particles and iron recycling.

In the research for safe-by-design efficient nanoparticles for nanomedecine, one should control not only their synthetic identity, but also their ever-evolving context-dependent structure and properties. Controlling the balance between short term efficacy in the relevant biological context and long term degradability or elimination is an important challenge that may be overcome by chemical design of functionalized nanoparticles.

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117. Destabilising Pickering Emulsions

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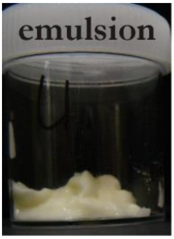
Emulsions stabilised by solid particles (Pickering emulsions) are remarkably robust structures [1]. Particle-coated drops can be squeezed together and the liquid evaporated to form porous solids [2,3]. The drop stability is attributed to the dense packing of strongly bound colloidal particles at the liquid interface. The particle layer is thought to behave like a 2-dimensional solid and provide a mechanical barrier to droplet coarsening [4]. Drops may coalesce, however, in emulsions under external stress. The mechanisms that cause the thin films to rupture are not well understood.

In this presentation, I will discuss our recent efforts at investigating destabilisation in aqueous emulsions of oil drops coated by silanised silica particles. We used confocal microscopy to follow the structural changes as drops are compressed together in emulsions. We characterised the elasticity and yielding behaviour of the concentrated emulsions. The elasticity is correlated with the salt concentration in the water and hence the particle aggregation in emulsions at a given drop volume fraction. Destabilisation is favoured by minimising the attractive interactions between particles, since deformation of the drops exposes interfacial area that is free of particles. Large shear strains cause the emulsions to yield and coalesce, rather than flow. By controlling destabilisation, Pickering emulsions have been used to form highly elastic gels and thin films.



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147. Pickering emulsions stabilized by soft microgels

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Some colloidal gel particles called microgels have the ability to adsorb at an oil–water interface and stabilise Pickering emulsions. Such particles are soft, deformable, porous and they can swell or shrink under the action of an external stimulus. These specificities makes them emulsifiers of special interest as they offer a large versatility to emulsions and materials elaborated thereof [1]. We took advantage of the limited coalescence process occurring in Pickering emulsions combined to cryo-scanning electron microscopy, to determine the surface coverage of the drops. Using non-polar oils, oil-in-water emulsions with different macroscopic properties have been prepared. We have studied the packing and morphology of the deformed microgels at the oil-water interface [2] and found a relation between their organisation and emulsion properties. We show that the packing density can be triggered through various microgel structural parameters such as cross-linking density [3] or size [4], and emulsification process like the stirring speed [5] or the temperature of emulsification [3]. At low surface coverage, emulsions are highly flocculated whereas at high surface coverage, the drops are free and the emulsion can flow easily. Water-in-oil emulsions are stabilized when the oil is a good solvent of the polymer (Figure). In this case, oil-loaded microgels are dispersed in the aqueous phase and give anti-Bancroft emulsions [6].

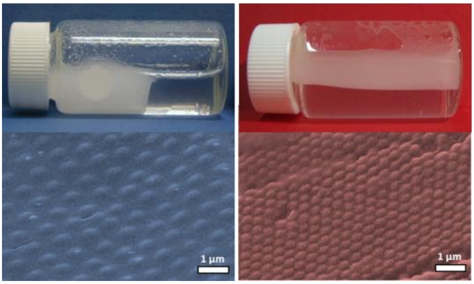

Figure. Relation between the emulsion properties and the microgel packing at the oil-water interface.

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183. Photoresponsive Aggregation of β-Cyclodextrin Capped Nanoparticles

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The general aim of this collaborative project is the investigation of light-responsive, self-assembled materials of multifunctional particles.

We could show that light-responsive supramolecular adhesion of cyclodextrin covered silica nanoparticles and a bifunctional, non-covalent azobenzene linker is possible. The self-assembly of these nanoparticles is photocontrolled due to the photoresponsive nature of the supramolecular recognition motifs – host guest inclusion of cyclodextrin cavities and azobenzene molecules. Switching experiments between aggregation and dispersion of the system show that aggregation is fully reversible over at least 4 cycles. [1]

It is also well known that nanoparticles can form pickering emulsions. In connection with the above described system, we investigated the control of the stability of emulsions consisting of cyclodextrin covered silica nanoparticles and an azobenzene linker.

Currently we investigate the preparation of anisotropic cyclodextrin functionalized silica microparticles using “*sandwich*” microcontact printing, in particular with the help of so-called “wrinkled” stamps.

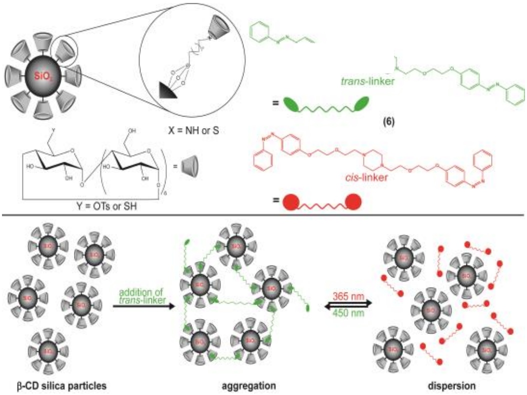

Figure 1: Photoresponsive aggregation and dispersion of β-cyclodextrin capped nanoparticles. [1]

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169. Stabilisation of Fluorinated Oil-in-Water Emulsions using Fluoroalkyl-Functionalized Silica Nanoparticles

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The unique physical, chemical and biological properties of fluorinated oils have generated much interest in their use in several biomedical applications such as propellants for pressurized metered dose inhalers (pMDIs) for direct delivery of drugs to lungs[1], ultrasound contrast enhancement[2] and for transport of oxygen in vivo in artificial blood[3]. Perfluoropropane (PFP) and hydrogenated perfluoropropane (HPFP) showed promise in the field of drug delivery and gene transfection[4].

All the aforementioned applications require that PFP and HPFP to be in the form of a dispersion. Emulsions of fluorinated oils and water are mostly formed using nonionic surfactants such as polaxamers and zonyls or a phospholipid (egg or soy lecithin). However, a problem inherent in such emulsion is the tendency of the emulsion to de-stabilize on storage and for the emulsion droplets to grow in size at the expense of small droplets (Ostwald ripening destabilisation mechanism)[5].

We have prepared a series of fluoroalkyl-functionalized silica particles by the treatment of silica particles with fluoroalkyl-functional chlorosilanes. Confirmation of covalent attachment was confirmed via X-ray photoelectron spectroscopy (XPS), while elemental analysis, thermogravimetric analysis and nitrogen adsorption isotherms were used to determine the different grafting densities.

The modified nanoparticles were used successfully to prepare stable HPFP-in-water Pickering emulsions. The emulsions stabilized by modified particles have i) higher stability compared to those prepared with unmodified ones; ii) low polydispersity, iii) stability at lower particle concentrations and iv) undergo no change in the average droplet size over the time course of six months.

Fluorinated emulsions stabilized by these modified silica particles exhibit preferential behavior to those stabilized by polymeric surfactants.

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62. Measuring the hydrophobic force in a soft matter system

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The hydrophobic attraction describes the well-known tendency for nonpolar molecules and surfaces to agglomerate in water, controlled by the re-organisation of intervening water molecules to minimize disruption to their hydrogen bonding network. Measurements of the attraction between chemically-hydrophobised solid surfaces have reported ranges varying from tens to hundreds of nanometres, all attributed to hydrophobic forces.

Here, by studying the interaction between two hydrophobic drops of fluorinated oil in water under well-controlled conditions, we were able to effectively suppress known surface forces in order to measure the intrinsic hydrophobic attraction. By introducing moderate repulsions of electrostatic, quantum electrodynamic and hydrodynamic origin, we probed the strength and range of the hydrophobic force.

In a wide variety of experiments using different conditions and velocities, we observe only a strong, short-ranged attraction with an exponential decay length of 0.30 ± 0.03 nm - comparable to molecular correlations of water molecules. Interestingly, there is no difference in the range or strength of the force when salts with very kosmotropic or chaotropic characteristics are added to the water.

This attraction is implicated in a range of fundamental phenomena from self-assembled monolayer formation to the action of membrane proteins and non-stick surface coatings.

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150. Cluster formation in fluids with competing short-range and long-range interactions

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We investigate[1] the low density behaviour of fluids that interact through a short-ranged attraction together with a long-ranged repulsion (SALR potential) by developing a molecular thermodynamic model. The SALR potential is a model of effective solute interactions where the solvent degrees of freedom are integrated-out. For this system, we find that clusters form for a range of interaction parameters where attractive and repulsive interactions nearly balance, similar to micelle formation in aqueous surfactant solutions. We focus on systems for which equilibrium behaviour and liquid-like clusters (i.e. droplets) are expected, and find in addition a novel coexistence between a low density cluster phase and a high density cluster phase within a very narrow range of parameters. Moreover, a simple formula for the average cluster size is developed. Based on this formula, we propose a non-classical crystal nucleation pathway whereby macroscopic crystals are formed via crystal nucleation within microscopic precursor droplets. We also perform large-scale Monte Carlo simulations, which demonstrate that the cluster fluid phase is thermodynamically stable for this system.

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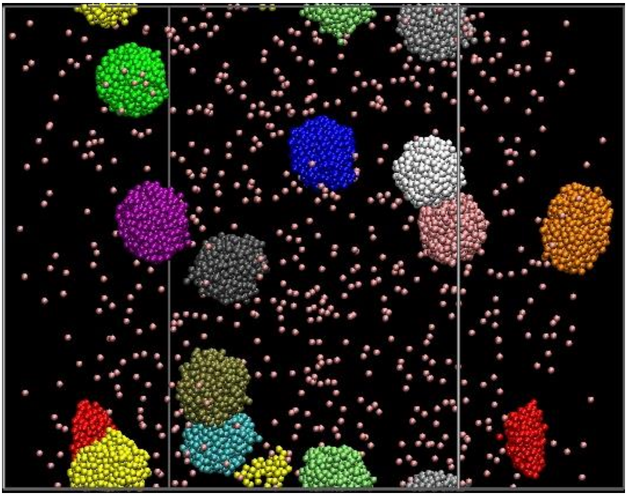

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4. Crystal nucleation kinetics in colloids

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It is shown that Classical Nucleation Theory (CNT) remains a sound basis upon which to understand nucleation in colloids. Speed of sound measurement is a very precise method for determining crystal solid content during primary crystal nucleation and in the induction phase, far more sensitive than turbidity measurement. It is shown that speed of sound determinations of dispersed temperature/time dependent phase solid contents measured in a number of different emulsion systems are fitted well by CNT. Computation of the energy barrier to nucleation for studied systems indicates that whilst homogeneous nucleation is unlikely at higher surface energies the addition of surfactant, lowering the interfacial energy may have a dramatic impact on surface nucleation rates. Data is included supporting this contention. The impact of reducing the size of colloidal particles to the point where the interfacial region occupies a significant proportion of the total volume of the dispersed phase is discussed and it is suggested that in these circumstances undercooling may fall significantly in comparison with the undercooling measured in micrometer sized emulsions. The measurement of collision induced nucleation in colloids permits the determination of the energy barrier established by different surfactants which can then be used as a comparison measure of the effectiveness of different surfactants as stabilisers.

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39. The breakup mechanism of biomolecular and colloidal aggregates in a shear flow

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The theory of self-assembly of colloidal particles in shear flow is incomplete. Previous analytical approaches have failed to capture the microscopic interplay between diffusion, shear and intermolecular interactions which controls the aggregates fate in shear. In this work we analytically solved the drift-diffusion equation for the breakup rate of a dimer in flow. Then applying rigidity percolation theory, we found that the lifetime of a generic cluster formed under shear is controlled by the typical lifetime of a single bond in its interior, which in turn depends on the efficiency of the stress transmitted from other bonds in the cluster. We showed that aggregate breakup is a thermally-activated process where the activation energy is controlled by the interplay between intermolecular forces and the shear drift, and where structural parameters determine whether cluster fragmentation or surface erosion prevails. In our latest work, we analyzed floppy modes and non affine deformations to derive a lower bound on the fractal dimension df below which aggregates are mechanically unstable, ie. for large aggregates df $\simeq$ 2.4. This theoretical framework is in quantitative agreement with experiments and can be used for the population balance modeling of colloidal and protein aggregation.

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44. Bio-inspired mini-eggs with pH-responsive membrane for enzyme immobilization

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Calcium alginate (Ca-alginate) hydrogel, which is featured with good biocompatibility and biodegradability etc, has been widely applied in biological and medical fields. Unfortunately, all previously reported carriers based on Ca-alginate hydrogels do not have pH-responsive characteristics; as a result, the efficiency of Ca-alginate-hydrogel-based carriers in practical applications is restricted and affected. In this study, a novel family of bio-inspired Ca-alginate-based capsules or so-called mini-eggs with a pH-responsive membrane are developed by a simple co-extrusion minifluidic approach and subsequent adsorption and biosilicification method. Such mini-eggs with a pH-responsive membrane are composed by two biocompatible materials, Ca-alginate and protamine, for enzyme immobilization. The average diameters of APSiE mini-egg with thin membrane and thick membrane are 4.2 mm and 3.5 mm, and the corresponding coefficient of variation values are 2.2 % and 4.2 % respectively. The wall of APSiE mini-egg with thin membrane and APSiE mini-egg with thick membrane are composed of inner Ca-alginate/protamine composite soft layer and outer silica surface rigid layer. The Ca-alginate/protamine composite soft layer provides the pH-responsive switching function driven by electrostatic interactions between Ca-alginate networks and protamine molecules at different pH values, and the silica surface rigid layer offers protection and restriction for the soft layer in order to guarantee the endurance and stability of the pH-responsive performance. The trans-membrane permeation results of VB12 molecules show that the critical pH value $pH_{critical}$ of the as-prepared capsule is about 4.5. The ratio of catalytic rate of invertase encapsulated in APSiE mini-eggs with the thin membrane and APSiE mini-eggs with the thick membrane at pH=5 to that at pH=4 are 2.38 and 123 respectively. The pH-responsive switching action of the prepared mini-egg membrane is rapid, reversible and reproducible. This work provides a new approach to improve the efficiency of Ca-alginate-hydrogel-based biomedical carriers.

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162. Life in extreme environments: The role of intrinsically disordered proteins under conditions of abiotic stress

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The ability of extremophile organisms to survive hostile conditions has caused us to reassess the requirements for life. Scientists and engineers strive to elucidate extremophile survival mechanisms that might allow the development of new technologies for preserving biological materials. LEA proteins are linked to the acquisition of cold and desiccation tolerance in plants and animals. As intrinsically disordered proteins (IDPs), LEA proteins are inherently tolerant to stress-induced denaturation, and LEA proteins have been shown to protect globular proteins, such as pig heart citrate synthase (CS) and rabbit muscle lactate dehydrogenase, and a human cell proteome from abiotic stresses [1].

The mechanism by which LEA proteins protect folded proteins is still unclear. Leading models of LEA protein protection include chaperone- and shield-like interactions. However, our aggregation assays, isothermal titration calorimetry experiments, and small angle neutron scattering experiments demonstrated that such bulk interaction mechanisms are insufficient to fully explain the observed aggregation protection of CS by LEA proteins.

Interfaces are known to nucleate and accelerate protein aggregation [2]. Our dynamic surface tension and neutron reflection experiments showed that LEA proteins are surface active, and these new results have led us to hypothesize that LEA proteins act by preferentially adsorbing onto surfaces generated during the freeze-thaw process, thereby excluding folded proteins from interfaces where they would otherwise undergo irreversible aggregation.

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190. Development of fluorinated colloidal gold nanoparticles as theranostic drug delivery systems

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In the last decades the use of nanoparticles (NPs) for biomedical applications has attracted a growing research interest, promoting NPs as a versatile tool with potential use in imaging, therapy, and drug delivery. [1] The possibility of combining diagnostic and therapeutic properties in unique nano-objects has led to the development of new theranostic systems, [2] which might improve the prognosis of many diseases. At the same time, fluorinated tracers represent a powerful diagnostic tool for in vivo imaging through 19F MRI detection, also showing the ability to provide quantitative information about the targeted disease area. [3] Thus, the use of fluorinated ligands for NP surface functionalization can bring to the development of innovative theranostic agents to be employed in nanomedicine.

In this contribution we report on a novel multifunctional nanomaterial based on gold NPs stabilized with highly fluorinated chains or with a mixture of hydrogenated and highly fluorinated ligands. These NPs were successfully transferred into an aqueous environment using two different coating

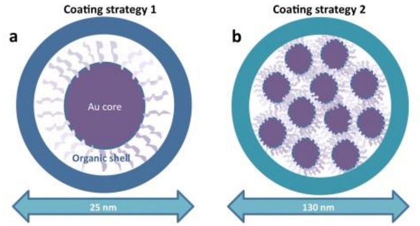

Figure 1: Schematic representation of the NPs structure by using the two coating procedures (a) coating procedure 1and (b) coating procedure 2

strategies, based on the use of different amphiphilic polymers, and the nano-dispersions were characterized by DLS, zeta-potential, 19F-NMR, FTIR, TEM and UV-VIS measurements. As shown in Figure 1, the two coating strategies produced different hybrid nanostructures. Indeed in one case we obtained NPs formed by a single Au core coated with a layer of polymer, while in the other the NPs were composed of Au clusters covered by a coating film. Overall, these systems can function simultaneously as 19F-MRI contrast agents and as drug delivery systems thus resulting in promising theranostic agents for biomedical applications.

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1. Multipod-like Polystyrene/Silica Clusters Designed by Seeded-growth Emulsion Polymerization: Towards Colloidal Molecules and Unconventional Inorganic Nanoparticles

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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 promoted at the silica surface, leading to multipod-like morphologies: bipods, tetrapods, hexapods, octopods, etc. While varying experimental conditions, the key parameters were evidenced.

The talk deals with recent insights in the high yield and repeatability of the synthesis process, the thorough characterization of some multipod-like clusters by cryo-electron tomography, the development of a model to help the understanding of the formation mechanism of almost pure suspensions of well-defined clusters, and the use of these clusters as precursors of dimpled silica particles and gold nanocages.

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I7. About the opportunity to include inorganic components in nanoscaled drug delivery systems.

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Recent progresses in nanotechnology offer exciting opportunities in the development of promising inorganic materials for medicine. Their possible insertion in drug delivery systems was recently investigated for protecting the drug molecules, making the systems biodistribution monitored by conventional medical imaging techniques or acting as heat converted for speeding the drug release.

The talk will be the opportunity to give general considerations on these aspects, discuss recent results and will be illustrated in particular by examples from our own research activity.

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I8. Synthesis and functionalisation of nanoparticles and some biological applications

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Molecular medicine is paving the way to new treatment paradigms for still untreatable diseases, by generating new diagnostic and therapeutic tools tailored to the needs of the individual patient. With engineered nanoparticles (NPs), a revolution is expected in the diagnosis and treatment of many diseases.

Concerning molecular imaging, the nanoscale materials owns their specific advantage to be used as probe for each imaging modalities and especially for magnetic resonance and optical imaging. Here we will described the synthesis optimization of two different kinds of inorganic NPs: superparamagnetic iron oxide NPs and persistent luminescent nanocrystals.

NPs surface must be tailored to insert molecules on the NP surface with control of their architecture and surface density to improve affinity and targeting efficiency or to impart additional properties. The design of multifunctional NPs is an exciting future challenge in the field. We will present several methodologies for the efficient NP surface functionalisation, allowing the attachment of passive or active targeting moieties (PEG and/or peptide and antibody). In-vitro assays and in vivo results will be presented.

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I9. Hydrophobic nanoparticles: a versatile platform to design colloidal silica-based nanostructures

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Hydrophobic nanoparticles (HBNPs) have been intensively studied because recent advances in synthesis through non aqueous approaches have allowed to easily prepare a wide range of nanoparticles and it has been shown that these routes are more efficient in producing stable colloidal nanoparticles with narrow size distribution, high crystallinity, tunable size and shape. However, their hydrophobicity often represents a limit for their applications in many field such as in biology and medicine. Thus, their conversion into hydrophilic systems is a crucial step toward their widespread use. Therefore, a suitable surface modification with organic or inorganic materials is needed. Hydrophobic nanoparticles made up of an inorganic core bound at the surface to the polar head of a long chain molecule (capping agent) represents an ideal building block to create composite systems with improved properties. This work shows how, starting from oleic acid-oleylamine capped nanoparticles, it is possible to design different silica-based colloidal nanoarchitectures. The homogeneous molecular coating and its affinity for the reactants chosen for their coating, more than the nanoparticle composition itself, are the key in order to orient the synthetic strategy versus the desired material. Following this general idea, monodisperse core-shell nanostructures with a core with different shapes and compositions and a low-porous silica shell have been achieved. This has been possible thanks to the high affinity of the capping agent for the inner core of the micelles inside which the coating process with TEOS takes place. Magnetic multicore nanosystems with high surface area and an ordered (hexagonal or cubic) porous silica structure can be also created due to the high tendency of oleic acid or oleylamine to be intercalated with cationic surfactants and triblock copolymers. This contribution provides a brief overview of the progress in the synthesis of silica-based colloidal nanoarchitectures

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K18. Engineering polymer micro and nanoparticles with controlled size, composition and morphology by microfluidics-assisted emulsification

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Most conventional processes for the production of polymer particles imply heterogeneous polymerization processes (emulsion, suspension) or precipitation processes in a non-solvent. Although these processes lead to polymer particles having a different size domain, the size is very sensible to the operating parameters and cannot readily be adjusted, not to mention the large particle size distribution which is often observed. Recently, microfluidic processes have been considered because of their unique capacity to generate micro and nanodroplets with a very narrow size distribution. Thus, if the dispersed phase is composed of a polymerizable liquid, it is possible to obtain polymer particles with well-defined characteristics like size, shape and morphology. Here we present our latest developments on microfluidic processes for the production of sized-, composition- and morphology-controlled polymer micro and nanoparticles.

Capillary-based flow-focusing and co-flow microsystems were developed to produce polymer microparticles of adjustable sizes (50 to 600 µm) with a narrow size distribution (CV<5%) while colloidal suspensions of highly monodisperse size-controlled polymer nanoparticles (60 nm and above) were obtained by means of elongational-flow or nanoprecipitation microsystems. Particles had different shapes (spheres, rods) and morphologies (core-shell, Janus, capsules). Influence of operating conditions (flow rate of the different fluids, microsystem characteristic dimensions and design) as well as material parameters (viscosity of the different fluids, surface tension) was investigated. Empirical relationships were thus derived from experimental data to predict particle overall size, shell thickness or rods length.

Besides the morphology, we will also present particles with various compositions and will emphasize their potential applications: drug loaded micro and nanoparticles for new drug delivery strategies, composed inorganic-organic multiscale and multidomain microparticles for sensorics and liquid crystalline elastomer microparticles showing an anisotropic reversible shape change upon temperature for thermal actuators or artificial muscles.

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153. Multi-Stimuli-Responsive Microcapsules for Adjustable Controlled-Release

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Smart microcapsules, which can control the release of the encapsulated contents according to various environmental stimuli, have attracted great interests from various fields in recent years. Because of their relatively faster response rate and other advantages such as small size, large inner volume, huge total surface area and stable capsule membrane, these environmental stimuli-responsive microcapsules are considered to be the most ideally intelligent drug delivery systems. In many cases, different environmental changes may occur at the same time, thus single stimulus-responsive microcapsules are insufficient for practical applications. More importantly, the patients' conditions are usually complex and diverse. To achieve best effects and reduce side effects of drugs, it is necessary to regulate the release dosage and the release rate in time according to patients' individual differences. Therefore, it is extremely favorable that microcapsules possess multiple stimuli-responsive properties and adjustable controlled-release rate, which are of great potential in drug delivery.

In this study, we report on a novel multi-stimuli-responsive microcapsules with adjustable controlled-release characteristics is prepared by a microfluidic technique. The proposed microcapsules are composed of crosslinked chitosan acting as pH-responsive capsule membrane, embedded magnetic nanoparticles to realize "site-specific targeting", and embedded temperature-responsive sub-microspheres serving as "micro-valves". By applying an external magnetic field, the prepared smart microcapsules can achieve targeting aggregation at specific sites. Due to acid-induced swelling of the capsule membranes, the microcapsules exhibit higher release rate at specific acidic sites compared to that at normal sites with physiological pH. More importantly, through controlling the hydrodynamic size of sub-microsphere "micro-valves" by regulating the environment temperature, the release rate of drug molecules from the microcapsules can be flexibly adjusted. This kind of multi-stimuli-responsive microcapsules with site-specific targeting and adjustable controlled-release characteristics provides a new mode for designing “intelligent” controlled-release systems and is expected to realize more rational drug administration.

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141. Janus Materials

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Janus materials with two different chemical regions compartmentalized onto the same objects are gaining growing interests. It is key to develop new methods to large-scale synthesize Janus materials with tunable morphology, strict chemical compartamentalization and precise control of microstructure.

Janus particles are fabricated by simultaneous biphasic grafting of different polymer brushes onto the two sides of a colloid at a liquid/liquid Pickering emulsion interface by atomic transfer radical polymerization. Similarly, Janus non-spherical colloids are prepared by asymmetric wet-etching the colloid frozen at the interface. We firstly developed large scale production of Janus composite colloids based on surface polymerization induced de-wetting onto a solid particle surface and polymerization induced phase separation against a polymer colloid during swell polymerization. Janus balance is tunable.

We further extend the Janus performance into hollow spheres by materialization of an emulsion interface. The materials may find potential applications in containers and controlled release. Janus composite hollow spheres with a porous shell are also synthesized by controlling the emulsion interfacial phase separation. After loading functional nanoparticles inside the cavity, the composite cages can selectively enrich desired reagents inside a confined environment for further manipulation.

Janus nanosheets are fabricated by crushing the as-prepared Janus hollow spheres, which can be used as solid surfactants to better emulsify immiscible fluids. Interestingly, stable "dry fluid" droplets can be achieved in air after the external continuous phase elutes. Functional Janus nanosheets can be derived by selective growth of materials for example paramagnetic ones by adsorbing Fe_3O_4 nanoparticles onto desired sides, which can be manipulated with a magnet. The dispersed droplets can be therefore manipulated, and the Janus nanosheets are easily collected for recycling. Janus polymer/inorganic composite nanosheets are synthesized by grafting polymer chains onto desire sides.

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168. Colloid – Liquid Crystal Gels

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Liquid crystalline materials occur in aqueous solutions of surfactant, DNA, peptide solutions, lipids and drugs in addition to the thermotropic materials used in liquid crystal displays. In many multicomponent biological systems and commercial formulations colloids are combined with liquid crystalline phases – therefore it is important to understand interactions between colloids and liquid crystals.

The nematic phase has orientational order and any defects caused by shear relax over time as the phase equilibrates. Immersing particles within a nematic phase creates defects since the uni-directional nematic must accommodate the surface morphology of the particle.

We examine the range of gel structures that form when hard-sphere colloids are dispersed in the nematic phase of 5CB. Through experiments and computer simulations we show that, when the surfaces of particles support homeotropic anchoring in a nematic solvent, colloidal structure is sensitive to concentration. Elastic mediation results in chain-like structures at very low volume fractions, $\phi < 2\%$. At intermediate volume fractions, $2\% < \phi < 22\%$, multi-particle clusters form and gather to form a percolating colloidal gel. For $\phi > 22\%$ the colloids are knitted together by percolating lines of defects that extend through the sample and lead to high elasticity [1]. All these structures are deeply metastable with percolating structures that persist for longer than 1 year.

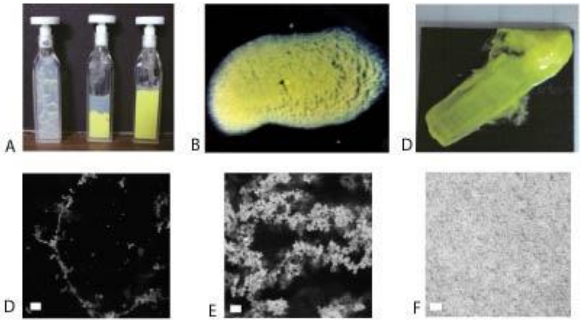

Figure 1: *Appearance of colloid dispersions in 5CB for different concentrations (A) in a vial after 10 months, from left to right ϕ = 1%, 3% and 5% (B) a drop of ϕ = 3% on a slide showing heterogeneous macroscopic texture (C) a spread drop of ϕ = 33% showing a smooth macroscopic texture. Confocal images of (D) the chain-like structures at ϕ = 0.5%, (E) percolating colloidal clusters at ϕ = 6% and (F) a densely knitted structure at ϕ = 33%.*

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70. Colloidal Suspensions of Pharmaceutical Solids in Non-aqueous Systems

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There are a number of reasons for attempting to understand and predict the behaviour of colloidal pharmaceutical solids in non-aqueous solvents.

Firstly, crystallisations in the pharmaceutical industry are often seeded with suspensions of active pharmaceutical ingredient (API) in order to provide control of solid state and particle size. This is often performed using daughter seeds for size control of the output crystallised material. An understanding of how seeds behave in a suspending solvent, in particular for sub-micron particles with high surface area, is therefore critical.

Additionally, by reducing the particle size of poorly soluble APIs to the colloidal range there is a potential to increase the drug dissolution rate and apparent solubility in vivo through increasing surface area.

In this work, an initial screening of factors expected to have an impact on the behaviour of colloidal suspensions of pharmaceutical solids in non-aqueous systems was performed using a d-optimal design of experiment (DoE). This study showed a number of the factors to be important individually such as API type and concentration as well as a number of 2 factor interactions in line with expected theoretical behaviour. In particular, the links between the concentration of surfactant and the 2 factor interactions of API:water and solvent:water have been investigated by use of rheology and settling rate analysis. The results of the work will be presented with particular attention being given to physical properties of the chemical components studied and their impact on colloidal behaviour.

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K19. Superspreading vs surfactant enhanced spreading: the role of adsorption on water/air interface

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Forcing water to spread quickly over hydrophobic surfaces is a challenging task for many industrial applications requiring covering large solid hydrophobic surfaces by water based compositions or their penetration into porous substrates. It was addressed in 1960s, when the extraordinary wetting properties of trisiloxane aqueous solutions were discovered [1]. The solutions spread very quickly covering a large area within a minute. That is why the phenomenon has been referred to as “superspreading” [2]. Systematic study of these compounds was started in 1990s to understand the mechanism of quick and extensive spreading and its relation to the surfactant properties [3]. It was shown later that other surfactants can also promote the spreading of water solutions considerably, but over the narrower range of substrate energies and therefore a more general term “surfactant enhanced spreading” was introduced [4].

Despite the intensive studies the mechanism of the surfactant enhanced spreading is not clear till now. Here we revisited the system first studied in [5] and containing aqueous solutions of sodium decanesulfonate and dodecyltrimethylammonium bromide. Each surfactant solution as well as their mixture spreads only slightly over the moderately hydrophobic substrates, whereas the putting a drop on one surfactant onto the top of another results in an enhanced spreading. Dynamic of spreading of this composition is studied as a function of concentration and compared with that of trisiloxane aqueous solution. The system behaviour is discussed as related to the surface tension of the mixture and bulk crystallisation processes.

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38. Achieving a ‘flatter’ film profile for applications in P-OLED displays: a numerical and experimental investigation of mixed solvent inks and their influence on film shape

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Polymer-Organic Light Emitting Diodes (P-OLEDs) are a technology where light is emitted as a function of the electrical operation. Such systems have the potential for use in the next generation of flexible electronics applications, such as bendable mobile telephones [1] and curved television displays [2, 3].

During the manufacturing process of P-OLED displays a solvent containing polymer ink, is dried. Depending on the processing conditions and ink properties, a variety of different film profiles can be achieved. Typically the profile has some form of undulation, which results in a non-uniform emission profile and less than optimal efficiency and display lifetime. The aim of this project is to model the dynamics of the drying process in order to determine the final deposit shape. It is hoped that the model will enable prediction of conditions that will lead to 'flatter’ profiles.

We present, to our knowledge, the first comprehensive numerical study of inks consisting of an ‘ideal’ binary solvent system. The ratio of solvent evaporation rates and surface tensions can alter the final shape, whilst the viscosity ratio proves to be less important. In addition, it is possible to determine the critical compositions that should lead to flatter profiles:

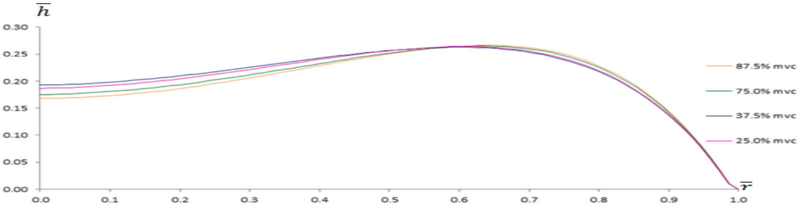

Figure: Final shape dependence on % more volatile component, for $\frac{E_1}{E_2} = 5, \frac{\gamma_1}{\gamma_2} = 1, \frac{\mu_1}{\mu_2} = 1$ and $\frac{\varphi_0}{\varphi_{max}} = 0.4$

Experimentally we use white light interferometry, to study an axisymmetric, ‘pinned’ droplet in which a ‘coffee-ring’ shape will develop due to an outward Capillary flow, as discovered by Deegan and co-workers [4]. The code that we have developed can also predict the final film profile for different initial and maximal volume fractions of polymer and for varying extents of evaporation suppression in the gelled region, towards the periphery of the droplet.

This work has relevance for a plethora of other applications in which droplets containing a dispersed material are evaporated, such as blood disease diagnostics [5], fabrication of micro/nanowires [6] and distribution of pesticides on leaves.

[1]. http://www.bbc.co.uk/news/technology-24238653

[2]. http://www.bbc.co.uk/news/technology-25633199

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[4]. Deegan et al., 1997, Nature, 389, pp. 827-829.

[5]. Brutin et al., 2011, J. Fluid. Mech., 667 pp. 85-95

[6]. Naqshbandi et al., 2012, Nature Communications 3:1188

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100. The evaporation of a capillary bridge between a particle and a substrate

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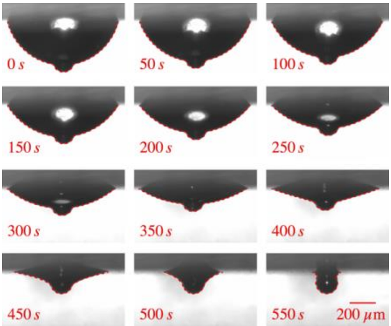
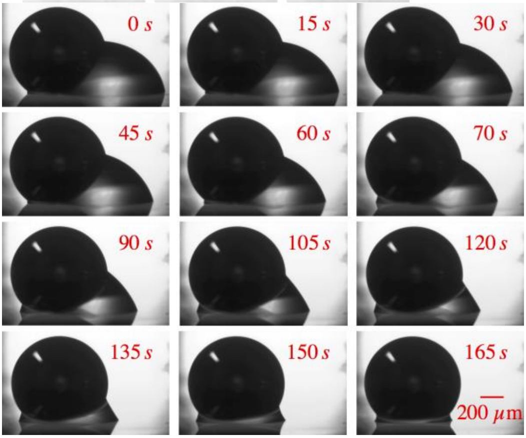
Capillary bridges are formed when a small volume of liquid sits between two solid surfaces. These bridges have wide ranging applications from particle-surface adhesion to evaporation and condensation in porous media. By considering a capillary bridge between a spherical particle and a flat substrate, we investigate how the physical properties of a given system affect the resulting configuration.

Through a careful analysis of the Gibbs free energy, the shape of the resulting configuration can be found, revealing a critical liquid volume for which the configuration switches from a spherical interface to an axisymmetric collar configuration. We also show that despite the gravitational forces being much smaller than interfacial forces (Bond number = 0.07), gravity plays a crucial role in determining the resulting configuration of these systems. Having established a theoretical model, a variety of key physical systems are presented. Fitting the theoretical model to experimental images allows the extraction of important physical quantities (Laplace pressure, capillary force, drop volume etc.), providing important physical insights into the underlying dynamics of such systems. Comparing the theory presented to surface-immobilised Janus drops of water and mercury, and we observe good qualitative agreement.





On the left, time-lapse images of an evaporating water capillary bridge between a silica particle and a silica substrate. The air-water interface is initially spherical, until the particle touches the substrate (~350s) at which point the configuration switches to an axisymmetric collar around the base of the particle. During the evaporation process, successive drops are compared to the Young-Laplace solution. On the right, time-lapse images of a compound mercury-water drop on a hydrophobic glass substrate with the water evaporating. During evaporation, the initially asymmetric interface forms an axisymmetric collar.

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96. On the Fate of Silver Nanoparticles in Simulated Primary Wastewater Treatment

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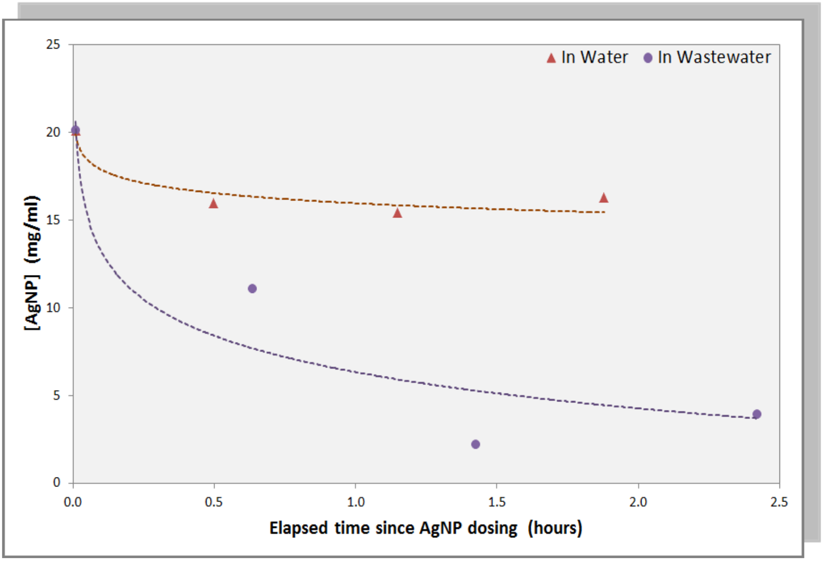
Our ability to synthesise, functionalise and manipulate matter at the nanoscale is revolutionising many product sectors, from energy to healthcare. Of particular note are the myriad of applications for different types of nanoparticles, global production of which already numbers many Mtonnes/year. Where there has been much less research, however, is into the environmental fate and behaviour of these nanoparticles. Of particular concern is the ecotoxicological impact of silver nanoparticles (AgNP) because of the known antimicrobial action of elemental silver, indeed often the very *raison d'être* for its use.

For a large proportion of nanoparticles their major route of release into the natural environment is through domestic and industrial wastewater discharges. This in turn makes wastewater treatment plants the 'gateways' to the wider aquatic and terrestrial environment. Understanding the colloidal behaviour of nanoparticles during wastewater treatment is thus of key importance for predicting their environmental fate.



This presentation will describe a series of SANS experiments exploring the time-dependent colloidal stability of a commercially-produced, sterically-stabilised, AgNP in *real* wastewater using a settlement microcosm. The results point to a significant and unexpected interaction between the non-ionic stabiliser and components of the wastewater, an effect duplicated using a model system with a completely different non-ionic stabiliser. These findings demonstrate the key role that surface coatings on functionalised nanoparticles play in directing the fate of nanoparticles in wastewater treatment.

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61. NMR Relaxivity Studies on Surfactant-free Superparamagnetic Iron Oxide Nanoparticles: the Effect of Particle Size, Magnetization and an Iron Oxidation State

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Searching for a novel material to be used as positive-image MRI contrast agent, alternative to gadolinium chelates, was a primary motivation of this work. Magnetite nanoparticles in the size range of 3.2-7.5 nm were synthesized with high yields under variable reaction conditions using high temperature hydrolysis of the precursor iron(II) and iron(III) alkoxides in surfactant-free diethylene glycol solutions. The average sizes of the particles were adjusted by changing the reaction temperature and time, and by using sequential growth technique. In order to obtain γ-iron(III) oxide particles in the same range of sizes, diethylene glycol colloids of magnetite were oxygenated at room temperature. As-obtained colloids were characterized by DLS and NMR; powdery products obtained by coagulating the same colloids with oleic acid, were characterized by TEM, XRD, TGA, FTIR and magnetic measurements. NMR r_1 and r_2 relaxivity measurements in diethylene glycol (for OH and CH_2-protons) and in water, have shown the decrease in r_2/r_1 ratio with the particle size reduction, which correlate with the results of magnetic measurements on magnetite nanoparticles. Saturation magnetization of the oxidized particles was found to be 20% lower than that for Fe_3O_4 with the same particle size, but their r_1 relaxivities are similar. Since oxidation of magnetite is spontaneous under ambient conditions, it was important to learn that the oxidation product has no disadvantages as compared to its precursor, and therefore it may be a better imaging agent due to its chemical stability.

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K20. Colloid uses and use of a colloid in enhanced oil recovery

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This paper gives an idiosyncratic review of the history of applications for colloids from 1910 to present and results of a patent search are used to identify current applications. It can be observed that while the patents for Colloid and Nanoparticle constituted only about 0.0256 percent of the total for the world over the first 13 years of this century, they have been consistently on the increase. It is concluded that the basic areas of use of colloids are developing, but more slowly than the underlying science, which has allowed access to smart materials and other impressive innovations. By way of example the principles behind the development of “smart”, thermal responsive particles for improved recovery of crude oil are presented. This includes design of a “popcorn” polymer particle incorporating thermal cleavable crosslinks, based on the desired properties before and after shape change. This leads up to a discussion of the action of the particles in blocking rock pore throats and an indication of the current level of commercial use.

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58. Model sheet structures for cement

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The hardening of cement is of crucial importance for many civil engineering projects. Despite cement's importance as one of mankind's most produced materials, fundamental questions remain unresolved.

One of these questions concerns the 3D morphology of the abundant hydration product, the calcium silicate hydrates (C-S-H), on length scales of 1 nm to 500 nm. They have been the topic of an intense debate. The two dominant viewpoints describe C-S-H either as a colloidal structure of layered particles [1] or a quasi-continuous layer structure [2, 3].

In this work, an algorithm to generate amorphous quasi-continuous layer structures is presented. The structure evolves from a number of seeds placed on the surface of the virtual cement particle, from which an extended sheet structure grows. New sheets can form aligned with previously deposited sheets. Resultant structures are shown in Figure 1 for different primary kinetic parameters.

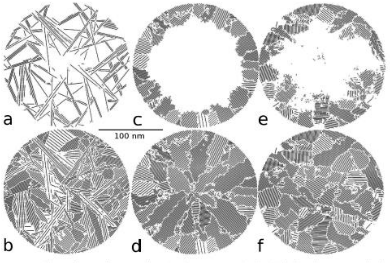

Figure 2: Cross sections through the sheet structures grown at different kinetic parameters. The first row shows intermediate, the second row fully evolved structures.

The resulting structures are characterised and compared against experimental data. It is demonstrated that sheet structures can be grown with a pore space corresponding to NMR T2-relaxometry. The small-angle scattering curves for these structures were simulated. Again, general agreement is observed with experimental data.

These results demonstrate that the proposed sheet structures are an alternative to colloidal structures for the nano structure of cement.

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[3] E. M. Gartner. Cem. Conc. Res, 27:665–672, 1997.

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204. Microparticle disassembly from fluid interfaces: remotely triggered particle delivery

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Self-assembly of colloids at fluid-fluid interfaces is exploited for the fabrication of selectively permeable capsules, tunable nanomaterials, and nanocomposites with complex morphologies. Disassembly of colloids from interfaces is equally important, for instance for green catalytic processes, advanced manufacturing, and drug delivery. Successful strategies to promote particle desorption include interfacial displacement by surfactants, changing interactions by tuning pH, and mechanically forcing the particles out of the interface by area compression. We developed a new technique for mechanically forced desorption where the fluid-fluid interface is manipulated remotely by ultrasound to trigger disassembly of an interfacial colloid monolayer. Different mechanisms of particle expulsion are observed depending on surface coverage: single particle expulsion, localized streams of particles, and delivery of blobs of particles of controlled size. This technique is up-scalable and can be used to precisely control the timing and dynamics of particle desorption and delivery.

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144. The effect of stabilizer choice on microcapsule morphology

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Polymer shell- liquid core microcapsules are of considerable interest in many industrial applications where it is desirable to protect the core from its surroundings. There are many available methods of fabricating core-shell microcapsules, and in this work we use solvent evaporation, well known and often used in the literature, to precipitate a polymer shell (poly-methylmethacrylate, PMMA) around a hexadecane, HD core.[1] This is achieved by dissolving PMMA in a good solvent, dichloromethane, DCM, and adding a poor solvent HD, and emulsifying with an aqueous phase containing either a surfactant or polymeric stabilizer. The DCM is allowed to evaporate, resulting in insolubility of the polymer which thus precipitates to form a shell around the HD. The choice of stabilizer is key in defining the final morphology of the capsules. Possible morphologies include core-shell, where the polymer forms a complete shell around a single core, acorn, where the polymer precipitates separately to the oil, and occluded, where the polymer precipitates around multiple cores. The final morphology of the capsules is determined by the spreading coefficients and interfacial tensions of the three immiscible phases – the polymer, the HD, and the aqueous phase. Previous work [2] found only polymeric stabilizers were suitable to form core-shell morphologies. However, by studying the effect of other classes of stabilizers on interfacial tension of the oil and water, in this work we have been able to systematically investigate the effect of increasing chain length of a surfactant family to obtain the desired core- shell morphology. Results show that a reduction in the chain length in a particular stabilizer family reduces the amount by which the oil-water interfacial tension is reduced, thus giving a higher percentage of core-shell microcapsules. In addition, we have found that by increasing the number of hydrophobic long hydrocarbon chains we are also able to reduce the oil-water interfacial tension to a lesser extent, once again resulting in core-shell microcapsules. Results also show that by altering the pH of a polymeric stabilizer, stable core-shell capsules can also be fabricated.

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158. Large-area patterning of the tackiness of a colloidal nanocomposite adhesive by sintering of nanoparticles under IR radiation

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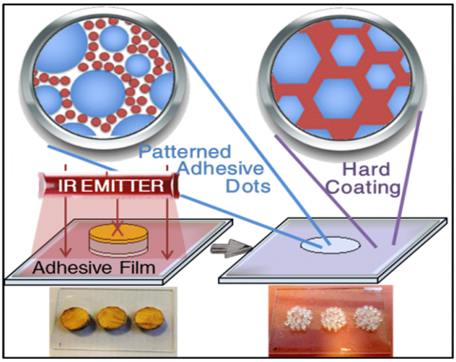
We present a simple technique to switch off the tack adhesion in selected areas of a colloidal nanocomposite adhesive. It is made from a blend of soft colloidal polymer particles and hard thermoplastic copolymer nanoparticles. The nanoparticles self-assemble around the larger colloidal particles when they are swept up by the receding air/water interface under fast evaporation. The addition of nanoparticles can be used to tune the viscoelastic and mechanical properties of the nanocomposite adhesive. In regions that are exposed to IR radiation through a mask, the nanoparticles are heated and sinter together to form a percolating skeleton, which raises the yield point and stiffens the adhesive. The tack adhesion is therefore lost locally where it has been heated. Masks can be made from silicone-coated disks, such as coins, or reflective plates containing an array of holes. Shadowed regions retain their tack adhesion, whereas the irradiated regions are non-tacky. The process enables the switching of the adhesive surface at specified positions to create a desired pattern (Gurney et al., *ACS Appl. Mater. Interf.*, (**2013**) 5, 2137).



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K21. Core@shell heterostructured nanoparticles for next-generation SERS applications

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Metal nanoparticles (NPs) have long been utilized for various types of chemical and/or biological sensing applications exploiting their localized surface plasmon resonance (LSPR) and/or surface enhanced Raman scattering (SERS) properties. At the same time, much of the knowledge being gained for manipulating NP structure or composition has focused on multimetallic type NPs. Such systems can display multiple properties arising from the individual components, but it is the observation of synergistic phenomena that is the most intriguing. Recently, we have synthesized various binary core@shell type NPs such as Au@Ag, Pt@Ag, Au@Fe and Au@Cu NPs. In all cases, it has been demonstrated that electron transfer from core to shell materials takes place and it modifies electronic/chemical states of shell materials. This synergistic effect enhances strengths and eliminates weaknesses of the shell element which is not achievable by alloying strategy. For example, Ag has superior SERS properties than Au, however Ag is easy to be oxidized. If one makes Au-Ag alloy NPs, both LSPR/SERS properties and oxidation resistivity would be in between those of Au and Ag NPs. In the case of Au@Ag NPs, however, we can combine LSPR/SERS properties of Ag and chemical stability of Au into single NPs. The electron transfer phenomenon has been confirmed for various core@shell NP systems by XPS and many other analytical techniques. We attempt to provide a unified explanation for those observations.

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133. Ultra-Small Functional g-Maghemite Nanoparticles: Surface Engineering for Effective siRNA/microRNA-Mediated Delivery/Gene Silencing Applications

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Iron oxide nanoparticles (NPs) have been quite widely used in numerous biotechnology applications (magnetism-driven cell separation, magnetic field-guided drug/gene delivery, non-invasive tissue MRI, anti-cancer hyperthermia). Serious drawbacks dealing with NP fabrication, *i.e.,* both *detrimental NP aggregation* and *controlled NP surface functionalization versatility* are extremely challenging issues calling for innovative solutions.

Our recent work in the field led to the discovery of a novel method/concept for the (i) aggregation control of ultra-small hydrophilic super-paramagnetic maghemite (γ-Fe_2O_3) NPs and for (ii) its successful use for NP functionalization toward siRNA/microRNA-mediated gene delivery/silencing applications. ***This nanofabrication method does not make use of any surface-passivating organic species***. Indeed, the controlled high-power ultrasound-assisted metal Ce(III/IV) cation doping of the surface of 45/50 nm-sized (DLS) maghemite NPs strongly modified the NP surface charge to highly positive values (+41.0 - +50.0 mV range) of ζ-potential. Such a $Ce^{3/4+}$ cation-doping process enabled (i) an effective charge control of NP aggregation, (ii) the full NP water compatibility for biological applications and finally (iii) the development of quite versatile surface engineering chemistries using the known rich $Ce^{3/4+}$ complex coordination chemistry for any biomolecule or organic species (polymer) binding.

This new NP ”*inorganic*” stabilization and surface functionalization approach afforded optimized (i) ultra-small core $Ce^{3/4+}$-doped γ-Fe_2O_3 NPs and (ii) various functional polycationic branched 25kDa *b*-PEI polymer-based decorated NPs for siRNA/microRNA *in vitro/in vivo* delivery applications. In addition, effective chemical strategies for NP toxicity mitigation have been successfully developed for successful ***in-vivo*** end-user applications dealing with safe siRNA/microRNA delivery.

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160. Stimuli responsive hybrid nanomaterials from synthesis to applications in nanomedecine

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Organic-inorganic nanoparticles (NPs) are an appealing class of colloids to be used in nanopharmaceutics. Recently their great potential not only for imaging and diagnosis but also for clinical therapeutics has started to flourish. Adequately choosing the constituents leads to systems that can response to external stimuli (magnetic or electric field, light, temperature…) that can be taken into account in biological applications.[1] Different nanohybrids based on the use of thermo- or pH responsive polymers were thus designed for such a purpose.[2,3]

As depicted in Figure 1, by designing new core-shell polymeric structures, we were able to get nanocarriers presenting a high binding affinity for copper ions and able to release these ions at low pH.[4] We demonstrate that the exact architecture of the core-shell system is a paramount parameter to control the maximum loading, the strength of complexation and the release profile of copper into the solution. Their low toxicity may open a new way to balance the Cu-homeostasis in neurodegenerative diseases, e.g., Alzheimer's disease.

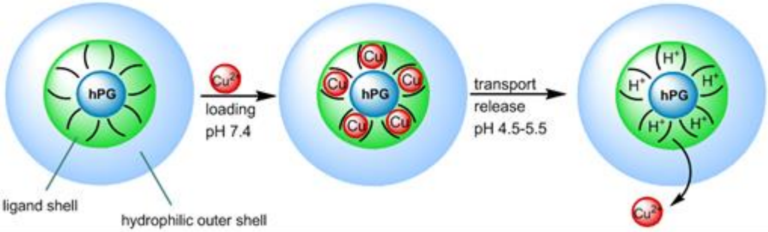

Fig. 1: Schematic illustration of the encapsulation and release of Cu-ions by core-shell nanostructures

Other examples take advantages of thermo responsive polymers. Thus nanohybrids with application as MRI, i.e. magnetic resonance imaging, contrast agent have been synthesized in presence of those polymers. The critical effect of polymer architecture and concentration on the morphology and relaxivity properties of the as-synthesized nanoparticles will be discussed.

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19. Patchy + Smart = Efficient? – Design of Advanced Micellar Carriers with Tunable Charge and Composition

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Block copolymers represent a unique class of materials for the generation of nanostructured materials in different environments – mainly driven by the inherent immiscibility of unlike building blocks.[1] Although being in the focus of research for decades, applications exploiting this potential to date are scarce. We present the use of (ampholytic) ABC triblock terpolymers for the design of efficient non-viral gene vectors or the preparation of core-shell-corona micelles with adjustable composition and charge. The first example, polybutadiene-block-poly(methacrylic acid)-block-poly(2-dimethylaminoethyl methacrylate) (PB-b-PMAA-b-PDMAEMA), forms soft and patchy multicompartment micelles which are able to react with changes of surface charge and morphology on subtle differences in the pH of the surrounding environment (Figure 1). We demonstrate that these structures can be used as superior non-viral gene transfection agents, outperforming even the “gold standard” poly(ethylene imine) (PEI).[2] Even one step further, we use mixtures of different polyether-based ABC triblock terpolymers to design sub 50 nm micelles with exact control over charge, charge density, and the content of possible targeting units.[3]

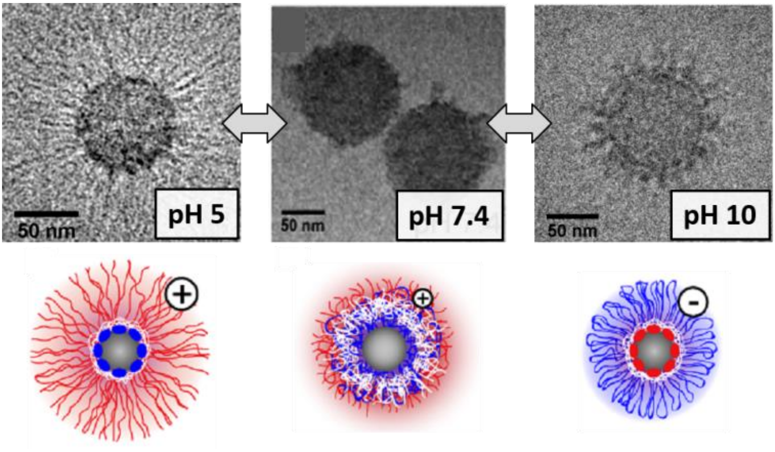

Figure 1: patchy PB-b-PMAA-b-PDMAEMA micelles at different pH.

References: [1] F. H. Schacher, P. A. Rupar, I. Manners, *Angew. Chem. Int. Ed.* **2012**, ***51***, 7898-7921; [2] A. C. Rinkenauer, A. Schallon, U. Günther, M. Wagner, E. Betthausen, U. S. Schubert, F. H. Schacher, *ACS Nano* **2013**, ***7***, 9621-9631; [3] M. J. Barthel, A. C. Rinkenauer, A. Träger, M. Wagner, S. Höppener, U. Mansfeld, M. Gottschaldt, F. H. Schacher, U. S. Schubert, *submitted*;

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80. Probing the True Near-Field Interaction between Metallic Nanoparticle and Fluorophore in Bulk Colloidal Solution Using Toehold-Mediated Internal Control

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Metallic nanoparticles (MNP) are known to alter the emission of vicinal fluorophores through the near-field interaction. Both quenching and enhancement have been observed in various systems, depending on whether the excitation and emission enhancement or the increased non-radiative decay rate dominates. While observations for substrate-bound or single-particle systems are largely consistent and in line with theoretical predictions, it is well-recognized that observations in bulk colloidal solution are difficult to reproduce. We hypothesize that interference from the inner filter effect due to the large absorption cross-section of MNP could play a significant role in masking the true near-field MNP-fluorophore interaction. We demonstrate that this far-field interference could be accounted for experimentally using the concept of DNA toehold to trigger the in situ dynamic assembly and disassembly of MNP-fluorophore conjugate within the same reaction volume. This ensured that both the sample and reference control remained in the same photophysical environment. Our toehold-mediated internal control system was used to evaluate the effect of nanoparticle size and MNP-fluorophore separation distance on the enhancement/quenching process. The trends observed were in line with theoretical predictions thereby validating the applicability of our proposed system. It is hoped that our DNA toehold design can serve as a central system to probe the near-field interaction of other MNP-fluorophore combinations more accurately so as to unify the diverse observations reported in literature to date.

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Plenary 3. Interactions between drops and bubbles in complex fluids

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In complex fluids, soft or deformable components, such as drops, bubbles, or capsules, respond to their surrounds in a far more complicated manner than rigid particle dispersions. This creates challenges in the processing and the characterization of these systems for a diverse set of applications. These applications range from the purification of minerals or pharmaceuticals using solvent extraction processes, to the formulation of emulsions and foams in food and personal care products. Through a combination of novel experimental methods, mainly using Atomic Force Microscopy (AFM) to visualize the collisions between micro-drops or micro-bubbles on the nanoscale, coupled with theoretical models, we have been able to quantitatively link the dynamic coupling of shape changes with external forces that control their behavior for a range of systems involving drops and bubbles.

This talk will focus on how oil-water and air-water deformable interfaces are mediated by the concentration, type and composition of stablisers in a complex fluid. First, we will discuss the direct measurement of colloidal forces between surfactant stabilized oil drops and air bubbles as a function of the type of stabilizer. Then we will examine the behavior of a mixed surfactant system of ionic and non-ionic surfactants. Through careful control of the ratio ionic to non-ionic surfactant, we are able to obverse significantly different charging behavior compared to the pure ionic system. This will be followed by measurements using highly concentrated surfactant systems or other nano-colloids (e.g. nanoparticles, micro-emulsions). We observe significant differences between the structural forces between these deformable interfaces compared to the periodic oscillatory structural forces commonly observed between rigid interfaces. In addition, quantitative comparison between these system types indicates that the deformable nature of droplets allows them to act as far more sensitive probes than solid spheres. Furthermore, the responsive nature of soft surfaces can give rise to unexpected behavior not encountered in rigid systems including reversible aggregation/flocculation for emulsion droplets and, potentially, spatial ordering within concentrated emulsion phases. More recent studies on the impact of hydrodynamic drainage effects on the resulting force behavior as well as changes associated with the aspect ratio of the nano-colloid will also be discussed. This work will showcase the utility of these methods to help bring new understanding to both fundamental and complex systems affecting microscopic drop and bubble behavior.

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K22. Interaction of particles with fluid-fluid interfaces quantified using magnetic tweezers

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A key challenge in point-of-care diagnostics is the miniaturization and integration of assay processes in lab-on-chip devices. Assay processes based on magnetic particles are particularly suited for miniaturization and integration, because the particles can be actively controlled using external magnetic fields [1,2]. The sensitivity and specificity of the assays crucially depend on the interaction of the particles with surfaces, interfaces and biological materials. Therefore we are investigating particle-based methodologies to characterize interactions of protein-coated particles with surfaces [3], protein-ligand systems [4] and cells [5]. Here, we extend the magnetic particle based toolbox to the characterization of interaction between particles and fluid-fluid interfaces, providing a novel tool for colloidal science studies [6].

In our experiments we use a magnetic tweezers setup with five electromagnets. Magnetic particles are first suspended in an aqueous phase and then trapped at a fluid-fluid interface. In a rotation experiment, a well controlled mechanical torque is applied to the trapped particles, using in-plane and out-of-plane rotating magnetic fields. The resulting particle rotation is tracked using optical imaging with fluorescent tags. In-plane rotation gives information about the in-plane mobility of the particles in the interface, thereby probing the local micro-rheology. Out-of-plane rotation induces an asymmetric deformation of the interface (capillary dipole) due to contact line pinning. By reconstructing the angular displacement and comparison with numerical simulations we are able to quantify the interface deformation. As a next step we will record data of contact line pinning and contact line friction forces on the microparticle surfaces. This novel technique represents a versatile tool to quantify and unravel the interactions of particles with fluid-fluid interfaces, with relevance for colloid science, active rheology, mesoscopic flow phenomena, and particle-based biosensing.

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6. Understanding Pickering Emulsions Using Mesoscale Simulations

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Although Pickering emulsions are becoming extremely popular in the academic community, few applications benefit from such interesting systems. We argue that better understanding their fundamental properties, especially related to their stability, will enable a host of practical applications. The stability of Pickering emulsions is related to structural and dynamical properties of interfacial nanoparticles. Our group has investigated such properties by means of multi-scale simulations (from atomistic to coarse-grained, to phenomenological). We considered several nanoparticle types, including spherical and elliptical, Janus or homogeneous with different amounts of hydrophilic/hydrophobic surface groups. We focused on (a) the effect of particle properties on self-assembled aggregates structure, (b) systems of different composition, (c) particles properties as a function of droplet size, and (d) particles with grafted polymers. For a given system composition, we investigated the effect of increasing nanoparticle density. We will present a survey of our recent results, quantified in terms of interfacial tension reduction, radial distribution function, order parameters, contact angle, self-diffusion coefficient, etc. The goal is to identify properties that could be tested experimentally.

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K23. The Versatile Properties of Hollow Silica Spheres

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Hollow silica nanoparticles are structurally simple colloidal building blocks. However, such silica capsules possess a vast range of interesting properties. Here, I will present a comprehensive overview on the optical, mechanical, and thermal properties of monodisperse hollow silica nanoparticles, which feature particle sizes of less 1 µm and shell thicknesses of only a few ten nm.

Individual hollow silica spheres feature an unique coloration effect, which originates from an incoherent scattering mechanism, namely Mie scattering. The low refractive index of hollow capsules suppresses multiple scattering, which is typically observed in solid colloidal particle powders. The large mean free path of light through such a hollow powder material therefore allows the observation of colorful Mie scattering with the naked eye.[1]

Arranging hollow spheres in a two-dimensional superstructure allowed us to determine the collective mechanical properties using nanoindentation. We investigated the elastic response as well as the plastic deformation. Such films feature mechanical properties comparable to solid polymer films. Their granular morphology reflects into an peculiar compression behaviour. Furthermore, such hollow particle films exhibit a large capacity to dissipate energy upon compression.[2,3]

Three-dimensional superstructures of hollow spheres can be regarded as an analogue to silica aerogels, however, with a much better defined internal structure and symmetry. The massive nanostructuring of the silica network and the interconnectivity at few, defined contact points between the spheres opposes the transport of thermal energy through such a material. The thermal conductivity through such films is therefore almost as low as in the case of silica aerogels. Without the need for supercritical drying, we can employ well established colloidal processing routes to fabricate highly insulating porous silica films. We present in great detail the influence of various structural parameters on the thermal conductivity.

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35. Can Polymersomes form Colloidosomes?

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Hydroxy-functional polymersomes (or block copolymer vesicles) were prepared via a facile one-pot RAFT aqueous dispersion polymerisation protocol and evaluated as Pickering emulsifiers for stabilisation of *n*-dodecane-in-water emulsions. Linear polymersomes produced polydisperse oil droplets of approximately 50 µm diameter, regardless of the polymersome concentration in the aqueous phase. Introducing an oil-soluble polymeric diisocyanate cross-linker into the oil phase prior to homogenisation led to block copolymer microcapsules as expected. However, TEM inspection of these microcapsules after an alcohol challenge revealed no evidence for polymersomes, which suggests that these delicate nano-structures do not survive the high shear emulsification process. Thus the emulsion droplets are stabilised by individual diblock copolymer chains, rather than polymersomes. Cross-linked polymersomes (prepared by the addition of ethylene glycol dimethacrylate as a third comonomer) also formed stable *n*-dodecane-in-water Pickering emulsions, as judged by optical and fluorescence microscopy. However, in this case the droplet diameter varied from 50 to 250 µm according to the aqueous polymersome concentration. Moreover, diisocyanate cross-linking at the oil/water interface led to the formation of well-defined colloidosomes, as judged by TEM studies. Thus polymersomes can indeed stabilize colloidosomes, provided that they are sufficiently cross-linked to survive emulsification.

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K34. Translational R&D in Healthcare Biomagnetics

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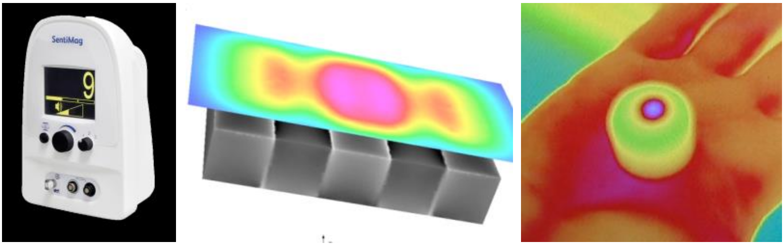
‘Healthcare Biomagnetics’ – the sensing, moving and heating of magnetic nanoparticles *in vitro* or in the human body – is a rapidly changing field that is attracting much interest worldwide.1 It offers the potential to develop safe and convenient alternatives for a diverse range of therapeutic and diagnostic healthcare applications, using injectable materials of proven safety and reliability. In doing so, it makes use of the three fundamental ‘action-at-a-distance’ properties of magnetic materials – their ability to act as remote sensors,2 mechanical actuators,3 and sources of heat fro both hyperthermia and thermoablation.4 The versatility of the field is leading to the emergence of multi-modal applications, combining two or more of the sensing-moving-heating properties in the same product. Similarly, certain applications are now entering or are close to beginning Phase I/II clinical trials, or in the case of *in vitro* products, are already entering the marketplace. Examples of work in the fields of targeted delivery of drugs and other therapeutic agents, and others, will be presented and discussed.



Representative images related to (from left to right): magnetic sensing, actuation and hyperthermia

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I9. Next Generation of Magnetic Nanoparticles

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High magnetic moment nanoparticles will have many potential applications in sensing, separation, diagnosis and treatment of diseases such as cancer, which is still a leading cause of disease worldwide. Magnetic nanoparticles offers an exciting new alternative treatment, with local heating of affected areas allows to eliminate the side effect of current radio-or chemotherapy. The most cutting edge research has recently focused on the combination of heat treatment with traditional cancer drugs. That synergistic effect with enhance the treatment efficacy of both hyperthermia and drugs. For many applications, the currently available MNPs namely iron oxide are sub-optimal in terms of their physical and biochemical properties. They have lower saturation magnetisation and often are not well biofunctionalised for specific biological target. In this presentation, novel class of MNPs with different size, shape (cube, octopods, rods, multipods, star), chemical composition (e.g., metallic Co, alloy FePt, trimetallic FePtPd, etc..;), coating and surface chemistry have been fabricated using wet chemical methods. Multifunctional/hybrid MNPs with noble metal Au and semiconductor quantum dots CdSe were also synthesised. Magnetic nanoparticles could also be used to track neural stem cells after a transplant in order to monitor how the cells heal spinal injuries or tracking of engrafted pancreatic islets for transplantation.

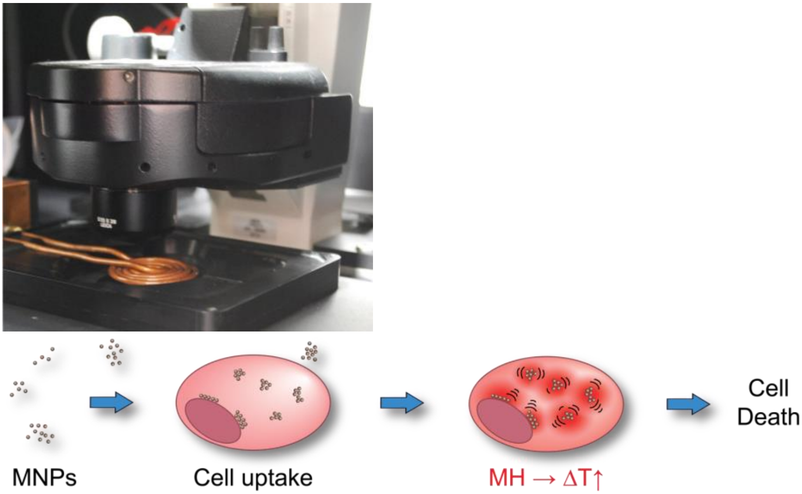

Fig 1. Magnetic AC field treatment applied via an in-house patented system

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K25. Chemotaxis of catalytic silica-manganese oxide "matchstick" particles

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Particles that can undergo directed self-propulsion are desirable for colloidal cargo delivery and self-assembly. Herein we describe the synthesis of silica–manganese oxide “matchstick” colloids that undergo catalytic self-propulsion by consumption of hydrogen peroxide. Chemotaxis is observed when particles are placed in a fuel gradient. Movement opposes convective flow which is tracked by following inert polymer microspheres simultaneously.

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118. Self-Diffusiophoresis of Chemically Active Colloids

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The challenge of enabling micrometer-scale objects to perform autonomous motion (so-called self-propulsion) in a liquid environment has received significant interest in the last decade. One route to achieve this is by covering part of the surface of a colloid with a catalyst for a chemical reaction in the surrounding solution (i.e., making a chemically active "Janus" colloid) [1,2]. In this way gradients in concentrations of reactants and products can be created along the particle’s surface and self-phoretic-propulsion emerges [2-4].

I discuss here two model systems of self-diffusiophoresis [3]. The first one is a Janus sphere (carrier) connected by a thin rigid rod to a spherical, catalytically inert particle (cargo). Generalizing previous results [4], I analyze this system in the most general setting of different radii (R_1, R_2), reactants-surface interactions (Ψ_1, Ψ_2), and as a function of the catalyst coverage.

The second one is that of a Janus sphere near a hard wall acting as a perfect sink for the reaction products, for which recent results [5] evidenced several non-trivial steady-states, including a “hovering” state. Taking advantage of the particular geometry of the hovering state (the axis of the Janus colloid is normal to the wall), the dependence of the position at hovering (height above the wall) on the percentage of catalyst coverage of the Janus particle and on the hydrodynamic boundary condition (stick or slip) at the wall is determined analytically.

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188. Formulation of electrostrictive materials for energy harvesting devices

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Embedded electronics have been used for weather database information, accelerometers and fatigue measurements. Nowadays, the main drawback of microsensors and actuators used in embedded electronics is their long term autonomy. In order to overcome to this problem, a promising approach is to harvest and convert mechanical energy from ambient vibrations to fulfill energy demands of micro-electromechanicals systems (MEMS). Variable capacitor composed of electrostrictive materials (i.e. for which dielectrics properties are modified under strain) are easily integrated to MEMS. A recent approach is based on the use of polymers loaded with conductive nanoparticles. Near percolated networks of conductive particles are expected to yield materials with giant dielectric constant and electrostriction coefficients [1]. Nevertheless, the validation of such expectations and the development of electrostrictive nanocomposites remain challenging. It is necessary to finely control the morphology of the particle networks formed by the particles within an elastic polymer.

The aim of the present work is the development of near percolated carbon nanotubes (CNT) networks within an elastic polymer matrix, such as polydimethylsiloxane (PDMS). A novel emulsion formulation route is employed to achieve a fine control over the structure of the materials. The nanotubes are dispersed in the continuous phase of an emulsion made of PDMS droplets in water. The CNT are segregated in between the PDMS droplets and can form near percolated networks of morphology controlled by the size of the emulsion droplets. The dielectrics properties of the composites materials will be driven by several factors such as (i) the droplets size, (ii) CNT loads and (iii) their aggregation state. The influence of these factors is investigated. A particular attention will be paid to the variations of the dielectric properties in response to a mechanical stress in order to assess the potential of these new materials for electrostriction and energy harvesting applications

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187. Controlling Shell Thickness of Large Core-Shell Drops in Non-Confined Microfluidics

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For numerous encapsulation applications such as nutrients, drugs, and long-term cell encapsulation, large core-shell droplets or particles are required.[1-3] Such structures exhibit greater stability with thin shells[4], while their permeability can be controlled via suitable material selections to tune release profiles.[5] Variation in shell thickness of core-shell droplets formed in a confined, flow-focused microfluidic approach is already known.[6] We introduce a non-confined microfluidic approach that produces giant core-shell droplets under the influence of buoyancy, which has so far remained unexplored. Two glass capillaries with selectively treated surfaces were coupled, aligned and housed inside a vessel containing the quiescent continuous phase. We demonstrate the production of giant core-shell drops, with droplet diameters ranging from 1.6 to 6 mm and typical shell thickness in the hundreds of micrometers. We also show an alternative approach for producing core-shell drops having ultra-thin shells using a single-step, biphasic flow using the same device. The relative thickness of shells was controlled by the relative flow rates of inner and middle phases (Figure 1). Droplets with diameters within 200 μm - 1.8 mm having shell thickness of 1 - 30 μm were produced. The facile nature of working with such systems by having a quiescent outer phase and non-confined geometry means scale up would be easy.

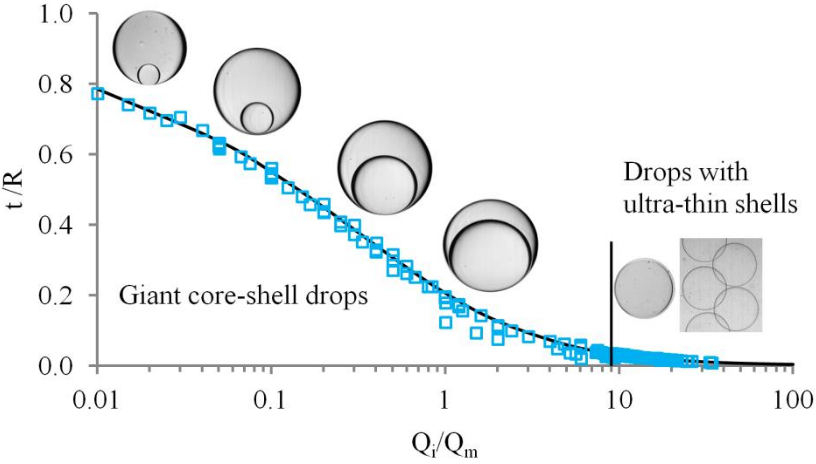

Figure 1. Relative shell thickness (*t*/R, *t*: Shell thickness, R: Drop radius) versus inner-to-middle phase flow rate ratio (Q_i/Q_m) curve showing the drops with thin shells obtained towards high Q_i/Q_m.

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K26. Using demixing, remixing & wetting to organize colloidal particles

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Formation of many soft composite materials involves the co-evolution of a host system that undergoes a phase transition with a dispersed constituent that alters or arrests that process. The host system is some solvent e.g. a phase-separating fluid or a liquid crystal while the dispersed constituent might be particles or polymers. In all cases the host can be thought of as creating effective interactions between the dispersed constituent. The resulting soft composite materials can have tuneable properties.

I will present experimental results demonstrating that phase-separating fluids can be used to organize colloidal particles: employing demixing to create bicontinuous gels stabilized by interfacial particles (bijels) [1]. I will then go on to present work showing pre-transitional clustering of particles approaching the phase boundary of a binary liquid [2]. Finally I will employ both these phenomena to create colloidal networks beginning with a partially miscible emulsion [3].

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157. Assembly of Colloidal Particles in Vertical and Lateral Directions in Thick Films

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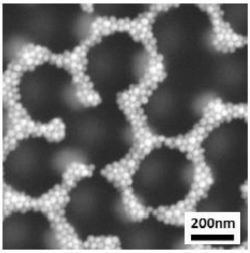
The controlled assembly of polymer particles and nanoparticles to create nanostructured films with functional optical properties and structures will be described. With a colloidal dispersion in a fluid, the competing effects of evaporation, which causes particle accumulation at the free surface, and Brownian diffusion, which smooths out concentration gradients, can be controlled to determine the concentration profile in the vertical direction. In blends of particles with differing size, a wide variety of structures, at sub-mm length scales, are created by adjusting these competing effects, as described through the use of a mean Peclét number (R.E. Trueman et al., J. Coll. Interf. Sci. (2012) 377, 207). Large particles are slowly diffusing so that they accumulate near the receding air/water interface. However, when nanoparticles are sufficiently small, they can pass through the interparticle voids to create templated structures (see Figure 1). In another type of assembly process, the evaporation rate laterally across a waterborne colloidal film is modulated by shining IR radiation through a shadow mask to heat locally. Colloidal particles are carried in a convective flow to fast-evaporating regions to build up thicker layers with lateral characteristic lengths on the order of millimeters (see Figure 2). Applications include drag-resistant coatings and microlenses (A Georgiadis, et al. Soft Matter (2012) 7, 11098). The addition of Au nanoparticles introduces plasmonic properties (A. Utgenannt et al, Chem. Comm. (2013) 49, 425) that are defined through the structural arrangement.

Figure 1. Au nanoparticles template around colloidal particles



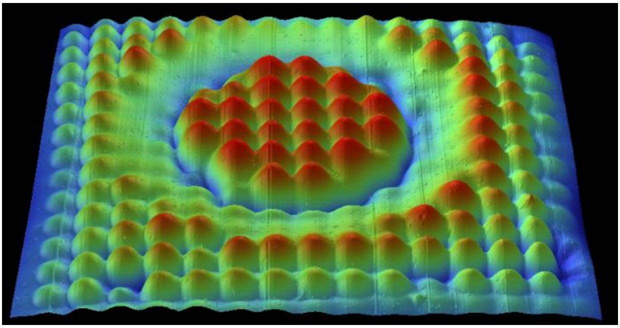


Figure 2. Patterned surface of colloidal film.

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22. How do Important State Variables like Particle Concentration and Strength of Attraction affect the Rheology of Cohesive Colloidal Suspensions?

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Concentrated colloidal suspensions found in nature and industry are almost invariably found to be cohesive to some degree, colloidally stable systems being rare outside of the university laboratory. The rheology and processing behaviours depend upon the usual state variables of particle size and shape (distributions), particle concentration and strength of interparticle attraction. Here I will focus on the latter two variables, since these together seem to conspire to produce a wide range of behaviours, to the point where, arguably, even the phenomenological catalogue of them is far from complete, let alone an understanding of them. It should be mentioned also that cohesive suspensions are very often adhesive too (of the dozen or so known mechanisms of inter particle attraction, the majority are non-specific), hence the phenomenology can depend also upon the nature of any solid bounding surfaces. Thus, even though the bulk flow behaviour of weakly-attracting particles (well-depth $<< 20\ k_BT$) is relatively simple (shear-thinning), complex time-dependent behaviour can be observed in the presence of smooth boundaries because of the slow development of adhesion. This can be mistaken for thixotropy.

More strongly attracting systems show a yield stress typically, although this does not mean that the rheology is universal in other respects. The linearity or otherwise of the viscoelasticity below the yield point seems to vary markedly from one system to another, for example. Some cohesive yield stress liquids (YSL) show history-independent and reproducible behaviour and some do not. It is tempting to suppose that the former are ergodic, i.e. that yielding in such cases involves tilting of the energy landscape until activated flow occurs (cf. Eyring), whereas the latter systems might just be uncompromisingly athermal: the horrors of irreproducible behaviour, shear-banding, irreversible history dependence do indeed seem to be associated with larger particles, higher concentrations and very strong attractions, in the speaker’s experience.

The rheology of cohesive suspensions is so rich that I will only be able to illustrate two or three aspects in the time available. My aim though will be to draw attention to aspects where, either, there is a dearth of experimental data, or, where there is an obvious need for systematic work.

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193. Taking a Look into the Black Box - New Perspectives of Nanoparticle Formation

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Colloidal nanoparticles have attracted much attention due to their unique properties and promising applications. Synthetic procedures are known and have been investigated since Faraday's groundbreaking experiments about gold colloids more than 150 years ago.[1] In the past 25 years, the synthesis, characterization and application of colloidal nanoparticles turned into one of the most vivid research fields.[2]

In this regard, it is surprising that the actual nanoparticle formation processes remain a black box. In general, progress in synthetic procedures is achieved by trial and error approaches without having a precise idea of the underlying growth mechanisms. Simple questions of fundamental interest such as (i) "What is the principal growth mechanism?", (ii) "What determines the final particle size?" or (iii) "How do the different synthesis parameters affect the growth mechanism and consequently the final size?" cannot be answered. In recent publications, we showed for several metal nanoparticle syntheses that time-resolved in-situ experiments can deliver a precise image of the particle growth. The deduced mechanisms are in contrast to classical and non-classical nucleation theories.[3-5]

The growth mechanisms and therefore the answer of question (i) can only be the first step to gain a profound understanding of nanoparticle formation. It is more complicated to deal with the other two questions and investigate the different physicochemical processes that occur during the synthesis, identify their influence on the growth mechanism and apply this knowledge to control the particle growth and final size.

Exemplified for syntheses of gold, silver and palladium nanoparticles, it will be demonstrated that the gained mechanistic knowledge allows improving and developing strategies for size controlled syntheses of nanoparticles without any stabilizing agents.

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K27. Colloid electrostatics at very low ionic strengths

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A charged colloid (of radius a) in solution is surrounded by a layer of ions which are attracted to the surface of the particle. In contact with an external reservoir of ions, the ionic atmosphere has a characteristic thickness of κ^{-1}(the Debye screening length). The range and strength of the double-layer repulsions between charged particles varies dramatically with κa.

In the large κa limit, where repulsions decay exponentially with separation, experiments are in excellent agreement with classical DLVO theory. The situation is however uncertain for $\kappa a \ll 1$, where double layers are diffuse and interactions are very weakly screened. Recent calculations[1], for instance, have suggested that for strongly overlapping double layers the strength and character of the repulsions between charged surfaces might change substantially at small separations. In contrast, earlier work[2] has even questioned if charged particles might not be repulsive at all at very low ionic strengths.

In this talk, we present an experimental study of the stability and interactions of highly-charged colloids with no added electrolyte and no external salt reservoir, so $\kappa a = 0$. We use a novel system[3] of ionic-liquid stabilized nanoparticles dispersed in a non-polar solvent to ensure that the dispersion contains only the exact number of counter-ions required for neutrality. We determine the structure of concentrated dispersions over an extended range of volume fractions using small angle X-ray scattering measurements. The variation of the structure factor with concentration is analysed to yield an effective pair potential. We find a surprisingly strong non-monotonic density dependence which we interpret in terms of counter-ion only solutions of the Poisson-Boltzmann equation. The finding has important implications for the operation of electrophoretic displays.

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195. Preparation of Soft, Responsive Nanogel Particles with Controlled Internal Structure

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The synthesis of responsive nanogel particles has attracted a considerable interest in the last decade.[1] To meet the challenges of nanotechnology, there is compelling need to develop synthetic methods for controlling the internal structure of the nanogel beads. In this contribution we provide information about the synthesis of soft, responsive poly(N-isopropylacrylamide) based nanogel particles with controlled internal structure. To achieve this goal the monomer conversion during the polymerization of pNIPAm nanogel particles has been investigated. Our results indicated that in agreement with literature results[1] the formed nanogel beads have inhomogeneous internal structure, which is the consequence of the different monomer reactivities. Based on our kinetic data we were able to control the internal structure of the prepared nanogel beads in a single pot reaction by controlling the monomer concentrations in the reaction mixture during the particle synthesis. This allowed us to prepare both nonagel particles with homogenous internal structure and unique core/shell particles, (i.e. pNIPAm particles with pure acrylic acid shell). Our investigations clearly indicated that the particle internal structure has a profound effect on the particle properties.

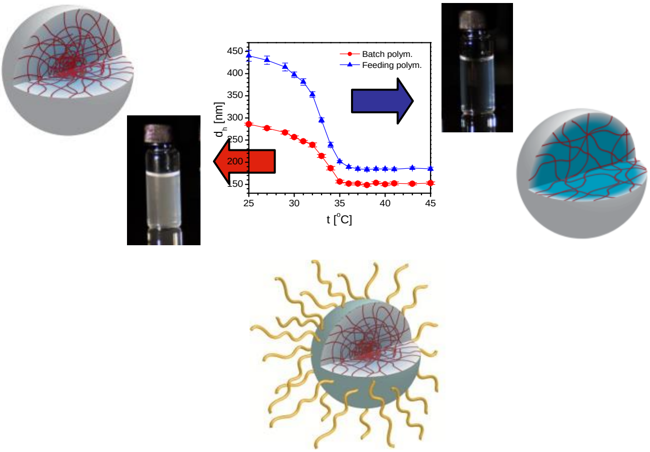

Figure 1 The optical appearance, the temperature dependant swelling, as well as the schematic representation of the internal structure of the microgel particles prepared by the traditional Batch method (on the left) and by our novel approach giving rise to either homogenous nanogel beads (in the middle) or unique core/shell structures (on the right).

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49. Self-Assembly of Poly (Methacrylate-co-Acrylic Acid) Copolymers of Varying Architecture Synthesised by RAFT Polymerisation

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Polymers with segmented amphiphilic structure possess numerous supramolecular properties leading to interesting nano-scale structures.[1] The study of this behaviour has largely been limited to linear block copolymers, but as the supramolecular organisation of the segments is expected to be controlled by architecture, consideration of other segmented architectures could lead to new and useful supramolecular and nanoscale structures. As a technique for producing segmented polymers of differing architectures**,** Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerisation[2,3] is possibly the most versatile of the controlled radical polymerisation techniques.[4]

Amphiphilic block copolymers with constant chemistry but differing architectures have been shown by transmission electron microscopy (TEM) and small angle neutron scattering (SANS) to self-assemble into micellar structures in water. RAFT polymerisation has been used to synthesise poly (alkyl methacrylate-acrylic acid) copolymers in a range of different architectures: graft, highly branched block and linear block, in addition to random versions of each of these copolymers. This set of model materials has allowed us to investigate the effects of architecture and composition on the properties of the copolymers. Additionally the hydrophobicity of the methacrylate block has been varied to study its effect on solution conformation.

These materials were designed to improve the adhesion of hydrophilic materials to a hydrophobic substrate via deposition from a fluid. However due to the amphiphilic nature of the materials they show potential for further use as surface active polymers in a range of nano- and bio- technologies.

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180. Elaboration of polysaccharide-covered polyester nanoparticles for the encapsulation of polyphenolic molecules

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Polysaccharide-covered polyester nanoparticles were prepared by two different methods: nanoprecipitation and emulsion/solvent evaporation. The core of nanoparticles was made of polylactic acid (PLA) while their surface was covered by dextran chains via the use of water-soluble randomly hydrophobized dextran (DexC6$_\tau$, Figure 1) as a polymeric stabilizer during either the nanoprecipitation or the emulsification step. These processes were optimized in order to obtain nanoparticles with reproducible size distributions well-below 1 µm. The encapsulation and release of homologous polyphenolic molecules (PM: confidential substances) in dextran-covered PLA nanoparticles was the targeted application. Investigated PM molecules varied by the length of alkyl group (R, cf. Figure 1).

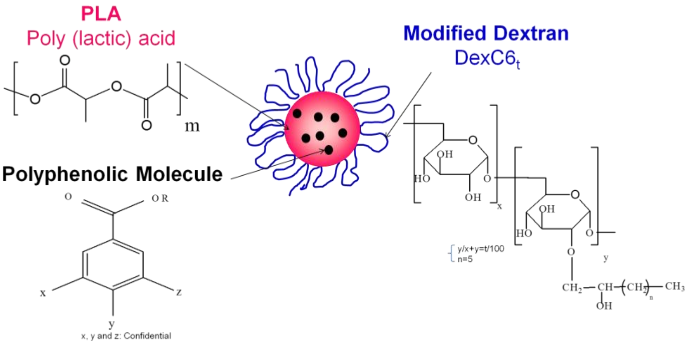

Figure 3. Dextran-covered PLA nanoparticles

The most hydrophobic substances appeared convenient for making the first attempts of encapsulation with significant yields. For these molecules, their miscibility with PLA in the solid state was characterized by Modulated Differential Scanning Calorimetry. The more hydrophobic the polyphenolic molecule, the lower the miscibility with PLA was. Loaded nanoparticles were characterized by measuring their size, evaluating their surface coverage as well as the thickness of polysaccharide superficial layer. We demonstrated that the use of polysaccharide-based stabilizers provided excellent colloidal stability in water and even in the presence of sodium chloride (from 10^{-4} mol/L to 4 mol/L) and allowed re-dispersion after freeze-drying. Nevertheless, the structure of dextran-based stabilizer appeared as an important parameter, particularly the number of attached hydrophobic groups (□, Figure 1). Finally, we compared the yields of encapsulation obtained by either the nanoprecipitation process or emulsion/solvent evaporation process.

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K28. Control over the Self-assembly of Nanoparticle Semiflexible Biopolyelectrolyte Complexes

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The electrostatic complexation between model negatively charged silica nanoparticles (NPs) with radius R=10 nm and chitosan, a natural polyelectrolyte bearing positive charges with a semi-rigid backbone of persistence length of Lp=9 nm, was studied by a combination of SANS, SAXS, light scattering, and cryo-TEM. In this system, corresponding to Lp/R=1, we observe the formation of (i) randomly branched complexes in the presence of an excess of chitosan chains and (ii) well-defined single-strand nanorods with monodisperse cross-section in the presence of an excess of nanoparticles. We also observe no formation of nanorods for NPs with poly-L-lysine, a flexible polyelectrolyte, corresponding to Lp/R=0.1, suggesting a key role played by this ratio Lp/R. The intermediate case obtained with the semiflexible biopolyelectrolyte hyaluronan and corresponding to Lp/R=0.5 is also discussed. In the intermediate range of nanoparticles concentrations, we observe an associative phase separation (complex coacervation) leading to more compact complexes in both supernatant and coacervate phases. This method might open the door to a greater degree of control of nanoparticles self-assembly into larger nanostructures, through molecular structural parameters like Lp/R, combined with polyelectrolytes/nanoparticles ratio.

L. Shi, F. Carn, F. Boué, G. Mosser, E. Buhler *ACS Macro Lett.* **2012**, *1*, 857-861. “Nanorods of Well- Defined Length and Monodisperse Cross-Section Obtained from Electrostatic Complexation of Nanoparticles with a Semiflexible Biopolymer”

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155. Many-body depletion interactions

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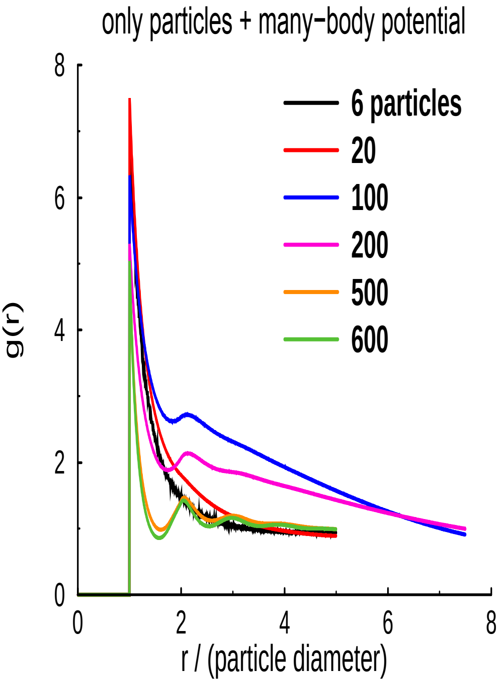
We have constructed a theory for colloid+non-adsorbing polymer dispersions, where an effective many-body Hamiltonian, acting between the particles, was derived. Explicit comparisons with simulations have revealed that the theory is able to predict structure and phase diagrams in these systems, with a remarkable accuracy (see examples in the graphs below). We have extended this theory to handle good solvent cases. We have also made theoretical calculations on a system of charged particles + depleting polymers, as studied experimentally by A. Stradner, P. Schurtenberger and colleagues (SANS, SAXS). We find excellent agreement with experimental S(k) curves at various concentrations of polymer and simple salt, provided that the former are modelled as “proper” chains, and not as spherical particles (the Asakura-Oosawa, AO, approach), and that the electrostatics is handled at the full non-linear Poisson-Boltzmann level, rather than its linearized (screened Coulomb) version. In these systems, the particles are an order of magnitude larger than the polymers, so there was no need for a many-body potential, i.e. the “pair potential approach” that fails so badly for the kind of systems studied in the graphs below, actually works fine in this case.

Simulations of a large number of non-adsorbing polymers + N particles, in a simulation box of a given size. The radius of gyration is twice that of the particle radius, so many-body interactions are very important. As the number of particles increase from the “gas”, the canonical system phase separates, until the concentration becomes “liquid-like”. These simulations are computationally very demanding.

The same system as above, but with implicit polymers, entering via a many-body Hamiltonian. These simulations are very simple and fast. Extremely inaccurate predictions are obtained if only the pair (two-body) part of the many-body Hamiltonian is used. In those cases, the simulated g(r) peaks are typically well above 100.



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106. Ostwald ripening of emulsions stabilized by a complex proteoglycan - gum Arabic

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Ostwald ripening is one of the main mechanisms destabilizing emulsions. It is driven by the Laplace pressure of the droplets. Gum Arabic produces very stable emulsions, due to the elastic film that it forms at interfaces1. For the first time, we study systematically the effects of Ostwald ripening on the size distribution of emulsions stabilized by gum Arabic. Our variables are: the concentration of gum Arabic, the composition of the oil phase and the emulsification pressure.

The results are contrary to intuition based on other mechanisms of destabilization:

1) Using less emulsifier can give more stable emulsions.

2) Higher emulsification pressures lead to droplets that are smaller initially, but with lower long-term stability, due to their higher Laplace pressure.

The existing theories of Ostwald ripening cannot completely explain our results. For pure oil, theory predicts two different behaviors, depending on whether the maximum diameter is above or below a critical value:

1) Maximum above critical: the average diameter increases without limit and the distribution has a universal form.

2) Maximum below critical: the size distribution is stable.

For oil containing a highly insoluble component, theory predicts that a bimodal distribution is possible. The small droplets are stable, but the large droplets increase in size without limit, exactly as though the oil were pure.

Our results show a previously unreported intermediate regime where the droplet distribution is bimodal, but the droplet diameters are fixed. Over time, the proportion of small droplets decreases and that of the large droplets increases. We discuss the role of interfacial elasticity for this intermediate regime and propose a “fate diagram” that uses the Laplace pressure and the osmotic pressure to parameterize our observations.

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84. Probing nanoparticle interactions with biological system for drug delivery applications

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Before any drug administered to the gastro-intestinal tract reaches the epithelium, it must traverse a layer of mucus. The main polymeric component of mucus is the glycoproteins collectively called mucins. These are complex gel-forming polymers which exhibit electrostatic, hydrophobic and H-bonding interactions and are responsible for the viscous and elastic gel-like properties of the mucus layer.

The efficacy of nanoparticles (NPs) to penetrate this layer, and deliver macromolecular drugs in therapeutic concentrations to the epithelium will depend on the surface chemistry (decoration) of the NPs. Quantifying the interactions between these NPs and the mucin gel is essential for designing successful drug delivery systems. In this project various decorations were fabricated, including zeta potential changing, slippery, and proteolytic enzymes. Figure 1 illustrates slippery and proteolytic enzyme decorated NPs penetrating a mucus layer that would stop conventional NPs.

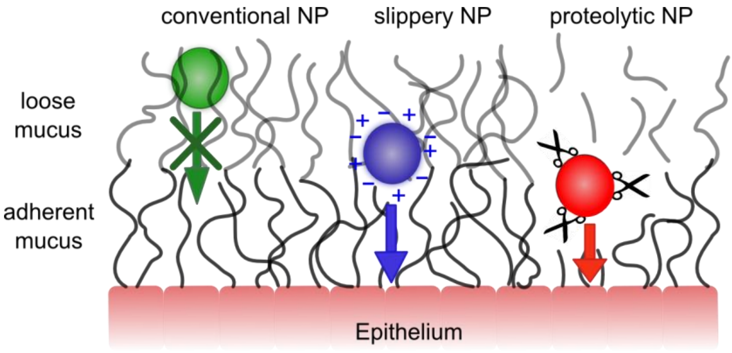

Figure 1: Possible scenarios of mucus interactions with particles of different surface chemistries

The effect of these NPs on the mobility of intestinal mucin gel was assessed by pulse-gradient-spin-echo NMR (PGSE-NMR); whereas the potential of the NPs to interact with the mucus and alter its tridimensional structure was investigated using two scattering techniques, small angle neutron scattering (SANS) and spin-echo SANS (SESANS).

The proteolytic strategy showed promising results, i.e. insertion of 0.5wt% of enzyme functionalized NPs to 5wt% intestinal mucin solution led to c.a. 2 fold increase in the mobility of the mucin molecules as measured by PGSE-NMR, this is indicative of a significant change in the structure of the mucin.

Scattering measurements also revealed a change in the mucus structure upon addition of functionalized NPs, occurring mostly at a lengthscale larger than 0.5µm.

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K31. Characterization of suspension separation in thickeners, by an acoustic backscatter system

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The measurement of suspended particle changes within settling multiphase systems is important to many engineering and environmental applications; particularly for example, in minerals processing and water treatment. Many industrial separation operations rely on gravitational settling of particles (such as clarifiers & thickeners) and the ability to monitor concentration and stratification *in situ* may greatly aid in optimisation and allow more accurate modeling of these processes. Acoustic backscatter systems (ABS) are potentially a practical and relatively cheap characterization technique, which can give the ability to profile depthwise particle segregation in large environments, although their application in concentrated industrial suspensions is largely unstudied. Here for the first time however, a collaboration between the University of Leeds and the University of Melbourne has investigated the use of an ABS to characterize a model mineral separation system, utilizing a bespoke continual-flow ‘mini thickener’ with inline pipe flocculator. The free-settling region of the suspension was studied by the use of 2 and 5 MHz transducers mounted in the top of the column; where the acoustic backscatter strength and attenuation from echo pulses were analyzed to study concentration changes with time. A 1 MHz probe mounted in the near-bed region was used to measure consolidated bed build-up and average density changes, also from the signal decay. Importantly, the influence of a scraper-rake on solids densification was observed by analyzing systems at two different scraper rotation speeds (0.1 and 1 rpm). In a second experimental programme in association with Yorkshire Water (UK), a full scale water treatment thickener was characterized by similar *in situ* measurements with the ABS. Here, the changing sludge interface and solids profile was measured from probes positioned at different radial locations from the centre. Again, rake densification of the sludge was analyzed by a deeper probe inserted within the consolidated sludge zone.

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95. Characterization of Graphene, Graphene Oxide and Nanographite Dispersions using NMR Solvent Relaxation

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Nanocarbon materials, such as graphene/graphene oxide and graphite, are increasingly attracting much attention owing to their stable physicochemical properties, low cost, excellent chemical stability, wide operating temperature range properties and long cycle life. They are being considered for use in all types of applications to deliver enhanced performance capabilities to products such as reinforced composites the development of new generation supercapcitors, sensors and electrode materials. However, studying these systems in-situ is not straightforward as the formulations are opaque and often highly concentrated dispersions in a variety of aqueous and non-aqueous liquids. The physical characterization of nanoparticulate dispersions poses challenges, especially at high concentrations. NMR solvent relaxation is a non-invasive technique that probes the molecular motions of species adsorbed onto the particle surface and so can be used to characterize the strength of interaction between a liquid (or other additives) and particle surface functional groups. A major advantage of the technique is that measurements can be made at virtually any solids concentration and in almost any fluid media. The ability to distinguish between molecules at the surface and those in the bulk solution can be used to obtain valuable information on the interfacial interactions and structure at industrially relevant concentration without dilution. In any dispersion, the available amount of wetted surface area depends not only on the amount of physical external/internal surface presented but also the physico-chemical nature of the particle-liquid interface (i.e., surface chemistry). In this paper we will show data, obtained using a small bench-top low field NMR device, on dispersions of porous and non-porous nanocarbon materials that illustrates the versatile utility of the technique.

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175. Functional Graphene-Polyelectrolyte Thin Films Formed By Hydrogen Bonding

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Electrically conducting thin films are essential for a variety of applications including solar cells, photonics and flexible electronics. Recently, graphene, a carbon allotrope consisting of single layer macroscopic carbon sheets, has attracted considerable interest in a range of research fields due to its unique 2D structure [1]. As a consequence of this unique structure, graphene possesses remarkable electrical conductivity, tensile strength, flexibility and optical transmittance, making it ideal for integration into thin films.

This study focuses on incorporating colloidal graphene nanoparticles into polyelectrolyte multilayers using hydrogen bonding. First, colloidal dispersions of pristine graphene nanoparticles were created from synthetic graphite using a method of surfactant-assisted exfoliation [2]. Thin films containing the anionic polyelectrolyte, polyacrylic acid and graphene nanoparticles were then constructed using the layer-by-layer approach [3]. Films were prepared using dip coating and a Quartz Crystal Microbalance (QCM) apparatus was used to monitor the deposition kinetics and adsorbed mass.

A range of analytical techniques were used to characterize the resultant film composition, surface features and mechanism of formation for the thin films. QCM measurements, Raman spectra and UV visible spectra indicate the successful formation of thin film multilayers through hydrogen bonding. However, atomic force microscopy imaging and optical microscopy indicate partial dewetting of the films from the silica substrates. It was also demonstrated that there was both a linear and exponential component to the film growth. These insights may guide further studies regarding graphene-based thin films.

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K29. CO2-Switchable Wormlike Micelles

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Recently, interest has emerged in the design of environmentally stimuli-responsive wormlike micelles (WLMs) due to their peculiar micellar structures and tunable rheological behaviours, as well as potential applications. Simpler “green” triggers for switching WLMs between an “on” and “off” state without compromising their inherent properties are also highly desirable.[1]

Here we developed three CO2-triggered wormlike micellar systems based on the following surfactants respectively: “pseudo”-gemini surfactants containing a commodity anionic surfactant and a diamine with molar ratio of 2:1,[2] a C18-tailed polyamine,[3] and a C22-tailed tertiary amine.[4] Before introducing CO2, all of these surfactant solutions are low-viscosity emulsion-like fluid; however, upon bubbling CO2 for only 2 minutes, they immediately transform into transparent viscoelastic gels with viscosity thousand times higher than that of the original solution. When CO2 is displaced with N2 or air, the gels restore to their initial low-viscous cloudy state. Of special interest is that such a CO2-responsive behaviour is reversible when cyclically bubbling and removing CO2, and could be repeated several cycles without loss of response to CO2. Cryo-TEM observation before and after CO2 streaming reveals a microstructural transition from spherical micelles to WLMs networks, NMR characterization of the corresponding species attributes the mechanism to the protonation and deprotonation of the amine groups in the systems. Compared with traditional trigger of HCl, CO2 does not produce contamination and accumulation of by-products in the solution, which may prolong the switchable cycles. These unique features furnish CO2-switchable WLMs to thicken and separate specific fluids for a myriad of technological applications, particularly water-alternate-gas oil recovery process.

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5. Realising Autonomous Transport Applications for Janus Particle Catalytic Swimming Devices

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Janus colloidal swimmers produce motion by asymmetrically decomposing dissolved fuel molecules around their surfaces. The goal for Janus swimming devices is to allow the delivery of drugs within the body, or transport of analytes in a microfluidic device. Here we survey the steps taken towards autonomous transport for these devices within our research group and highlight the challenges that still remain. The key to controlling Janus particle device trajectory is to influence rotational diffusion rate. If left to undergo unrestricted Brownian rotational motion, swimmer trajectories are rapidly randomised; because their direction of travel is determined by the Janus particles orientation. Consequently, without control, the propulsion force manifests as super-diffusion at time scales beyond the rotational diffusion constant, rather than the more useful directed motion required for applications. So we describe and compare the wide range of methods we have investigated to modify and control rotational diffusion; including stimulus responsive size change, magnetic quenching, interfacial confinement, self-assembly, gravitational bias, and control of the catalyst patch geometry, Figure 1.

We discuss how these phenomena can be exploited to achieve new applications such as the active separation of devices according to properties such as spin, or velocity. Combined with self-assembly, this can allow swimmers with particular properties to be autonomously manufactured. In addition we show how the interaction of swimmers with interfaces can allow them to follow surface patterned features, providing a method to direct and control their motion.

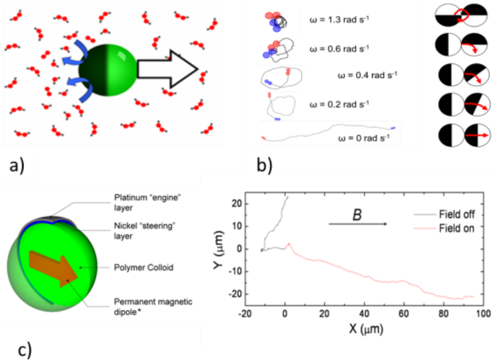

Figure 1: (a) Schematic of Janus colloid (b) control via self-assembly (c) control via magnetic fields

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181. Switching between two modes of coalescence in dense thermo-responsive emulsions

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We apply a new method of micro-centrifugation to directly study the coalescence in densely packed emulsions, under well-defined conditions. By combining microfluidic centrifugation and high-speed imaging we are able to obtain direct and quantitative measurements of temperature-dependent critical disjoining pressures and coalescence rates. In experiments using a thermoresponsive emulsion we find two distinct modes in which a dense emulsion coalesces. A small change in temperature allows switching from coalescence occurring exclusively at the oil-emulsion front to coalescence occurring randomly throughout the entire packed layer of emulsion. These findings shed new light on the mechanisms of coalescence in dense emulsions at the length scale of the individual droplets.

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Dynamic arrest in soft colloidal matter

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Understanding how dynamic arrest takes place in disordered systems such as glasses or gels is an important problem in condensed matter physics. A molecular glass is normally formed by cooling of a liquid. Upon entering the supercooled state, the structural dynamics slows down dramatically, eventually leading to the formation of a non-equilibrium glassy state. On route towards the glass, the behaviour shows a range of highly general, near universal characteristics, such as stretched exponential behaviour of dynamic correlation functions and cooperative dynamics. Such generalities exist even though molecular glasses can be formed from liquids encompassing a wide range of molecular structures and interactions. Glass formation also occurs in altogether very different systems. One of the most interesting, both from a fundamental and an applications point of view, is that of colloidal suspensions. The high degree of control that can be achieved regarding colloidal particle size, shape and interactions makes this a fantastic model system for learning about glass-formation in general. Moreover, in colloidal systems with attractive interactions dynamic arrest into gels can also take place and the interplay between glass- and gel-formation is often both important and complex. We will here discuss both glass and gel formation in colloidal model systems and will also discuss how concepts from colloid physics might be important for understanding dynamic arrest also in molecular polymer systems which undergo gelation.

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K32. Exfoliation of layered materials for energy, water and biomedical applications

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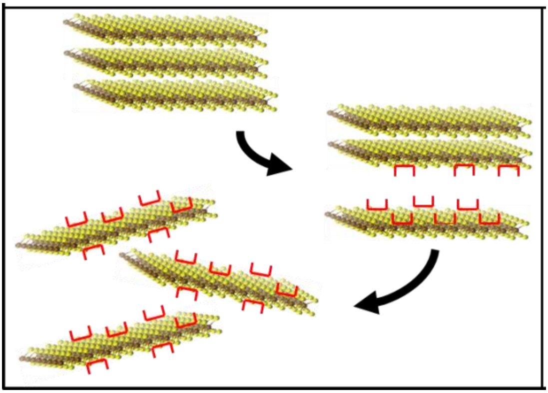
The exfoliation of van der Waals bonded solids has been of great recent interest with the formation of graphene from graphite the most notable. Other materials such as the transition metal dichalcogenides have received less attention however MoS2 and WS2 also display interesting properties in the limit of 2D. In principle, any layered solid material held together through weak dispersion forces can be exfoliated to single sheets using a range of techniques such as the “scotch tape method”, solvothermal and intercalation routes, chemical oxidation and reduction as well as surfactant assisted liquid phase exfoliation. All of these techniques have advantages and limitations, indeed few are capable of generating large volumes of exfoliated sheets whilst maintaining sheet integrity. One method that shows great promise and can be scaled to meet industry needs is the aqueous based surfactant assisted liquid exfoliation technique. Here, the properties of material such as graphene, MoS2 and WS2 will be discussed as will potential applications of exfoliated sheets generated in this manner.



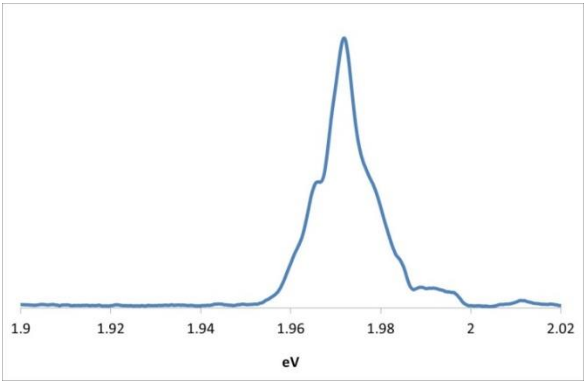


Figure 1. Schematic representation of exfoliation of MoS_2 and the PL spectrum of particles generated using this technique.

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107. Influence of particle shape and concentration on the pattern of dried colloidal droplets

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Inkjet printing is a widely used technique to deposit small volumes of liquid with high precision, both for volume and spatial location, onto a great variety of substrates. Although this is a very efficient deposition technique, being able to control the dried deposit pattern of particulate inks upon solvent evaporation is an important challenge that is yet to be overcome.

Our work studies the deposit patterns of particles of various shapes onto well-defined substrates. Our aim is to gain a better understanding of the phenomena involved during the droplet drying process and thus, provide us with tools to control the dried deposit structure regardless of the initial ink composition. This work investigates the drying behavior of colloidal suspensions as a function of particle shape, size and weight fraction. For spherical colloids (silica Ludox nanoparticles, 25 nm in diameter), a "circular stain" is observed due to an outward flow of particles upon solvent evaporation as the drop contact line is pinned by the presence of nanoparticles. This circular pattern indicative of a "coffee ring effect" is observed regardless of the particle concentration, whereby a steady increase in the height and width of the drop edge is observed with increasing particle concentration up to 2 wt% in mass. Meanwhile, for a disk-like particle system (Laponite-clay nanoparticles, 30 nm in diameter and 5 nm thick), the “coffee ring effect” is only observed at low particle concentrations, and a complete film across the deposit is observed at higher concentration. The study of the dried deposit structure of rod-like, cubic and other shapes colloidal nanoparticles has also been investigated.

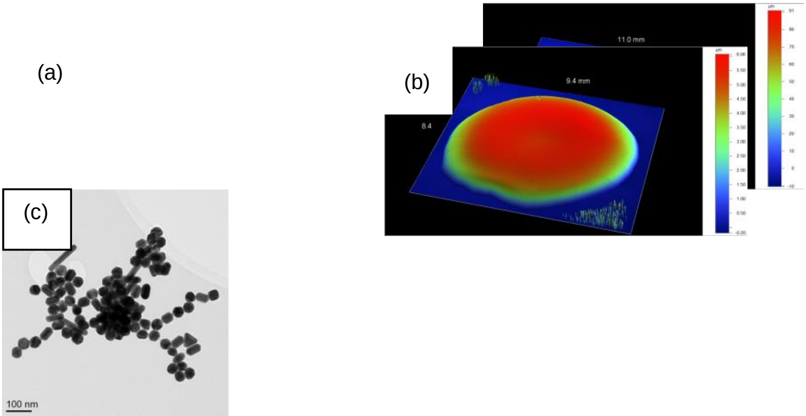

Figure 1: 3D images of the whole dried deposit structure of (a) spherical silica Ludox ® ,(b) disk-like clay Laponite at 2 wt% by an interferometer and (c) TEM image of faceted gold nanoparticles (rod-like, cubic and other shapes)

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173. Carbon nanoparticle colloids for facile and multifunctional superhydrophobic surfaces

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Colloidal dispersion of a hydrophobic polymer with nanoparticles would be well suited to prepare nanocomposite coatings with superhydrophobic properties. However, in general, it is challenging to form stable particle colloids in hydrophobic polymer solutions. Herein we overcome this problem by employing a commercially available, short chain fluoroacrylic copolymer solution to disperse carbon nanoparticles. The copolymer has perfluoro (hydrophobic) and acrylic (hydrophilic) components. The latter facilitates particle dispersion. The hydrophobicity of the perfluoro chains and the texture from the nanoparticles provided a facile means to produce superhydrophobic surfaces by casting. Using different nanoparticles, multiple desirable properties could be simultaneously attained such as the ability to resist impalement by impacting drops, electrical conductivity, the self-cleaning ability (i.e., low contact angle hysteresis) and the ability to separate oil/water mixtures. Three different carbon nanoparticles, namely, carbon black (CB), carbon nanotubes (CNT), graphene nanoplatelets (GNP) and their combinations were employed. At 50 weight% of either CB or CNT, the coatings resisted impalement by water drops falling down at 3.7 m/s, the highest attainable speed in our setup. The coatings were also tested with 5 volume% IPA-water mixture, which has a surface tension of 47.8 mN/m and thus poses a stiffer non-wetting challenge. Only the CB coatings could resist impalement by the IPA-water mixture drops up to 3.7 m/s. GNP based surfaces featured very high conductivity ~1000 S/m, but the lowest drop impact resistance. The optimal performance was obtained by combining the carbon fillers, for example, excellent impalement resistance up to 3.5 m/s with the

IPA-water mixture drops and electrical conductivity of ~1000 S/m. All the synthesized coatings were superhydrophobic and oleophilic. This property was used to separate mineral oil and water through filtration of their mixture.

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K30. Use of Particle Technology in Development of Advanced Functional Materials

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Cabot Corporation is a world leader in the production of carbon black, activated carbons, and fumed metal oxide particles. These materials are critical enablers of functions such as color, conductivity, reinforcement, rheology, and adsorption that drive performance in a range of applications in key industrial segments. Engineering materials for these industrial applications requires considerable capabilities: (i) High volume production of particles with controlled size and shape, (ii) Surface modification of particles to enable certain key functions; e.g. processing, and (iii) Incorporation of particles in a matrix of interest for a variety of end uses; e.g., conductive plastics. Case studies highlighting the use of particle surface engineering to improve product performance will be presented.

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32. Micromolding in Capillaries for Nanopatterning of Rare-Earth-Ion-Doped Nanoparticle films on Plastic Sheets

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We report calcination-free micromolding in capillaries1 for the nanopatterning of rare-earth-ion-doped nanoparticle films on flexible plastic sheets. We synthesized polyethylene imine-modified NaYF4 nanoparticles doped with Er3+ and Yb3+ as upconversion luminescent material. The diameter of the NaYF4 nanoparticles was estimated to be about 50 nm using scanning electron microscopy. Figure 1a shows an experimental scheme of the patterning of the NaYF4 nanoparticle films on flexible plastic sheets. A small droplet of the NaYF4 nanoparticle dispersion was placed at the open end of polydimethylsiloxane (PDMS) molds on flexible plastic sheets, leading to spontaneous inflow of the NaYF4 nanoparticle dispersion into the channels by capillary force. After drying, the samples were analyzed mainly by optical, fluorescence, and scanning electron microscopies. Figure 1b shows a scanning electron microscope (SEM) image of the NaYF4 nanoparticles on a flexible plastic sheet. The NaYF4 nanoparticles are aligned along the walls of the PDMS mold. Fluorescence microscopy showed that visible upconversion luminescence and near-infrared fluorescence appeared from the NaYF4 nanoparticles. These results demonstrate that calcination-free micromolding in capillaries allows for the nanopatterning of inorganic phosphor films on flexible plastic sheets.

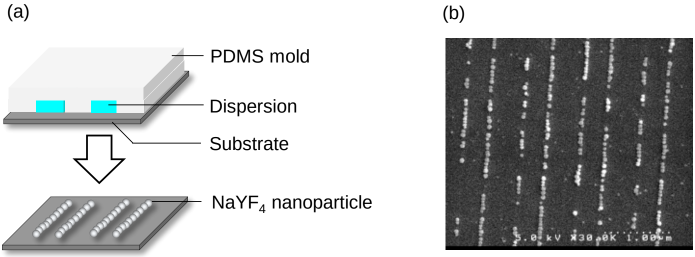

Figure 1 (a) Experimental scheme and (b) SEM image of polyethylene imine-modified $NaYF_4$ nanoparticles on flexible plastic sheets.

[1] S. Watanabe et al., *Adv. Funct. Mater*. **2010**, 21, 4264–4269; *Langmuir* **2013**, 29, 11185−11191; *J. Colloid Interface Sci*. **2014**, in press.

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206. Designing bimetallic nanoparticles for high catalytic performance

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The rapid advances in colloid chemistry over the last decade have resulted in the synthesis of monometallic nanoparticles with tunable size, shape and composition, which have been used as model catalytic systems to investigate synthesis-structure-activity correlations in a range of chemical processes. Besides the development of monometallic catalysts, a new set of catalysts prepared by mixing two metal components and resulting to a bimetallic system has been introduced in the area of catalysis. We have developed Au-based nanoparticles where the control of size, shape and morphology of structure (alloy or core-shell) (Figure 1) is achievable.1 Here we present case studies where the influence of preparation in catalytic performance of Au-based nanoparticles synthesised by colloidal methods in a variety of important reactions in terms of activity and selectivity is evident, such as (i) the oxidation of benzyl alcohol and glycerol, (ii) CO oxidation, (iii) synthesis of H2O2 via in situ processes and (iv) the production of H2 via photocatalytic processes using bio-refinery “waste” chemicals. The catalysts have been characterised using a combination of techniques, (i) UV-vis spectroscopy, (ii) transmission electron microscopy, (iii) STEM HAADF/XEDS and (iv) X-ray photoelectron spectroscopy. An overview of the UK Catalysis Hub (facilities at Harwell Campus) and the benefits in terms of collaborations and objectives will be presented.

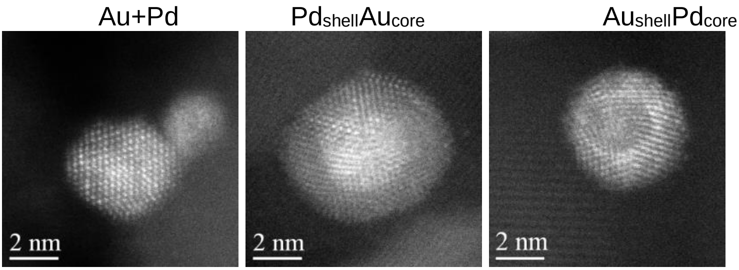

Fig.1 Representative STEM-HAADF images of individual sol-immobilized Au+Pd, Pd$_{shell}$Au$_{core}$ and Au$_{shell}$Pd$_{core}$ supported nanoparticles on activated Carbon.

References

1 N. Dimitratos, J.A. Lopez-Sanchez, G.J. Hutchings, *Chem. Sci.,* 2012, 3, 20 ; Q. He *et al*, *Faraday Discuss.,* 2013, 162, 365; R. Su *et al, ACS Nano*, 2014, *in press*.

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131. Catalyzed H-D Exchange Reaction in Micelles of Ionic Liquids

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Ionic Liquids (ILs), as well as common ionic surfactants, can be constituted by a charged hydrophilic headgroup and one or more hydrophobic tails. These species are able to self-aggregate as micelles in aqueous solution. Typical ions of ILs are asymmetric organic cations containing nitrogen (imidazole, pyridine, etc) and a wide variety of anions. Long-chain ILs composed of the 1-alkyl-3-methylimidazolium cation ([Cnmim+]) are among this novel type of amphiphiles.

In 1964 Olofson et al. reported for the first time the facile deuterium (D) exchange of the C(2)-H of the 1,3-dimethylimidazolium cation in D2O. For [Cnmim+]-based ILs the H-D exchange reaction has been explained in terms of three main effects: the IL concentration, the length of the chain, and the nature of the counterion. The goal of the present work is to determine the weight of each factor in the kinetic process in a wide number of new ILs. The kinetic study starts with the evaluation of the effect of the concentration of the ILs on the exchange process. The second step in this work is to analyze the effect of the anion. Finally, for amphiphilic ILs we determine the role that self-aggregation plays in the exchange process for cationic and anionic micelles. The kinetic study of the H-D exchange reaction for IL-based micelles provides relevant information about the studied systems.

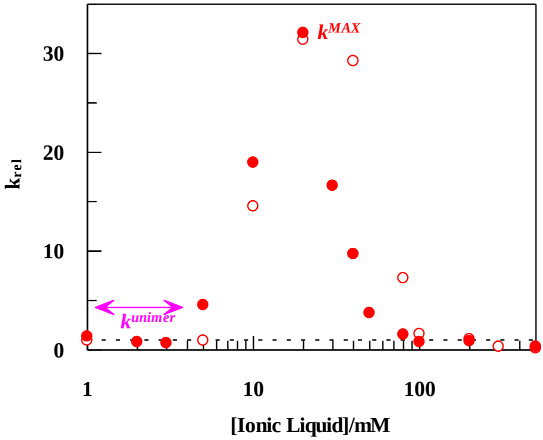

Figure 1. Variation of relative rate constants with [C_{12}mim][Cl] (Θ) and [C_{12}mim][C_1SO_4] (α) concentration. The H-D exchange reaction was performed in D_2O at 25ºC.

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K33. High-performance doubly crosslinked microgels for biomaterial applications

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Recently, we developed a technology that transforms injectable microgel dispersions into hydrogels via inter-linking of the particles. These new hydrogels are termed doubly crosslinked microgels (DX MG) and have been shown to restore the mechanical properties of degenerated intervertebral discs (IVD). DX MGs have a unique advantage from the biomaterials perspective because most of the assembly is conducted outside the body and the particles are simply linked together in vivo using free-radical chemistry under mild conditions. This presentation briefly discusses our DX MG work in the context of IVD repair and highlights the potential applications of these hydrogels from the perspective of a potential treatment for some types of lower back pain. Two new types of high performance DX MG composites are also discussed. We will show that the use of additives provide major increases in both DX MG elasticity and ductility. Future biomaterial challenges will also be identified and the role that injectable DX MGs could play in solving them will be highlighted.

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40. Liquid Crystal Emulsions for Efficacy

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Much research has been carried out to investigate the effects of various formulations to deliver active ingredients to the skin, including emulsions for dermal and transdermal delivery. Although there are many factors which affect the degree of skin penetration for active ingredients, it is very difficult to draw general conclusion due to differences in composition and physicochemical properties. Recently, liquid crystal emulsions (LCEs) have been extensively used in the cosmetic and drug industry. Because LCEs have multi-lamellar structures similar to the structure of human stratum corneum, they are expected to enhance the skin penetration of actives. However, according to many of the previous studies, it is hard to maintain formulation stability with LC emulsions due to swelling and re-crystallization. In this study, we prepared LCEs and these formulations showed long-term stability up to 6 months under a variety of temperature conditions, including -20ºC, 4ºC, 25ºC and 50ºC. Polarizing microscopy and electron microscopy were used in order to observe LCEs. Maltese cross patterns could be observed using polarizing microscopy, which means that these emulsions are optically anisotropic. Furthermore, we observed multi-lamellar structures using electron microscopy. In this study, the visualized multi-lamellar structures in LCEs were obtained using Mueller matrix polarimetry. This might be due to the retardance of light between the short-axis and the fast-axis. To the best of our knowledge, this is the first time that an extensive study of the quantitative assessment of multi-lamellar structures has been performed using the Mueller matrix. We used in vivo confocal Raman spectroscopy in order to monitor human skin penetration. This method is a non-destructive and label-free technique, which can be applied directly to human skin. LCEs and ordinary O/W emulsions were applied once and measurements were performed up to 6 h after treatment. Remarkable differences between LCEs and ordinary O/W emulsions in the delivery of retinyl palmitate can clearly be observed.

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82. Heterogeneous Dynamics of Polymer Chains and Spherical Nanoparticles in Nanocomposites

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By performing molecular dynamics simulations, we investigate the structural and dynamical properties of polymer melts containing probe spherical nanoparticles. Generally speaking, the behaviour of these polymer nanocomposites is strongly affected by the interaction strength established between the nanoparticles and the chain monomers, and by the nanoparticles' size. We highlight that this dependence is not always evident and some intriguing properties, such as the heterogeneous dynamics of both polymer chains and nanoparticles, and their non-Gaussian behaviour at short and long time scales, are not particularly influenced by the degree of attraction between nanoparticles and polymer for the range of interactions we study (up to 6 kT). We find the existence of weakly ordered interdigitated structures with sequential arrangements of particles and polymer chains, which separate each other and hence inhibit the formation of nanoparticles' clusters. This is especially evident with big nanoparticles, being less prone to aggregate than small ones, even when their interaction with the polymer chain is as low as 0.5 kT. Moreover, by integrating the stress-tensor autocorrelation functions, we estimate the shear viscosity and determine its dependence on the strength of the polymer-nanoparticle interactions and on the nanoparticles' size. By acting as plasticizers, small nanoparticles decrease the viscosity, especially at low-to-moderate interactions with the polymer. By contrast, big nanoparticles that establish strongly attractive interactions with the polymer chains, behave as thickening agents and significantly increase the viscosity. This complex, and perhaps still scantily understood, balance between nanoparticles' geometry and their interaction with the polymer is key to predict and fully control the macroscopic response of nanocomposite materials and hence suitably tailor their mechanical properties.

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Abstracts for Poster Presentations

P1. Comprehensive Study of Catastrophic Phase Inversion Emulsification

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This research aims to uncover the mechanistic basis of catastrophic phase inversion (CPI) in producing fine emulsions. It also investigates the conditions under which CPI can produce finer emulsions than direct emulsification. Phase inversion process can be altered by the surfactant affinity toward phases and the dynamic effects caused by variations in process parameters such as agitation intensity or the rate of addition of phases as examples. In this study both aspects have been considered. The effective value of HLB (hydrophilic-lipophilic balance) of the surfactants has been altered either by changing the surfactant composition (the ratio between the oil soluble surfactant and the water soluble surfactant) or by altering the emulsification temperature. While the dynamic effects have been explored by changing the mixing rate.

This work focused on emulsification process using a model of cyclohexane-water emulsion and two non-ionic surfactants (Igepal Co-720 with HLB of 14.2 and Igepal Co–520 with HLB of 10). A series of experiments has been carried out at constant phase ratios to produce oil-in-water emulsions. In some cases the surfactant or surfactants mixture was dissolved in the oil phase and in other cases it was dissolved in the water phase. Microscopic images of the emulsions have been acquired using optical microscopy and the average droplet size was measured. The onset of phase inversion was monitored via variations in conductivity and where a large increase in conductivity occurred. The effects of different process and formulation parameters on the inversion time, the effective dispersed phase ratio as well as the Sauter mean diameter of drops in the final emulsions were studied. It has been found that these parameters can play a key role in controlling the emulsion morphology and drop size. In all systems used throughout this study CPI emulsification was found to produce finer oil droplets than direct emulsification. It was also concluded that in order to obtain an emulsion with a finer droplet size, it is better to place the surfactant/surfactants mixture in the oil phase.

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P2. Stability of Natural Rubber Latex

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Natural rubber (NR) latex is a widely used natural compound for industrial applications. NR latex is extracted from a tree, Hevea Brasiliensis. This natural latex is a colloidal dispersion mainly made up of polyisoprene 1, 4-cis particles in an aqueous serum. These particles are stabilized by a complex layer of phospholipids and proteins. Coagulation of latex naturally occurs on the tree after tapping, but the underlying physicochemical mechanisms involved are still not well understood. Here, we report an experimental investigation on the peculiar destabilization pathways of NR latex.

Originality of this work is found in the biological origin of the latex. Usually, the coagulation of natural rubber is realised by neutralisation of acidic groups by adding acidic solution. However, irreversible coagulation of natural latex is possible with other compounds such as hydrophobic carbon black (CB) or divalent cations. The natural latex quickly coagulates when mixed with CB powder. We have shown that NR is destabilized when hydrophobic particles are incorporated into the dispersion via a bridging phenomenon. Moreover, this heteroaggregation is controlled with the help of a surfactant adsorbed onto the CB. Finally, this process results in the fabrication of composite materials with a NR matrix and well-dispersed CB particles. It is also observed that divalent cations lead to an irreversible aggregation that forms a slightly elastic coagulum. These observations led us to describe the phenomenology of coagulation with these two different chemicals.

This interesting surface reactivity of NR particles is studied with the help of surfactants that allow one to modify their interfacial composition and thus the interactions between them. Moreover, we use fluorescent molecules to tag the surface by specific reaction with primary amines. This allows us to show the role of surface species in the destabilization process and to image the final structure of the coagulum.

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P3. High-Yield Synthesis of Monodispersed Gold Nanostar with Highly Tunable Optical Property for Biomedical Applications

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We developed a surfactant-free synthesis route to produce highly-monodispersed gold nanostar (AuNS) in high yield (ca. 100 %) using hydrogen peroxide as the “green” reducing agent. The mechanism underlying the anisotropic growth of AuNS was elucidated. Multiply-twinned gold seed was necessary in initiating the formation of bumps on the gold core while Ag+ was the main shaping agent in promoting the preferential elongation of spikes along certain crystallographic directions. The morphology of the as-synthesized AuNS was stable for months under room temperature condition and surprisingly, did not reconstruct into a more thermodynamically-favored spherical shape. The LSPR peak could be tuned predictably across a wide optical wavelength range of ca. 560 – 850 nm, including the important biological optical window, by changing the Ag+ concentration. The AuNS was synthesized reproducibly within the size range of 70 – 150 nm by adjusting the Au^{3+}-to-seed ratio. We also demonstrated the ease of modifying the relatively “clean” surface of our AuNS with different biomolecules and biocompatible molecules. Overall, this synthesis protocol is versatile in controlling the size and spikiness of the AuNS while maintaining good homogeneity and stability which should yield high quality, functionalized AuNS for downstream biomedical applications.

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P4. Adsorption mechanisms of model antigens on aluminum-based vaccine adjuvants

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Aluminum-based adjuvants, i.e. aluminum hydroxide and aluminum phosphate, have been used for over sixty years in vaccine preparation. They are known to induce a strong, durable and protective immune response. Antigen adsorption on adjuvants is a crucial but still not well understood step of vaccine formulation. The objective of this work is to better understand the interaction between antigens and aluminum-based adjuvants used in vaccines. Two $AlPO_4$ and two $Al(OH)_3$ were characterized in terms of surface chemical composition, particles morphology and crystallinity. Bovine serum albumin, maltoheptose and dextran were chosen as model antigens representative of protein and low/high molecular weight polysaccharides, respectively. Quartz Crystal Microbalance (QCM), which records frequency shifts of a piezoelectric crystal upon adsorption, is a powerful tool to monitor adsorption in situ and in real time. The potentialities of QCM to probe antigen-adjuvant particles interactions were explored.

Surface chemical composition of the adjuvants was determined by X-ray photoelectron spectroscopy, and their morphology was studied by scanning electron microscopy. Aluminum hydroxide particles are lamellar and composed of amorphous $Al(OH)_3$ and crystalline AlOOH. Aluminum phosphate particles are round shaped, amorphous, and have an $Al(PO_4)x(OH)y$ formula, x and y depending on production conditions. Strategies to cover the surface of QCM sensors with a homogeneous layer of adjuvant particles were then developed, with a view to monitor antigen adsorption on the designed sensors. Sensors were coated by electrostatically-driven deposition of adjuvant particles. An optimal pH for deposition of each adjuvant was identified.

Model antigen adsorption was monitored on the adjuvant-coated QCM sensors. Very low amounts of maltoheptose and dextran seem to adsorb to all adjuvants. In contrast, BSA adsorbs well to $AlPO_4$ and $Al(OH)_3$. Further work is now needed to validate the adsorption measurements using QCM. More experiments will be done in different conditions of pH and ionic strength to clarify the role of polysaccharides in the adsorption process of conjugate vaccines.

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P5. Novel Polymer Coated Super Paramagnetic Iron Oxide Nanoparticles (SPIONs): synthesis, colloidal stability and evaluation for cell tracking

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Stem cell therapies have potential to combat many diseases, especially those that have no known cure. Stem cells can be monitored in vivo using non-invasive imaging techniques such as magnetic resonance imaging (MRI), where cells are labelled with a contrast agent prior to transplantation. MRI contrast agents are normally split into T1 and T2 categories. Super paramagnetic iron oxide nanoparticles (SPIONs) generate much attention as T2 agents, and are often preferred due to high sensitivity and biocompatibility. This high sensitivity allows the visualization of stem cells within certain organs. Synthesis of SPIONs for biomedical applications typically involves synthesis of an iron oxide core, followed by some type post modification technique to render the materials hydrophilic.

Our focus is to manufacture chemical coatings that lead to nanoparticles with high cell labelling efficiency, whilst exhibiting no toxicological effect on cell function. They must also be stable in aqueous conditions. This work follows on from our group’s previous work involving the biocompatible polymer poly[2-(methacryloyloxy)ethylphosphorylcholine]. We use controlled radical polymerisation techniques to produce polymer coated SPIONS with different surface charge and investigate how this can influence cell uptake and colloidal stability in buffer solution and acidic cell-like environments.

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P6. Dynamics and structure: A study of arrest in a non-aqueous colloidal system

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Overbased detergents are a class of engine oil additive, comprising a metal carbonate core (typically 1-10 nm in diameter) surrounded by a sheath of surfactant molecules which are adsorbed to the particle surface. They are included in the lubricant to prevent deposit formation on the metal engine parts and to neutralise acids. With the increased use of bio-diesel, an increase in the volume of small polar molecules (such as water and acetic acid) contaminating the lubricant has been observed. The mechanism of water interaction with overbased detergents has not been fully understood, however, it is known that water hinders their efficacy.

The effect of water on the overbased detergent is largely determined by its interactions with the surfactant molecules. When water was added to samples of sulfonate overbased detergents, sedimentation of surfactant and some metal carbonate occurred in the following 24 hours. Upon the addition of water to solutions of a particular salicylate

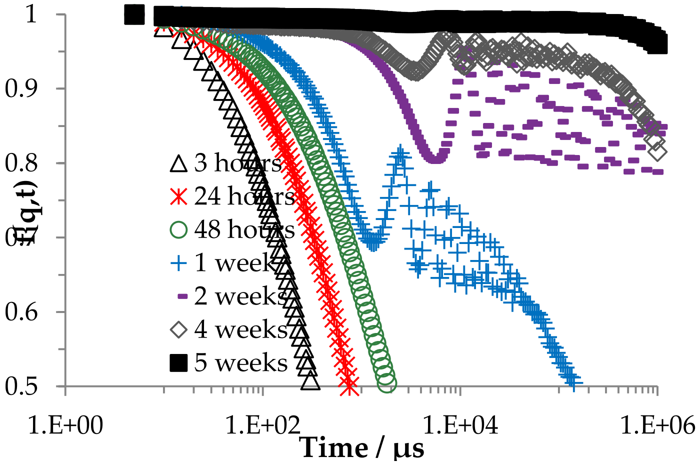

Fig. 1. Normalised intensity correlation functions, f(q,t) of one gelling sample over 5 weeks.

overbased detergent in n-dodecane, gelling occurs over a period of weeks. The dynamics of gelling and mechanical properties of the gel have been found to vary depending on the volume fraction of particles and the volume of water added. This system has been studied by dynamic light scattering (see fig. 1) and small angle neutron scattering. The gels have been characterised using controlled stress rheology and thermogravimetric analysis; results have shown different compositions and rheological properties at different sample heights. The arrest is hypothesised to be due to a depletion interaction, induced by the formation of aggregates of surfactant. Varying the particle volume fraction, volume of contaminant and free surfactant concentration have all been found to have an impact on the arrest.

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P7. Synthesis of multi-voided polymeric particles

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Porous micro-particles have very broad applications and may be synthesised using emulsion non-solvent induced phase separation (NIPS). The properties of a colloidal emulsion may be exploited in order to control key manufacturing features, such as particle size and porosity.

A polymer may be dissolved in a good solvent to make a polymer solution of a desired concentration. The polymer solution is added to a non-solvent along with a surfactant to form an emulsion. Stirring rate allows to control droplet size. Each droplet of polymer solution becomes an independent system, and the droplet size is directly related to the final polymer particle size. When the emulsion is transferred to a “precipitator” solvent for quenching, the precipitator/solvent exchange determines polymer precipitation and vitrification, leaving particles with a porous morphology. A smaller particle allows a higher precipitator/solvent exchange rate, affecting the pore size. This way both particle and pore size may be controlled.

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P8. Non-aqueous microgels and the Flory Rehner theory

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Microgels are cross linked polymer latex particles that form stable colloidal dispersions. Their typical sizes range from 10 to 1000 nm in diameter and they can display a swelling – de-swelling transition in response to external environment (pH, temperature and solvency). However, in non-aqueous solvents, microgels have only been shown to swell in response to solvency and the scope for observing any swelling transition is more limited.

The Flory-Rehner theory (FRT) [1, 2] describes the swelling behavior of macroscopic polymer gels and is an extension of the phase theory for polymer solutions. In principle, the theory can also be applied to microgel particles, however a quantitative verification of the FRT as applied to microgels does not appear to be available.

The FRT highlights three key parameters in the swelling transition of gels: the average molecular weight between cross links, the solvent molar volume and the Flory-Huggins solvent parameter. These three parameters can be used to predict how gels will behave.

Microgels made of styrene and divinylbenzene monomers are swollen in various organic solvents and from this a swelling ratio of the particles can be determined. It is shown that, at least qualitatively, the FRT provides a useful guide to swelling behaviour of non-aqueous microgels.

[1] P.J. Flory and J. Rehner, *J. Chem. Phys.*, 1943, **11**, 512-520.

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P9. Zwitterionic SiO2NH2-Au Particles with Tunable Patchiness via Wrinkle Templating

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In this work we present a template-based approach utilizing wrinkled surfaces to obtain zwitterionic SiO2NH2-Au patchy particles. Templates are prepared by stress release on a bilayer system consisting of an elastic PDMS basis and a rigid silica top layer, generated by air plasma oxidation. In the next step amine-functionalized silica particles are assembled on top of the wrinkles, immersing a defined part of the particle into the wrinkle grooves and leaving only the accessible surface area available for further modification. In an electrostatic adsorption step gold nanoparticles are added on top of the substrate for partial modification of the silica surfaces. Ultrasonication or wetting of the surface with a water droplet releases particles with two oppositely charged hemispheres. Variation of wrinkle dimensions offers the ability to control the patchiness of the resulting SiO2NH2-Au particles. Additionally alignment on wrinkle templates allows for further modification like enhancement of the gold to a closed structure.

We performed interfacial tension measurements to prove the surface activity of the SiO2NH2-Au patchy particles at an oil/water interface. Depending on charge and charge distribution of the particles, shown by ζ-potential measurements at different pH-values, orientation at the interface relative to the curvature and the Janus character correlating with the coverage of the interface the differing values could be explained.

The ability to adapt waterborne patchy particles towards system requirements by variation of patchiness and surface charges should surpass standard surfactants as emulsion or foam stabilizers.

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P10. New method to predict the surface tension of colloidal polyelectrolyte/surfactant mixtures

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While the surface tension of complex mixtures determines the fate of important natural processes like the stability of aerosol droplets in clouds and the biological function of lung surfactants, the property is notoriously difficult to interpret and model. For example, it was established over a decade ago that some strongly interacting colloidal polyelectrolyte/surfactant (P/S) mixtures exhibit a peak in their surface tension isotherms [1]. Recently we have systematically linked the peak of a strongly interacting P/S mixture to slow dynamic changes in its bulk phase behavior [2], and we went on to demonstrate the non-equilibrium nature of the system [3]. Here we present a new approach that successfully predicts the surface tension of two synthetic mixtures (Pdadmac/SDS and NaPSS/DTAB) and one biologically-relevant mixture (DNA/DTAB). The approach is based on the non-equilibrium framework of comprehensive precipitation of kinetically-trapped aggregates followed by their transport under gravity away from the probed interface. Importantly our approach does not need any measurements of the surface properties of the mixtures; only the surface tension isotherm of the pure surfactant and some bulk measurements of the mixtures are required. This simplification in our understanding of the surface properties of strongly interacting mixtures may lead to the optimization of applications involving commercial synthetic polymers, DNA and proteins at surfaces, such as in common household formulations as well as drug and gene delivery applications.

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P11. Key factors regulating the mass delivery of macromolecules to model cell membranes: gravity and electrostatics

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An immense effort has been invested to understand the mechanisms of interactions between macromolecules and lipid membranes [1]. A key challenge is to develop drug delivery systems involving the efficient transport of therapeutic agents to cell membranes [2]. One approach is to position reservoirs of the drug in contact with the membrane for continuous delivery in the form of self-assembled aggregates in colloidal systems [3]. This approach can provide a way to reduce dosages and the frequency of injections administered to patients. In this poster we show that both gravity and electrostatics can be key factors regulating interactions between model cell membranes and self-assembled lamellar aggregates of dendrimers and phospholipids [4]. The system is a proxy for the trafficking of reservoirs of therapeutic drugs to cell membranes for slow diffusion. Neutron reflectometry measurements were carried out on supported lipid bilayers of varying charge and on hydrophilic silica surfaces. Translocation of the macromolecule across the membrane and adsorption of the lamellar aggregates occur only when the membrane is located above the bulk liquid and has sufficient charge. We emphasize the dramatic directionality effects to researchers involved in biochemical investigations of complex formulations. Further, our findings indicate the potential to switch on the interaction through tuning the charge of the aggregates and/or to specific cell types, which is discussed in the context of potential future targeted drug delivery applications

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P12. Measurement of Partition Coefficient of a mutually soluble solvent in oil/ mixture of polymer + salt + water systems

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Solvents that are soluble both in water and in oil can enhance oil recovery from oil reservoirs. The mutually soluble solvent is always dissolved in the aqueous phase and then it is carried through the reservoir. Upon contact with oil phase, the mutual solvent migrates into the oil phase and it mobilizes the trapped oil. The extra oil recovery is critically depends on the partitioning of the solvent in the oil phase. Here the concentration ratio (partition coefficient) does not depend on the relative volumes of the oleic and the aqueous phase; and it is a constant parameter for such a system.

The partition coefficient of two mutually soluble solvents in different water-NaCl-polymer / oil systems has been investigated. The mutually soluble solvents were dissolved first in polymer solution in a flask. Then the oil phase was added to the mixture and the flask and it has been shaken for a period of about 24 hours over a shaker. Afterwards, the volume fraction of the solvent in the oleic phase and the volume fraction of the solvent in the aqueous phase were measured.

The effect of oil type, polymer concentration, presence of NaCl in the aqueous phase and the solvent concentration in the aqueous phase has been investigated. The result shows the presence of NaCl increases the partition coefficient. The higher solvent concentration leads to a higher partition coefficient. The partition coefficient was first increased with the increasing of the polymer concentration, after a pick it was decreased. Moreover, increasing the oil viscosity decreased the partition coefficient. The partitioning coefficient of solvent A is always bigger than the partition coefficient of solvent B. However, the above mentioned behaviour of the partition coefficient for the presence of NaCl, the polymer concentration, the oil viscosity and the solvent concentration is the same.

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P13. On the design of supracolloidal chirality

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Understanding how chirality is expressed, controlled, and propagated at the microscale is of much topical interest for bottom-up routes to functional materials [1, 2]. This presentation will describe computational approaches to programmed assembly of supracolloidal chiral architectures with achiral building blocks, maintaining a close tie with contemporary experimental research. Illustrative case studies will be presented, demonstrating how chirality can emerge from the interplay between two competing length scales for anisotropic interactions [3], how helix-handedness inversion can potentially be exploited [4], how the pitch of a supracolloidal helix can be controlled [5], and how a minimalist design rule for a Bernal spiral with patchy colloids can be derived [6].

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P14. Synthesis of Magnetic Polystyrene Nanoparticles using Amphiphilic Ionic Liquid stabilized Miniemulsion Polymerization

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In our study, we have synthesized polymer magnetic nanoparticles (PMN) using miniemulsion polymerization (MEP) process. We have investigated the use of imidazole based amphiphilic ionic liquids as surfactant in MEP of styrene to prepare PMN. Following the demand for producing magnetic colloidal nanoparticles with nice stability as well as with high content of magnetic nanoparticles (MNP) for several applications, we have explored an efficient pathway to increase the MNP content in the composite through RAFT mediated MEP. A carboxyl-terminated chain transfer agent (CTA) has been proved to be useful to increase the MNP content in PMN. The content of MNP as well as morphology of PMN was possible to adjust by controlling the initiator to CTA mole ratio. The type of initiator (water soluble or water insoluble) had also an effect on the morphology of PMN. The influence of MNP on the molar mass distribution of polystyrene in PMN both in absence and presence of CTA has been investigated. The characterization of the materials has been performed by TEM, SEC, DLS, and TGA. Finally the magnetic property of the materials was determined by vibrating sample magnetometer (VSM) analysis.

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P15. Controlling Shell Thickness of Large Core-Shell Drops in Non-Confined Microfluidics

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For numerous encapsulation applications such as nutrients, drugs, and long-term cell encapsulation, large core-shell droplets or particles are required.1-3 Such structures exhibit greater stability with thin shells4, while their permeability can be controlled via suitable material selections to tune release profiles.5 Variation in shell thickness of core-shell droplets formed in a confined, flow-focused microfluidic approach is already known.6 We introduce a non-confined microfluidic approach that produces giant core-shell droplets under the influence of buoyancy, which has so far remained unexplored. Two glass capillaries with selectively treated surfaces were coupled, aligned and housed inside a vessel containing the quiescent continuous phase. We demonstrate the production of giant core-shell drops, with droplet diameters ranging from 1.6 to 6 mm and typical shell thickness in the hundreds of micrometers. We also show an alternative approach for producing core-shell drops having ultra-thin shells using a single-step, biphasic flow using the same device. The relative thickness of shells was controlled by the relative flow rates of inner and middle phases (Figure 1). Droplets with diameters within 200 µm - 1.8 mm having shell thickness of 1 - 30 µm were produced. The facile nature of working with such systems by having a quiescent outer phase and non-confined geometry means scale up would be easy.

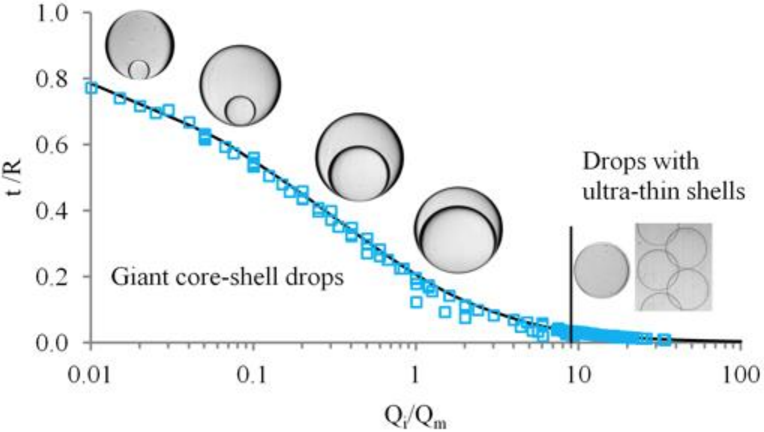

Figure 1. Relative shell thickness (t/R, t: Shell thickness, R: Drop radius) versus inner-to-middle phase flow rate ratio (Qi/Qm) curve showing the drops with thin shells obtained towards high Qi/Qm.

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P16. Dextran-covered nanocapsules prepared by interfacial “click” reaction

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Submicron polymer particles have attracted a great interest in the past few decades. They have been extensively investigated in drug delivery systems or as other active substances carriers1. Nanoparticles can be divided into two main groups: nanospheres, with homogenous structure in a whole particle, and nanocapsules (NCs), which have a typical core-shell structure. The liquid core of nanocapsules allows facile encapsulation of hydrophilic or hydrophobic substances. It is possible to control their release by adjusting the nature and thickness of the polymer shell, but also the polarity and the volume of the liquid core2. Taking into account these advantages, we focused our interest especially on polymer nanocapsules.

To assure the biocompatibility and biodegradability of NCs, we choose polylactide (PLA) as inner hydrophobic polymer shell and Miglyol 810 (a neutral oil widely used in biochemistry and cosmetics) to form the liquid core. NCs were also surrounded by a hydrophilic shell of Dextran (a natural polysaccharide), to ensure their colloidal stability.

There are many different methods to prepare the oily core-polymer shell objects3. Based on our previous works4, to obtain NCs with well-controlled morphology, we combined the classic method of emulsion-solvent evaporation with the interfacial in situ “click” CuAAc reaction. By varying four parameters: power and time of sonication, chemical nature of catalyst and amount of Miglyol 810 in the organic phase we successfully optimized the “click” reaction between α-alkyne PLA and reactive surfactant DexN3 at the oil (dichloromethane mixed with various Miglyol 810 amount)/water interface. The obtained objects were characterized in terms of size, colloidal stability and dextran coverage stability with or without the “click” reaction as well as copper residual amount.

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P17. Preparation of sterically stabilized aqueous nanodispersions using modified poly(ethyleneimine)s

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New approaches of producing aqueous dispersions of nanosized particles prepared from water insoluble actives (e.g. drugs, paints, optoelectronic nanodevices) have attracted much attention in the last decade. Due to their inherent instability, these particles require special means of treatments to provide colloid stability. Numerous surface modification agents ranging from alkyl chains to macromolecules have been applied for this purpose. Our aim is to perform a systematic investigation how efficiently hydrophobically modified poly(ethileneimin)s (hf-PEI) can perform for this purpose. PEI is hyper-branched weak polyamine that is widely used both in research and industry when surface modification is required. To enhance its interaction with hydrophobic nanoparticles we grafted the PEI molecules with various hydrophobic chains. We investigated the effect of graft and charge density, the alkyl chain length and the effect of PEI molecular weight. To test the efficiency of the hf-PEIs we used model nanoparticles stabilized in an organic solvent and the solvent exchange technique to prepare an aqueous dispersion. The characteristics of the prepared aqueous dispersions were investigated by turbidity, dynamic light scattering, and electrophoretic mobility measurements as a function of sample age and ionic strength.

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P18. Superhydrophobic Silicone Nanofilaments for Coating Solid Surfaces

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Silica nanoparticles, which can usually be prepared via Stöber reactions in the presence of a suitable amount of ammonia catalyst, are frequently used in the fabrication of self-cleaning surfaces. However, to achieve superhydrophobicity, the nanosilica-modified surfaces need to be further functionalized with low-surface-energy materials. Here, we describe the preparation of polymethylsiloxane nanofilaments in a facile way, i.e., the hydrolysis of trichloromethylsilane in toluene in the presence water without using any catalyst. With such a technique, a dense SNF layer can be grown on various substrates, including glass, silicon, ceramics, Titanium, Aluminum, cotton fabrics, silk, wood, polyethylene, and so on, by liquid (wet toluene) phase deposition of trichloromethylsilane (TCMS) in the presence of a trace amount of water (ca. 50 ppm to 200 ppm) at room temperature. The water repellent properties can be controlled by a variety of reaction parameters, such as silane precursor, reaction time, water content, etc. Besides, such a coating exhibits excellent chemical and environmental stability.

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P19. Development of nanoparticulate systems for delivery of novel oligonucleotide antibacterials

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DNA-based therapeutics such as transcription factor decoy (TFD) oligonucleotides are being developed as new antibacterials to combat the emerging threat of antibiotic resistance in the clinic. TFDs mimic the binding sequence of transcription factor proteins, to competitively block expression of essential bacterial genes, thus preventing infection. In our group, this technology has been successfully applied to stop bacterial growth in vitro and treat infections in animal models. The major technical challenge is delivery of these oligonucleotides, which as large, highly charged molecules cannot permeate membranes and are also susceptible to enzymatic degradation in biological fluids. In order to improve the bioavailability, a dequalinium analogue is being developed as a delivery system. The analogue readily forms nanoparticles that encapsulate the TFD. Nanoparticulate TFDs are not only protected from biological degradation but also have the ability to deliver the oligonucleotide to the bacterial cytoplasm. Further, this has been demonstrated with Gram-positive and Gram-negative bacterial pathogens with markedly different cell walls suggesting that the delivery mechanism is robust. We refer to these nucleic-acid based therapeutics as SnareTM antibacterials. Our current efforts are focused on the development of stable formulations and on the physical and structural characterization of the complex formed between the TFD and the dequalinium analogue. In order to define key biophysical parameters of the lipoplexes to scale up production and allow progress to clinical trials, but also to understand to what extent the properties can be engineered to control the biodistribution and PK/PD of the SnareTM antibacterials and therefore the range of infections they may be designed to treat.

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P20. Particle-stabilised aqueous ethanol foams

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It is possible to encapsulate various liquids in particle-stabilised materials, such as liquid marbles, particle-stabilised emulsions and "dry water". Encapsulation may allow for controlled release of an active component dissolved in the encapsulated liquid, and this may be manipulated by appropriate selection and variation of the particles comprising the shell. We investigate how liquids may be successfully encapsulated by solid particles until they are required at the point of use. To control this process, the behaviour of particles at various aqueous liquid-air interfaces should be understood. Therefore we have investigated the effect of reducing surface tension of the aqueous phase on the colloidal behaviour of a range of particles. Our results show that with decreasing surface tension, a transitional behavior from liquid-in-air systems (dry water, liquid marbles) to air-in-liquid systems (foams) is observed. With further decrease in surface tension, particle dispersions were formed. We have explained this behaviour by direct measurement of the particle contact angles at the aqueous ethanol-air interface. The information gathered helps our understanding of the boundaries of encapsulation for application in forming dry water and liquid marbles with active components in the liquid core.

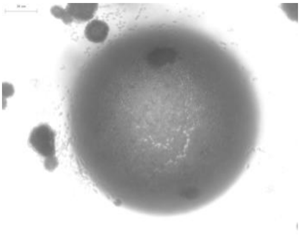

Figure 1. Microscopy image of an air bubble in an aqueous foam stabilised with hydrophobised silica particles (2 µm diameter) Scale bar – 30 µm

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P21. RAFT Dispersion Polymerisation in Non-Polar Solvents: Facile Production of Block Copolymer Spheres, Vesicles and Thermo-responsive Worms in n-Alkanes

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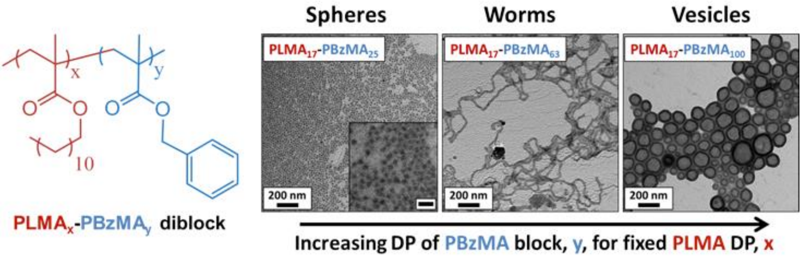
Well-defined poly(lauryl methacrylate-benzyl methacrylate) (PLMA-PBzMA) diblock copolymer nanoparticles are prepared in n-alkanes via RAFT dispersion polymerization.1 Using a relatively long PLMA macromolecular chain transfer agent (macro-CTA) leads to the formation of well-defined spherical nanoparticles. In contrast, using a relatively short PLMA macro-CTA enables both worm-like and vesicular morphologies to be produced, in addition to the spherical phase. Particular attention is paid to the worm phase, which forms soft free-standing gels at 20°C due to multiple inter-worm interactions.2 Such worm gels exhibit thermo-responsive behavior: heating above 50°C causes a worm-to-sphere transition that leads to de-gelation. This worm-to-sphere thermal transition is irreversible in dilute solution (0.01 % w/w), but more or less reversible in concentrated solution (20 % w/w). Surface plasticization of the worm cores is invoked to account for the observed change in morphology, since this is sufficient to increase the copolymer curvature and hence induce a worm-to-sphere transition.



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P22 The Application of Mixed Surfactant Systems to developing Hierarchical Porous Silicas

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Hierarchical porous silica structures are widely used in various applications in the field of adsorption, sensing and catalysis in terms of their high specific surface areas and wide pore size distribution. These materials are used as substrates to produce catalysts as they have ordered porous structures, and the efficiency of these catalysts depends on the morphology of the silicas. In addition, adding macropores (>50 nm) to the mesoporous (2-50 nm) system, the properties of both meso network and macropores could be exploited simultaneously which results in increased mass transport and accessibility to the active sites, leading to enhanced performance the materials.

In this work, hierarchical porous silicas have been synthesised in order to display multimodal pore sizes in the silica network which are desirable to provide improved flow performance coupled with high surface areas. Hydrocarbon surfactant hexadecyltrimethylammonium bromide (CTAB) has been used with a fluorocarbon surfactant, Zonyl-FSN-100 which has an average chemical structure of C8F17C2H4 (OC2H4)9OH. Perfluorohexane was used as an oil phase in the emulsion solution, and is used as a variable parameter to show how the mixed or demixed micelles form in the emulsion, which acts as a template to form bi-modal mesoporous silicas. The phase behaviour of these surfactant/water/PFH systems has been studied. The resulting silica materials possessed high surface area over the range 600-1110 m2g-1), mesopore volumes of 1.2- 2.3 cm3g-1 and pore diameters of 2.5-3.4 nm. Sulfonic acid functionalization was realized to yield mesoporous solid acid catalyst using postgrafting techniques.

The catalytic performance was estimated using palmitic acid esterification as a benchmark reaction. Thus, the synthesis of porous silica network and its characterization in this study have been considered based on emulsion chemistry using hydrocarbon and fluorocarbon surfactants.

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P23. Characterization of lipophilic and hydrophilic dye-loaded red blood cells as delivery carrier

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Natural and biomimetic concept have extensively developed and optimized for application in drug delivery system (DDS). Among the intrinsic cellular based carrier the most have been attention are red blood cells. Red blood cells are biocompatibility and biodegradable sourced from endogenous cells which can avoid provoking an immune response and prolonged the circulation in bloodstream. In terms of the structure, red blood cells own unique biconcave discoid feature and large inner space. It provides sufficient space to entrap the active pharmaceutical ingredients which enable to provide sufficient space for encapsulating various types of active pharmaceutical ingredients. In the present work, we employed hypotonic dialysis method to prepare red blood cell ghosts in order to disrupted membranes of red blood cell empty out the haemoglobin. The aim of the study was to investigate the influence factor in preparation process and to validate the drug-loaded red blood cell ghosts. Rhodamine 6G (R6G; lipophilic dye) and fluorescein isothiocyanate (FITC; hydrophilic dye) are as model drug. The results demonstrated that gradient isotonic solution, dialysis time, dialysis bag volume and concentration of dye were influence in entrapment efficiency. Scanning electron micrographs of red blood cells presented biconcave discoid feature and inner space can load active pharmaceutical ingredients.

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P24. Highly Charged and Salt Free Nonpolar Colloids

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The low dielectric constant which defines nonpolar media results in long ranged electrostatic interactions, with interesting ramifications for colloids. In particular the phenomenon of counterion condensation, an important facet of some aqueous polyelectrolytes such as DNA [1], is also important in nonpolar systems. For a polymer charged above a critical value, counterions are predicted to condense into a tightly bound layer on the polymer, with a diffuse phase of surrounding counterions. While well established for aqueous polyelectrolyte systems, spherical colloids have never shown this behaviour due to geometric dependent entropic considerations.

By using spherical particles containing a covalently bound ionic liquid and dispersed in dodecane, a highly charged, salt free and unique system is prepared with which the aforementioned phenomena can be studied. Prior results on this counterion only system have shown strong evidence for a condensation effect dependent on particle volume fraction [2]. In this poster, pair potentials measured with the aid of blinking optical tweezers [3] will be presented. The results will be discussed in the context of more traditional aqueous potentials as well as more complex systems such as Pickering Emulsions.

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P25. Effects of native and modified cyclodextrins on the aggregation behaviour of poloxamines in water

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Amphiphilic linear surfactants based on polyethylene oxide/polypropylene oxide (PEO/PPO) triblock copolymers, known as poloxamers or Pluronics, exhibit a rich polymorphism in water, which can be tailored by modifying the molecular weight, the PEO/PPO ratio, and the distribution of the hydrophilic and hydrophobic blocks1,2. Their structural features and physicochemical properties, as well as their potential applications in drug delivery and targeting, are well documented3,4. An interesting and less studied family of polymeric surfactants based on PEO and PPO are poloxamines, or Tetronics. These are four-armed (X-shaped) copolymers containing a PEO and PPO block per arm. For the purpose of developing drug delivery vehicles, Tetronics show advantages over Pluronics, in particular because of the central ethylene diamine spacer, which makes drug loading and release pH-sensitive and offers the possibility of site-specific delivery5,6.

Cyclodextrins (CDs) are known to direct micellization processes either by the formation of inclusion compounds or by other modes of interaction7. The combination of native CDs with Pluronics may lead to the formation of pseudo-polyrotaxanes and gels8, which have obvious applications for sustained release, while the effect of substituted CDs is highly dependent on the nature of the substituents, leading in specific cases to full micellar rupture, which is envisaged as a trigger for controlled release7.

In this contribution, we study the effect of native and substituted CDs on the micellization process of three Tetronics (304, 904, 1307 and the reverse 90R4), having different HLB and aggregation properties, by using a combination of techniques (SANS, DLS, and NMR). We have also explored the rheological behaviour of the gels formed at high concentration of poloxamine as a function of temperature, as a first step towards the development of drug delivery systems.

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P26. Manipulating the large scale structure of plate-like clay colloids in aqueous suspension

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Known for their anisotropy in shape, clay minerals have found wide industrial use due to the formation of low volume fraction colloidal gels and the ability to fine-tune the properties of these materials using surface chemistry. The formation of liquid crystalline phases in these systems has been a long running academic pursuit as gelation often intervenes. Despite this, their exact structure is still under debate for static systems and is poorly understood under flow.

Aqueous suspensions of the plate-like clay montmorillonite have not been reported to form a thermodynamic liquid crystalline phase unlike other clay minerals of similar particle shape. This is thought to be due to weaker electrostatic repulsion between particles, reducing the excluded volume effect and allowing gelation before the liquid crystalline phase is able to form.

It has recently been shown that the rheological properties of montmorillonite suspensions can be dramatically altered by adsorbing an amine terminated amphiphilic polymer to the surface of the platelets as a means of masking electrostatic interactions [1]. The most striking effect being a near doubling of the weight percentage of clay required for a sol/gel transition. We present scattering measurements showing that the only structural change accompanying this is the prevention of a tenuous 1 dimensional structure forming at length scales corresponding to tens of microns. This is at odds with more established surface treatments such as sodium pyrophosphate [2] which exhibits similar rheological modification yet does not appear to prevent the formation of this 1-dimensional structure.

These results suggest the existence of multiple mechanisms of structural modification that can alter the flow properties of plate-like clay suspensions. Such mechanisms appear to be both large scale and controlled by the interactions between particles.

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P27. Synthesis and Characterisation of Poly(amidoamine)-BSA conjugates

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Although the development of therapeutic proteins has increased over the last decades, their general use as therapeutic agents has been hindered by their immunogenicity and their ability to reach intracellular targets. Several polymer-protein conjugates have been developed with success to overcome some of these limitations 1. However, efficient intracellular delivery remains a challenge and restricts the use of proteins with an extracellular target. Poly(amidoamine)s 2,3 (PAAs) are pH responsive polymers and have been used to promote intracellular delivery of different macromolecules via interpolyelectrolyte complexes. Our objective was to develop a method to obtain a poly(amidoamine)s-protein conjugate that could promote cytosolic delivery.

PAA with vinyl end groups was synthesised by Michael addition polymerisation and characterised by NMR, FT-IR and GPC (Mw = 13.2 kDa, PDI= 1.92). PAA-BSA conjugates were synthesised by hydrogen-transfer between the PAA vinyl groups and the NH2 groups present on the surface of the protein 4. The bioconjugation was carried out at pH 8 and 9 for 24 h, 4 days and 8 days. The reaction mixtures were recovered by freeze drying followed by ultrafiltration. The samples were analysed by native and SDS PAGE electrophoresis. A conjugate was only observed after 8 days, at both pH. The conjugates showed different elution times compared to BSA and PAA. SDS PAGE gels showed the presence of a high molecular weight conjugate (~200 kDa) suggesting that there are approximately 10 chains of PAAs (13.2 kDa) per BSA (66.4 kDa). The conjugates were further purified by anionic exchange chromatography to remove any unconjugated protein.

The method developed in this study could be used to develop a bioconjugate using a therapeutic protein with an intracellular target.

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P28. Development of novel functional magnetite nanoparticles for evaluation of human mesenchymal stem cell (hMSC) labelling in a tissue-engineered airway

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With the successful transplantation of a tissue-engineered larynx into a patient1, the clinical use of stem cell therapy is promising. The cellular distribution, function and viability of human mesenchymal stem cells (hMSCs) must first be evaluated in a safe and non-invasive manner.2

Several studies using commercially available (Feridex® and Resovist®) or synthesised iron oxide nanoparticles have allowed labelling and tracking of hMSCs in vitro by magnetic resonance imaging (MRI).3-5 However, most of these materials are not suitable for biomedical applications as they are made in organic solvents and require complex post-synthesis phase transfer by ligand exchange. To overcome this, we present the use of a microwave-assisted simple one-pot synthesis of iron oxide nanoparticles by the polyol method for their use as contrast agents in MRI. This novel method is reliable and leads to mono-disperse, water-soluble and stable nanoparticles further functionalised for biomedical applications with different coatings such as citrate or fluorescent silica coating. Their enhanced cellular uptake and magnetic properties allow their use in cellular tracking by MRI.

In this study, experiments are carried out to optimize the synthetic method, properties (size, coating), and dose of the nanoparticles for their uptake by hMSCs. MRI of hMSCs labelled with nanoparticles as contrast agents is a useful tool towards further understanding their role in tissue-engineered organs. While active targeting of magnetic nanoparticles with specific antibodies has been thoroughly studied to control their biodistribution, a novel strategy to obtain information on the differentiation stages of transplanted hMSCs in vitro was studied. The use of a superparamagnetic iron oxide nanoparticle based imaging modality could be therefore applied to assess the success of stem cell therapy.

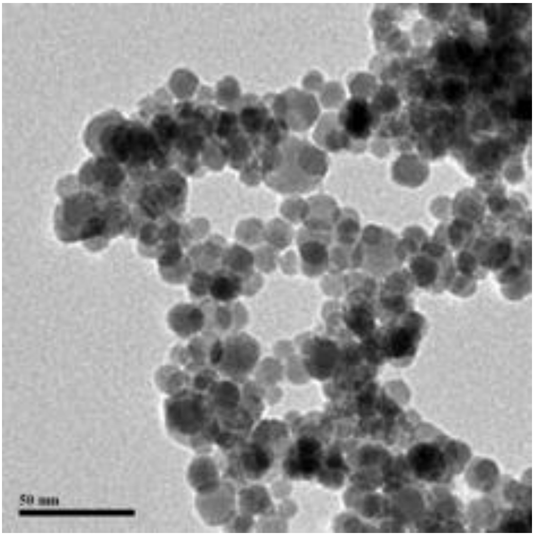

Figure 1: TEM image of novel magnetite nanoparticles synthesised by the polyol method

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P29. Template-directed Synthesis of Hybrid Mineral Hollow Capsules via o/w Emulsions

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Nature provides intelligent solutions for the design of novel hybrid materials of various shape and compositions under mild and energy efficient conditions.

Functional materials containing hydroxyapatite have a growing demand in medical applications. We are able to synthesize mineral hollow capsules of hydroxyapatite *via* a template-directed synthesis. The basis of this biomimetic synthesis is a protein stabilized oil/water emulsion. The oil phase serves as a template for the mineral hollow capsules, whereas the protein serves at the one hand as an emulsifier and on the other hand as a matrix where ions - like calcium and phosphate ions - can bind and crystallization of hydroxyapatite can be induced. Among other proteins, the small globular protein hydrophobin fulfils these two functions due to its self-assembly properties and amphiphilicity resulting from its hydrophilic and hydrophobic patches. Influencing the scaffold *via* the choice of protein or oil, we can tune the morphology of the mineral capsule wall. Furthermore, we use different low molecular agents to alter the morphology even further.

Moreover, we investigate the dynamics of protein adsorption *via* pendant-drop-measurements, since the matrix protein plays a crucial role in the crystallization step. Here, we focus the denaturation and reorientation processes of the protein that can be reached by adapting the measured time-dependent interfacial tension to protein models.

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P30. Controllable Nitric Oxide Release in the presence of Gold Nanoparticles

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A major problem associated with nitric oxide (NO) donors is the release of the desired amount of NO at a specific site. A number of platforms have been developed for the regulation of NO dosage. We present the use of citrate stabilized gold nanoparticles as a platform to regulate NO release. Because of the affinity between gold and thiols, the characteristic -S-NO bond of S-nitrosothiols (RSNOs) breaks in the presence of gold nanoparticles, thereby releasing NO and modifying the gold nanoparticle surface with the corresponding thiol. This system allows for surface-controlled NO release, where the amount of NO released is proportional to the number of thiols bound to the gold nanoparticle surface. Moreover, by employing an amperometric technique to detect the maximum NO release, we were able to estimate the stoichiometry of the reaction, that is, the number of adsorbed RSNO molecules per gold nanoparticle1. The obtained values agree reasonably well with those found by a direct technique such as Isothermal titration calorimetry (ITC) 2. A kinetic model for NO release and its subsequent decomposition is proposed and used to fit the experimental results. The reaction order was found to be zeroth- and first- order with respect to RSNO and gold nanoparticles respectively.

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P31. Ink-jetting stabilised colloids with polymers

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Mixtures of ethylene glycol and water (EGW), with ≤ 1 wt% extra polymer (10 kDa PEG - polyethylene glycol - or 100 kDa PEO - polyethylene oxide), and ~15±1 wt% dispersed polystyrene particles, were jetted from a drop-on-demand (DoD) print head (MicroFab ABP 80 µm diameter) with a range of actuation drive voltages. Spark flash shadowgraph imaging established the break-off times and drop speeds achieved. No significant differences between the observed break-off times were found for these fluids (i.e. for the EGW mixture alone, for EGW with the extra polymer at various concentration levels, and these with the colloid suspension). This result is consistent with the measured near-Newtonian rheology for the colloidal solutions. Effects of the ~400±40 nm hydrodynamic particle diameter with ≤ 1 wt% extra polymers appear to be rather small for inkjet printing, thus aiding applications. Jet break-off was located near the nozzle exit for the colloidal jets whereas without colloids the jet break-off moved from the head end for low added polymer towards the nozzle exit for higher extra polymer concentrations or molecular weight. The jets without colloid tended to produce more satellites than the colloidal jets at given DoD drive voltage, but most probably because they also produced jets with higher total volumes and drop speeds. Added 100 kDa PEO at ≤ 0.1 wt% produced similar effects to added 10 kDa PEG at 1.0 wt%, a similar factor to that observed in other comparisons of PEO and PS jetting.

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P32. Self-Assembly of Cyclodextrin Covered Particles at Interfaces

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The main aim of this collaborative project is the investigation of light-responsive, self-assembled, cyclodextrin covered particles at interfaces. These particles could be silica particles as well as modified microgels. We investigated the light-responsive supramolecular adhesion of cyclodextrin covered nanoparticles and a bifunctional, non-covalent azobenzene linker. The self-assembly of these particles is photo-controllable due to the photo-responsive host-guest interaction of cyclodextrin cavities and azobenzene molecules.

In our project, we are focus on the investigation of silica particles in a range from nanometres to micrometres. Using atomic force microscopy, we could show that - depending on different parameters (e.g. particle size, concentration etc.) - these silica particles can be aligned in wrinkled structures to form chains. Furthermore, especially cyclodextrin covered silica nanoparticles can form pickering emulsions. In connection with the above described properties, we investigated the stability of emulsions consisting of cyclodextrin covered nanoparticles and an azobenzene linker. Additionally, we measured the interfacial tension of these silica particles in the absence as well as presence of an azobenzene linker. First results show the influence of the azobenzene linker on the interfacial tension due to a better stabilization at the interface. Currently, we investigate the preparation of photo-responsive chains by cross-linking the aligned cyclodextrin covered particles with an azobenzene linker.

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P33. Addition of water to an alcoholic RAFT PISA formulation affects both polymerisation kinetics and copolymer morphology

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The efficient synthesis of amine-functional diblock copolymer nano-objects via RAFT alcoholic dispersion polymerisation has been recently reported. Benzyl methacrylate (BzMA) is polymerised in ethanol using a poly(2-(dimethylamino)ethyl methacrylate) (PDMA) chain transfer agent at 70˚C. Depending on the packing parameter, p, polymerisation-induced self-assembly (PISA) can produce spherical micelles, worm-like micelles or vesicles. High monomer conversions (> 99% by 1H NMR) are achieved within 24 h, while THF GPC studies indicate low copolymer polydispersities (Mw/Mn < 1.30), suggesting good pseudo-living character. When transferred from ethanol to water, the nanoparticles remain colloidally stable and acquire appreciable cationic character, as judged by DLS and aqueous electrophoresis studies respectively. Utilising an ethanol/water mixture leads to a significantly faster rate of BzMA polymerisation, with 80% conversion being achieved at 70oC within 7 h. This is presumably because water is a poor solvent for the BzMA monomer, which partitions into the growing micelles; thus enhancing the local monomer concentration and increasing the polymerisation rate. Moreover, the addition of water also affects the final copolymer morphology, with only kinetically-trapped spherical micelles being obtained when targeting diblock compositions that produce well-defined vesicles when utilising pure ethanol. This suggests possible protonation of the PDMA stabiliser chains in the presence of water. The resulting charge repulsion between neighbouring chains means that more asymmetric diblocks (i.e. longer PBzMA blocks for a fixed PDMA block) are needed to achieve non-spherical morphologies.

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P34. Gold Nanoparticles and Biological Structures

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Understanding the interactions of nanoparticles with skin is of high importance for the development of new ways to deliver drugs efficiently but also in order to realize potential toxicity risks. Certainly, the study of the penetration of skin with nanoparticles is a complex research task because it involves a number of parameters that can not be easily controlled related to the complexity of the skin and the type of nanoparticles.

In this presentation we take a thorough analytical approach to answer key questions concerning these interactions. We will particularly focus on how the charge, shape and function of nanoparticles influence the penetration through skin. For our studies we chose to work with gold nanoparticles due to the ease of their surface modification.

To gain a good understanding, we employ a number of techniques such as ICP-OES to quantitatively measure the penetration of nanoparticles, as well as two-photon photoluminescence microscopy and tem cross sectioning to analytically detect the particles in the skin. Moreover we will hypothesize potential mechanisms of penetration.

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P35. Applications of silica / polymer colloidal core shell particles for antireflective coatings

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Antireflective coatings on a substrate such as glass can be prepared as an interference-type multilayer coating or as a low refractive index gradient coating. In order to obtain a one layer coating with good antireflective properties, very low refractive index materials are necessary. The optimum refractive index n for a one layer antireflective coating is 1.23. There are, however, no low index solid materials that display a refractive index lower than 1.37, therefore the best method to realize materials with a low n, is to reduce their packing density or increase porosity.

DSM managed to develop a coating technology based on silica modified, cationic polymer colloids. For the synthesis of these hybrid nanoparticles, small in-situ produced silica nanoparticles were deposited on cationic polymer colloids. Parameters that influence the growth rate and the density of the silica shell are e.g. pH, temperature and the addition rate of TMOS. The alcoholic particle dispersion is then treated with a silica binder. To obtain an antireflective coating, this formulation is applied on glass in a thickness of $\lambda/4$ and thermally treated at 450-650°C, to introduce the porosity into the coating. The resulting antireflective coating has a porosity of 30-40%, is mechanically robust, with a transmission of 98% or higher, and shows excellent durability.

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P36. Stable vesicle formation from glycolipid biosurfactant and its applications

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Glycolipid biosurfactants, such as mannosylerythritol lipids(MELs), are produced by different yeasts belonging to the genus Pseudozyma and have been attracting much attention as new cosmetics ingredients owing to their unique interfacial action and moisturizing properties. In this study, stable vesicle formation from glycolipid bio surfactant and its mechanism were investigated using a biocompatible Mannosylerythritol lipid(MEL)/phospholipid mixture by varying the composition. The mixed vesicle was investigated dynamic light scattering, TEM and fluorescent microscope. Mannosylerythritol lipid efficiently self-assembled in water to form giant vesicles. Interestingly, the addition of mannosylerythritol lipids into phospholipid liposomes brought various effects on their properties, especially on their structures. Dynamic light scattering(DLS) measurements revealed that the average size of the vesicles at the compostion of XMEL=0.25 was 230nm , which is small compared to other compostions. Moreover, the mixed vesicle was kept its dispersion stability at 25 ℃ for more than 2month, indicating the formation of a thermodynamically stable vesicle. Also, we studied the effect of biosurfactants on cell penetration by liposome. Our results showed that a biosurfactant of mannosylerythritol lipids increased the efficiency of cell penetration mediated by phospholid liposome.

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P37. Particularities of agglomeration of nanoparticles in aqueous colloids

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Experimentally studying water colloids with nanoparticles of silica, we found some unusual agglomerations. First, in the vicinity of the outer edges of the films of the suspensions of water and amorphous SiO2 particles, poured onto a glass substrate, optically anisotropic agglomerates of the nanoparticles were found. Their optical anisotropy was determined by enlightenment of their images in crossed polarizers. In the optical microscope agglomerates looked like sticks of length 10 - 15 micrometers and a thickness of a few micrometers , forming clusters in a bandwidth from the edge of about 100 micrometers. With the placement of the suspension between the electrodes with the gap between them of 10 - 20 mm, application of a potential difference of 100-600 volts produced at the positive electrode a set of quasi-periodic rows of silica particles oriented parallel to the electrode. These microparticles , unlike the first case have a circular shape , and showed no optical anisotropy. Row spacing amounts to a few tens of microns. When applying electrical field we observed droplet ejection slurry onto the lower surface of the cover glass (detached above the suspension at 0.3-0.5 mm), with the formation of parallel rows of droplets in the vicinity of the positive electrode. Simultaneously we observed at the negative electrode increase of anisotropic agglomerates like sticks described above. Discovered phenomena are explained by two particularities of liquid water: formation around the silica particles of an electrical double layer of micelles and abnormally high dielectric permittivity of water ($\varepsilon = 81$). Due to decrease of surface tension of water by silica particles they are attracted to the edge resulting in creation of an electric field perpendicular to the edge and leading to the formation of chains of particles having the appearance of stick and the above described optical anisotropy. Due to the fact that the outer surface of the micelles has a positive charge, the anisotropic particles are concentrated at the negative electrode. If a double layer of micelles is destroyed by the electric field of the capacitor, its remaining shell is negatively charged and they are attracted to the positive electrode of the capacitor. But these micelles can’t enter into direct contact with an electrode, due to the fact that they have much lower dielectrical polarization in comparison with water. Due to negative electrical polarization these micelles are pushed away to the regions with lower field. So the equilibrium distance between the rows corresponds to the balance between the attraction and repulsion forces. Therefore, as a result of balancing a row of the particles is formed being parallel to the electrode. Remaining from the shattered micelles positive charges for the same reasons form the next row,eyc. This version can explain the formation of quasi-periodic rows of SiO2 particles, parallel to the electrodes, and the expulsion of these rows on an outer cover glass. The distance between the rows is determined by size and charge of the particles, so the variation of these parameters will provide preparation of regular nanostructures with controlled spatial distances.

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P38. Study of structural changes of water confined in the AOT and Brij-30 reverse micelles by UV-visible spectroscopy

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The microemulsion systems represent a good artificial model of biological membranes due to the likeness of their structure. The analogous picture of normal membrane structure in cell is created by reverse micelles, besides water dissolved in the core of micelle represents the best model of the confined water in biosystems [1]. Complexity of water structure becomes enormous when it is confined to nanometer-scale cavities. Therefore investigation of the properties of water core of the reverse micelles is urgent and topical [2].

The goal of the proposed work was to study the influence of kosmotropic and chaotropic ionic additives introduced in the water nanopools of AOT sodium bis(2-ethylhexyl) sulfosuccinate and Brij-30 (polyoxyethylene (4) lauryl ether) reverse micelles, also in their mixed (AOT+Brij-30) micelles by using ultraviolet-visible spectroscopy.

The microstructure of AOT and Brij-30 reverse micelles were investigated using ultraviolet-visible spectroscopic method. The binding constants of optical probe o-nitroaniline (o-NA) with reverse micelles were calculated. The different influence of kosmotropic and chaotropic ions on water core structure of reverse micelles is reflected in the changes of values of binding constants of optical probe with AOT and Brij-30 reverse micelles, viz., binding constants of o-NA with AOT reverse micelles are greater in the presence of acetate, than in the presence of perchlorate in the water core of AOT reverse micelles. Vice versa, the values of binding constants of o-NA with Brij-30 reverse micelles in the presence of perchlorate ions exceed their values in the case of acetate ions additives in the water pockets of Brij-30 reverse micelles. Results may be useful in the study of properties of water aggregates close to the ionic center of the surfactant.

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P39. A supramolecular route towards hierarchical colloids in water via cucurbit[8]uril complexation

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A supramolecular route towards hierarchical colloids in water based on cucurbit[8]uril (CB[8]) host-guest interactions is proposed. Core–shell polymeric microspheres with a cleavable shell were prepared in water using the supramolecular route as show in Figure 1a. CB[8] was employed to bring together functional polymeric microspheres and functional polymers via CB[8] host-guest interactions. This supramolecular approach offers a powerful tool to switch the cytotoxicity of polymeric microspheres, leading to potential applications in the eradication of cancer cells.

This supramolecular route was further employed to build up hybrid raspberry-like colloids (HRCs) in water as shown in Figure 1b. CB[8] was employed as supromolecular linking reagent to lock methyl viologen functionalised polymeric nanoparticles onto 4-hydroxyazobenzene functionalised silica microspheres via the formation of CB[8] ternary complexes. The formed HRCs are photoresponsive and the disassembly/assembly of the HRCs can be reversibly controlled upon light irradiation. This facile supramolecular route provides a platform for the preparation of hierarchical colloids with advanced structures.

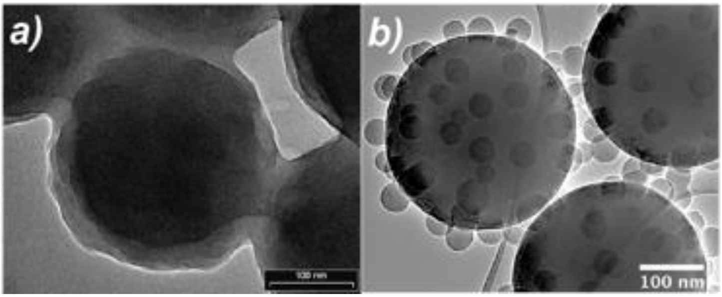

Figure 1: TEM image of a) core-shell polymeric microspheres and b) hybrid raspberry-like colloids based on cucurbit[8]uril host-guest interactions.

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P40. An AFM Study of Droplet-Droplet Interaction with Different Surfactant Concentrations

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The instrument of Atomic Force Microscope (AFM) was used for measuring the force behaviour of two approaching droplets and the influence of experimental conditions including ramp size, trig threshold and drop size on droplet-droplet interaction were explored. The dynamic interaction and deformation of two oil droplets submerged in deionised water phase approaching/retracting each other under different velocities were measured and analysed, which shows a similar velocity dependent trend with Dagastine et al. finding 0 and is believed to be caused by dynamic film drainage process. An experiment to demonstrate the deformation behaviour of droplets containing certain amount of oil soluble surfactant was carried out and the role of surfactant was discussed. Concentrations of surfactant varied in a wide range from far below critical micelle concentration (CMC) to above CMC. Force curves of 8 sets were compared and further converted into drop deformation behaviour. Results show that droplet deformability is sensitive to the amount of surfactant adsorption onto the interfacial film between the two droplets in situ. With surfactant concentration below CMC, the ability of droplets against deformation initially shows an increasing trend and then decreases. As the surfactant concentration continues to increase above CMC, the drop deformability is strengthened further. Interestingly, this trend is similar with that of interfacial dilational modulus curve, which demonstrate that drop-drop interaction and drop deformation is strongly related to the dilational elasticity of the interfacial film.

Reference

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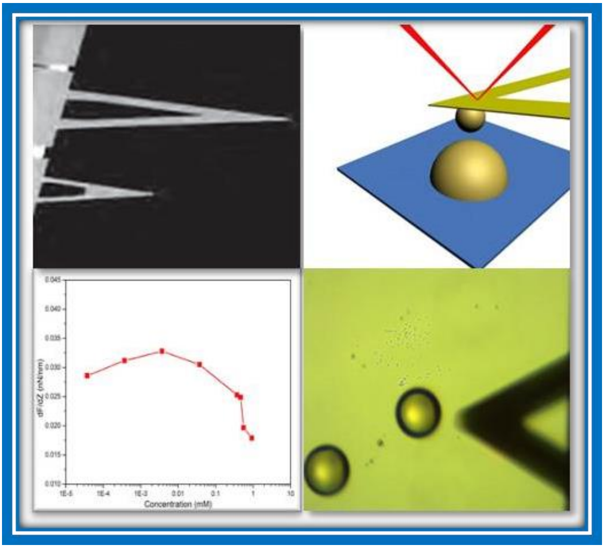

P41. Iron oxide micro-rods at liquid interfaces

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Rod-like particles can induce some interesting properties at liquid interfaces. The structural transitions within rods monolayers are more complex than those of spheres with the similar dimensions or surface chemistry. More interesting, in an external magnetic field, rods with magnetic moments can be used to reorganize the networks at the liquid interface. In the present work, the behavior of monolayers of monodisperse akaganéite rods with or without a permanent moment has been studied in a Langmuir trough. These iron oxide micro-rods have the same size and surface chemistry. Phase transitions and in-plan rearrangements are observed with the increasing of the surface pressure during the compression process. From the microscopy observations, some individual rods flip into a perpendicular position relative to the interface to relieve the compressional stress. For the monolayer of magnetic rods, an applied magnetic field is introduced to fix the rods' ordering direction. The competition of magnetic forces with other kind of forces is evaluated. We hope that our work will aid in understanding the complex interaction between the rods at interfaces.

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P42. Janus Container

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In 1991, P. G. de Gennes in his Nobel lecture firstly employed the term of two faceted Roman God "Janus" to describe characteristics and performances of such particles with two different components districted onto the same surface. In analogous to molecular surfactants, Janus particles of amphiphilic performance were predicated to stack densely at an interface forming a porous monolayer, where small molecules can transport. The non-centrosymmetric Janus materials have been extensively reported with varied shapes including particle, rod, and disc which own two different compositions are compartmentalized onto the same surface.

Beside of Janus particles, we extended the concept of Janus to hollow spheres achieving Janus cages. We realize that an emulsion interface is Janus with both hydrophilic exterior and oleophilic interior surfaces, which can act as a temporal template to prepare Janus shell after duplication. Hydrophilic and lipophilic species self-organized at the interface forming a silica shell which can spontaneously face towards the external aqueous and the internal oil phases, respectively. Micelle-like Janus hollow spheres are achieved. Hydrophobic organic components can be selectively captured inside the cavity from their aqueous surroundings. Selective grafting responsive polymers for example thermal responsive onto the interior surface, the Janus hollow spheres can load oil at high temperature. At lower temperature, the cavity becomes hydrophilic and the oil is released. Janus micro-reactors are further derived after incorporating catalysts such as photocatalytic nanoparticles P25. Decomposition of organic pollutants is completed at a local higher concentration after being collected from their aqueous surroundings.

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P43. Material characterization and CO2 adsorption ability of mesoporous silica synthesized via P123 combined with F68

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Ordered mesoporous silica is the popular adsorbent in pollution removal and separation. For the past few years, mesoporous silica have been considered as potential adsorbent for CO2 removal, due to the high specific surface area, tunable pore size and well-defined pore structure. Especially, SBA-15 with unique micro/mesoporous structure, thicker wall thickness and higher hydrothermal stability is one of the suitable candidates for CO2 capture.

Porous structure has been discussed that was the important parameter affecting on the adsorbent's performance, and then modifying adsorbent with the appropriate porous structures to enhance the adsorption efficiency is concerned. Therefore, P123 combined with F68 is utilizing as the dual-template surfactant to synthesize the mesoporous silica, in order to altering porous structure and improving adsorption capacity. The material characterization of synthesized mesoporous silica in this study are discussed as specific surface area, pore distribution structure and transmission observation of pore structure. In addition, the CO2 adsorption capacity of the synthesized mesoporous silica is also described and compared with the common SBA-15.

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P44. An effective approach to the fabrication of plasmonic structures on graphene based on self-assembly and nanosphere lithography

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Introducing plasmonic structures on top of graphene can be important for sensing and optoelectronic applications, e.g. for the enhancement of photoresponsivity of graphene photodetectors. Electron beam lithography (EBL), which has been used to control their structural and spectral properties [1-2], is not a viable option for the fabrication of patterns over large areas, due to cost and time burden. We propose nanosphere lithography as an effective approach to the fabrication of large area plasmonic structures on graphene and apply proper strategies to avoid possible damage to graphene resulting from surface treatment and further processing steps, which could deteriorate graphene properties.

Self-assembly of polystyrene nanospheres at liquid/air interface is carried out, followed by transfer of the nanosphere monolayers on large area graphene covered by protective layers chosen according to the further processing steps and used to prevent possible graphene damage. The fabrication process is completed by performing reactive ion etching and metal deposition.

Periodic patterns with different spectral characteristics and shapes can thereby be created on graphene, in a more effective way compared to EBL. The plasmonic properties are tuned by proper control over the self-assembly process and reactive ion etching parameters. The approach can be adapted to create other different patterns, e.g. via self-assembly of binary colloids.

This work was supported by the Swiss Innovation Promotion Agency CTI-KTI.

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P45. Oleanolic Acid Delivery using Biodegradable Nanoparticles for Cancer Therapy

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Oleanolic acid (OA) is a naturally occurring pentacyclic triterpenoid widely found in Chinese herbs. It has been extensively studied owing to the beneficial effects such as hepatoprotection, anti-inflammatory and it is recently found to have anti-tumor ability. However, resembling the other hydrophobic drugs, it has poor water solubility and therefore very limited intestinal absorption when administrated orally. Investigations concerning the delivery of OA have been carried out to enhance its dissolution and bioavailability. Nanoparticulate systems involve the reduction of drug particle size into nano-scale thereby increasing the interfacial surface area. As a result, absorption of drug in the body system could be enhanced. Biodegradable polymer-based system can be metabolized by the body system into harmless compounds so it is regarded safe and promising. This study was conducted to evaluate the efficacy of four types of biodegradable copolymers as potential OA delivery nanoparticulate system.

Co-polymers consisting a hydrophilic block: poly(ethylene) glycol (PEG) and a hydrophobic block of either poly(lactic-co-glycolic) acid (PLGA) or poly(lactic acid) (PLA) were used to fabricate a novel nanoformulation to improve OA bioavailability. The OA-loaded mPEG-(D,L)PLA, mPEG-(L)PLA, mPEG-(D,L)PLGA and mPEG-(L)PLGA nanoparticles (NPs), prepared by nanoprecipitation, were observed to be spherical in shape under transmission electron microscope. Results indicated that narrow size distributed NPs with mean hydrodynamic diameter of 200±16.0, 233±13.9, 211±10.1 and 229±10.1nm respectively were obtained. mPEG-(D,L)PLA NPs attained the highest encapsulation of OA with 75.8% efficiency while mPEG-(L)PLGA NPs displayed the lowest encapsulation efficiency at 40.8%. The in vitro anti-tumoral activity was evaluated on A549, lung carcinoma epithelial cell lines using MTT assay. All the four types of OA-loaded NPs demonstrated better anti-cancer ability than saturated OA in medium. Moreover, NPs without OA exhibited significantly lower cytotoxicity towards A549 indicating induced cell death was due to the effective delivery of OA as an anti-cancer therapeutic agent.

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P46. Controlling Competitive and Synergistic Interactions in Formulations

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Amphiphilic block copolymers of the poly (ethylene oxide)–poly (propylene oxide) (PEO–PPO) group (commercially available as Pluronic or Poloxamers) are widely used in numerous applications, especially the pharmaceutical, consumer, technological and formulation areas. Whilst, mixtures of small molecule surfactants and Pluronics have previously been examined, as has the effect of alcohols on Pluronic behaviour. There are far fewer studies of the quaternary systems; Pluronic/small molecule surfactants/alcohol/water.

Against this background, we have employed a range of techniques including surface tension, pulsed gradient spin-echo nuclear magnetic resonance (PGSE-NMR) and small- angle neutron scattering (SANS) to quantify the interaction between these small molecule surfactants (sodium dodecyl sulphate, dodecyltrimethylammonium bromide and polyoxyethylene (23) lauryl ether) and short, medium and long chain alcohols (ethanol, hexanol and decanol respectively) on the critical micelle concentration (CMC) and subsequently the micellar structure. SANS data for aqueous Pluronic solutions with added alcohols fitted to a charged spherical core/shell model for the micelle. The addition of the surfactants led to significantly smaller, oblate elliptical mixed micelles in the absence of alcohols. Addition of ethanol to the system led to a decrease in the micelle size, whereas larger micelles were observed upon addition of longer chain alcohols. NMR studies provided a complementary estimate of the micelle composition using average diffusion coefficients. These observations extend our understanding of the synergistic interactions between the Pluronic and small molecule surfactants when the partitioning of the added alcohol perturbs the interaction between the two types of surfactants.

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P47. Design of silicone-in-water emulsions for use as release agents

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With their high chain flexibility, low glass-transition temperature and low surface tension, polyorganosiloxanes are often the molecules of choice when one needs to formulate lubricants and release agents [1]. Among the various industrial processes requiring release agents, metal die casting is one of the most important, but also one of the most demanding since high thermal- and corrosion-resistance is needed. Specific functional silicones must be designed and synthesized, in order to comply with all performance requirements [2]. Then, those functional silicones should be properly emulsified, since – particularly for health, environmental and safety reasons – the preferred vehicle for such applications is water.

After a rapid overview of the key chemical routes for silicone functionalization, we will explain why such functional silicones are particularly difficult to emulsify. Next, we will present some aspects of silicone emulsification, with emphasis on the interplay between stability, droplet size, interfacial tension, shear, and respective viscosities of silicone and aqueous phase. The underlying choice of emulsification route will be discussed [3]. Finally, we will show the impact of various formulation parameters on release properties.

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P48. Preparation and in vitro characterisation of rapamycin-loaded solid lipid nanoparticles for the brain-targeted therapy

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Neurodegenerative disorders, such as Alzheimer, Parkinson or lysosomal storage diseases belong to most delibitating diseases of affluence which continuously remain without any efficient, low-cost remedy. Much effort has been paid for inventing effective brain-targeted drug composites to sufficiently overcome the blood-brain barrier, that constitutes a natural system strictly regulating the transport into the central neural system from the blood or cerebrospinal fluid. At the same time, specific inhibition by rapamycin of the mTOR complex, i.e. mammalian target of rapamycin displaying Ser/Thr kinase activity, responsible for autophagy, metabolism and cell proliferation, has been recently demonstrated to repair the cognitative behavior in a Alzheimer mouse model. Hereof, design of well-defined solid lipid nanoparticles carrying rapamycin becomes a powerful strategy to cross the BBB and treat the central nervous system-localized lesions.

Rapamycin-loaded SLN (10 and 20 % w/w), based on cetyl palmitate, Compritol® ATO888 and Geleol® as matrixes and stabilized with 1% polysorbate 80, were prepared using a cold high-pressure homogenization, solvent evaporation and dialysis protocol. Drug content and thermal stability of the nanoformulations were established exploiting DSC, UV-NIR and Raman spectroscopy, whereas DLS, zeta-potential and SEM measurements revealed their colloidal size distribution (50, 100, 200 nm). These favorable properties made the rapamycin-loaded SLN useful for in vitro treatment of a SH-SY5Y neuroblastoma cell line, i.e. an in vitro model for neurodegenerative diseases. Long-term studies of MTT toxicity and mTOR activity provided a promising evidence for controlled rapamycin release from lipid matrixes in cytosol, what confirms a potential biomedical application of the nanoformulations.

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P49. Squeezing an emulsion with two continuous phases: centrifugal compression of the bijel

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Bicontinuous interfacially jammed emulsion gels or bijels are a class of soft material where two partially miscible liquids are quenched and phase separate via spinodal decomposition. This results in a short-lived bicontinuous structure; the interface can then be stabilised by solid particles which jam causing a long-lived stable structure to be formed [1]. We have investigated the mechanical response of bijels using centrifugal compression (as for droplets in [2]). This was combined with imaging in order to observe internal changes to the particle network and gain insight into potential new structures which could be formed. We find that the bijel structure is preserved only at low centrifuge speeds at around 10 g with a complete destruction of the structure occurring for speeds around and above 100 g. The distorted bijel does not exhibit an elastic response because it has two continuous phases, which following compression at 10 g, sit one above the other. Therefore, one of the liquids is trapped and cannot regain access to the particle stabilised structure. The treatment at low speeds results in domains which are elongated in the direction perpendicular to the axis of rotation. The final structure can be controlled via the temperature and the initial domain size of the bijel.

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P50. The effect of electronic configuration on the catalytic activity of gold nanoparticles in the solvent free oxidation of alcohols

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It is well known that spherical gold nanoparticles are good catalysts for various oxidation reactions, but there has been little reported data on the catalytic ability of non-spherical gold nanoparticles. The plasmon resonances of rod shaped and spherical gold nanoparticles are very different with rod shaped particles having two resonances, one of which can extend into the near infra-red region of the electromagnetic spectrum, which suggests they would behave differently as catalysts. In this report, we demonstrate a robust method to synthesize gold nanoparticles in different configurations and subsequently use them to catalyse the oxidation of alcohols to analogous carbonyl compounds. Specifically, we developed a reproducible method to synthesize monodisperse rod-shaped as well as spherical gold nanoparticles by a seed-mediated synthesis technique using CTAB as a stabilising agent, $AgNO_3$ to control the growth and L-ascorbic acid as the reducing agent. The nanoparticles are used as catalysts for the oxidation of non-activated alcohols in a base free aqueous environment with H_2O_2 as the oxidising agent. Reaction yields from these tests display noteworthy differences in the catalytic activity based upon the shape of the nanoparticles.

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P51. Formulation and characterization of 1-monoacylglycerols-loaded microemulsions

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Microemulsions have recently attracted attention as useful carriers of active substances, which offer opportunities for the encapsulation of both water-soluble and oil-soluble compounds. Due to their beneficial physicochemical properties, they are applicable in the cosmetic, pharmaceutical and food industry. The objective of our study was to investigate the effect of various co-surfactants on the formulations of o/w microemulsions containing 1-monoacylglycerols (1-MAG) with fatty acid of different chain length, namely capric (C10:0), lauric (C12:0) and myristic (C14:0) acids. Medium-chain length alcohols (ethanol, 1-propanol, 1-butanol, 1-pentanol) were used as co-surfactants, and Tween 80 as a surfactant. Phase behaviour of the emulsion systems was studied with the help of pseudo-ternary phase diagrams, which were then used to determine the final composition of microemulsions. On the optimum formulations, the size of the microemulsion droplets was determined using photon correlation spectroscopy and their antibacterial properties against the most common pathogens were studied. The results indicate that the largest region of limited miscibility exists for microemulsions with the pentanol as co-surfactant. For systems wherein ethanol, butanol and propanol were used, the reduction of immiscibility area compared with pentanol was determined. Phase diagrams based on the data proved that the area of limited miscibility for the respective 1-MAG increases with increasing chain length of the alcohol used. Regarding size, emulsion droplets diameters were of about 12-24 nm and the best antibacterial properties were determined for 1-MAG C12:0 microemulsions irrespective of the co-surfactant used.

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P52. Preparation of Colloidal Inkjet Inks by Emulsion Polymerisation

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Nanoparticles are widely used in ink formulations as they offer some very desirable advantages, including a long shelf life due to the high stability of the dispersions, and controllable jetting behaviour. The aim of this project is to produce high solids content, sub 100 nm monodisperse latex particles to be used as model inkjet inks. Highly concentrated (up to 45 wt% solids content) stable PMMA latex particle dispersions have been prepared via emulsion polymerisation. More specifically a chain transfer agent has been utilised to enhance particle nucleation efficiency, aiding the preparation of polymer particles with a narrow weight distribution and increased monodispersity. Our initial work has found that high nanolatex concentration can be achieved with a relatively low emulsifier concentration, without sacrificing the colloidal stability of the dispersions. Waterborne nanoparticles around 50 nm have been obtained with a 45 wt % solids content. These dispersions do not require any lengthy processing to perform rheological experiments in regions where the particle suspensions show clear shear thinning behaviour.

In this study, we compare the use of a surfactant and a block copolymer as emulsion polymerization stabiliser. In addition, we also systematically study the effect of the emulsifier, initiator and chain transfer agent concentration on final particle size and polydispersity of the synthesised particles.

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P53. Coalescence stability of oil-in-water emulsions prepared using microchannel emulsification

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Pickering (or Ramsden) emulsions are dispersions of oil and water stabilised by colloidal particles[1]. One of the most important parameters in stabilizing the Pickering emulsions is wettability of colloidal particles against oil/water interfaces, which is quantified by a contact angle measured through water phase (θ). The energy of adsorption of particles at oil/water interfaces is given by an equation: $\Delta G = \pi\gamma R^2(1-|\cos\theta|)^2$, where γ is an interfacial tension of an oil and water and R is a particle radius. When $\theta < 90°$, the ΔG value increases and the particles become strongly adsorbed at oil/water interfaces with increasing θ, leading to the formation of emulsions stable against coalescence.

Metal oxide particles, such as silica and alumina, are widely used as particulate emulsifiers. The metal oxide particles are positively charged when pH is lower than isoelectric point (IEP), while they are negatively charged when pH is higher than IEP. For macroscopically flat surfaces of metal oxides, it has been shown that the surfaces of metal oxides are most hydrophobic when pH is around IEP[2].

In this study, we have used alumina-coated silica (ACS) particles and prepared Pickering oil-in-water (o/w) emulsions using microchannel emulsification. The emulsions were made as a function of pH and NaCl concentration (m_{NaCl}) of aqueous dispersions of ACS particles. The pH region where oil drops are stable against coalescence was determined, on the basis of monodispersity of oil drop size, at each m_{NaCl}. Combining results of emulsion stability against coalescence and those of zeta potential measurements, it is found that monodispersed stable o/w emulsions are formed when pH of the aqueous dispersions is around IEP, indicating that relatively less charged particles are relatively hydrophobic, so that they are more strongly adsorbed at oil/water interfaces than those when pH is apart from the IEP.

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P54. Physisorption of Π-conjugated polymer Onto Silica Surface in Toluene

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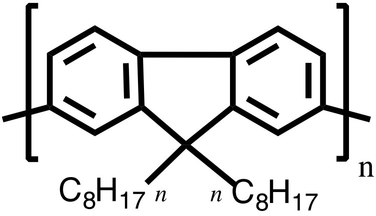

Fig.1. Chemical structure of PF8.

A physisorption is one of the most common phenomena at the interface between soft matter and hard matter. Even among them, definitive difference in physisorption at the solid surface between polymers and small molecules might mainly be due to large numbers of conformation freedom (entropy) that is a uniqueness of floppy chains. An open question is what is the inherent nature on solution-phase physisorption of polymer at the surface, which might be a long-standing issue in the realm of surface and interfacial science. To address this question, we desighned a new solution depletion system, consisting of uncharged poly(dioctylfluorene) (PF8) chosen as a chromophoric probe (Fig.1) and spherical silica with smooth surface (0.5 µm in diameter) dispersed in toluene. Long-range van der Waals and other noncovalent forces may be responsible for this physisorption. The present outcome may lead to an import pillar of several innovative hybridized materials consisting of various pi-conjugated polymers and inorganic directed toward printable solar-conversion and white-light-emitting systems in the future.

Experimental: The spherical silica was dispersed in toluene solution of PF8 and stirred at room temperature. The crude silica core-shell particles were purified by washing with toluene removes non-adsorbed PF8.

Results and discussion: Herein we found spontaneous physisorbed PF8 onto the silica surface without any specific treatment. PL spectrum of the particles and observation by the naked eye revealed that PF8 on the silica surface is physisorbed. Indeed, the PF8-silica showed cleary intense four regression PL signals due to phonon-side bands at 440/470/500/530 nm, reponsible for crystaline □-phase of PF8 (Fig.2).

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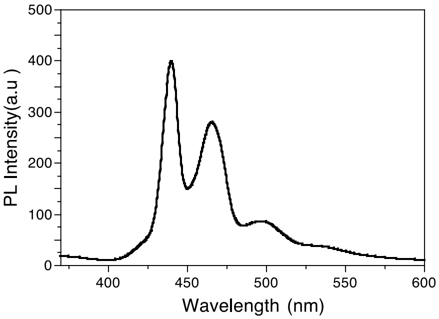

Fig.2. PL spectra of PF8/0.5μm spherical silica composite.

P55. Estimating the power absorption of tailored iron oxide nanoparticles from AC susceptibility measurements

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The US nanomedicine industry totals around $34.2 billion and the demand for biomedical nanosized products is expected to grow a 17.1% in 2014.[1] Due to the growing market needs, the introduction of a cost-efficient, high-yield and reproducible method for the synthesis of magnetic nanoparticles would revolutionize the market by improving the properties of the generated materials. Microwave reactors have the potential to offer this possibility thanks to the introduction of new high performance bench-systems (e.g. MARS 6, CEM Corporation) that could generate around 500 g of particles per week in a high controlled and reproducible manner.

Techniques such as magnetic resonance imaging (MRI), magnetic hyperthermia and magnetic particle imaging (MPI) heavily rely on the magnetic relaxation properties of magnetic nanoparticles. Understanding the mechanism of relaxation in working conditions is crucial for their routine use. Nonetheless, small changes to the synthetic conditions can lead to drastic variations on the frequency range of maximum imaginary component (χ'') of the complex susceptibility leading to products with unpredictable behavior or non-reproducible properties, as seen in the case of magnetic hyperthermia.[2] To this aim we have investigated the effect of the synthetic conditions with a microwave reactor in the final magnetic relaxation properties by AC susceptibility measurements on iron oxide nanoparticles. Citric acid and dextran ligands were used in the system to exemplify the drastic changes on the frequency of maximum susceptibility loss with the concentration of ligand in solution.

The frequency of maximum χ'' was found to increase along with the concentration of ligand in solution. The results reveal that it is possible to match a targeted frequency of maximum χ'' for a specific application through a carefully programmed microwave-based synthesis.

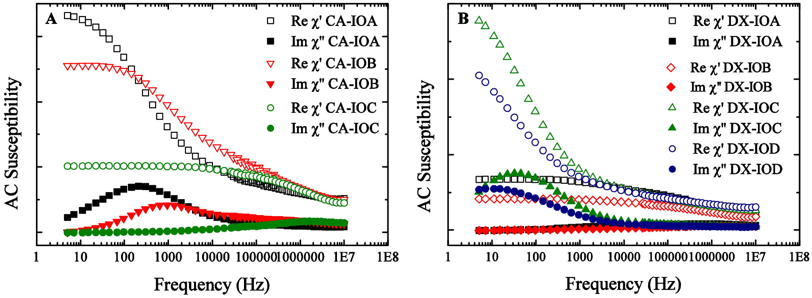

Figure 4. AC susceptibility (Re: real part, Im: imaginary part) measurements of A) citric acid-iron oxide NP series and B) dextran-iron oxide NP series.

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P56. PNIPAAM Brushes Grafted from Two-Dimentional Phase-Separated Structures

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Surface-initiated graft polymerization has been attracting considerable attention as a tool to modify the surface properties of solids. In particular, surface-initiated atom transfer radical polymerization (ATRP) yields polymer brushes with high graft density and with smooth surfaces. PNIPAAM is a representative thermoresponsive polymer with lower critical solution temperature (LCST) at 32°C

The Langmuir-Blodgett (LB) technique has been used to fabricate organic ultrathin films with well-defined structures. Mixed LB films form two-dimensional phase-separated structures with patterns of the size of a micrometer or nanometer length scale. These patterns can be controlled by adjusting the intermolecular interactions. Mixed LB films containing a silane-coupling agent can be converted to templates on which materials can be patterned. In this study, we grafted PNIPAAM brushes from two-dimensional patterns fabricated from mixed LB films.

We prepared mixed LB films of $CH_3(CH_2)_{18}COOH$ (H19A)/$CF_3(CF_2)_7(CH_2)_2SiCl_3$ (F8H2SiCl) = 1/3, heated them and treated them with organic solvent, followed by the reaction with a silane-coupling agent bearing an amino group, with a subsequent reaction to immobilize a polymerization initiator. The graft polymerization of NIPAAM was carried out for specific times at room temperature. The PNIPAAM brushes were characterized using AFM in air and in water at 25°C, 30°C, and 34°C. In situ AFM revealed that the PNIPAAM brushes were in a swollen state at 25°C in water due to hydration. On the other hand, the PNIPAAM brushes contracted in water due to dehydration when the temperature was raised to 30°C.

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P57. Designing Disorder Using DNA-Functionalized Colloids

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Understanding and controlling the properties of amorphous materials is essential in the design of new materials. Among different amorphous structures, colloidal gels play an important role. We use the short-ranged attractive interactions between colloids provided by selective DNA bonding to build ramified amorphous space-spanning structures that can sustain mechanical stress. [1] The mechanism of aggregation in our system occurs through arrested demixing in binary colloidal mixtures. This leads to the formation of bigels - a new class of materials. We obtain these materials by end-grafting highly specific single-stranded (ss) DNA. As ssDNA can only bind to its complementary counterpart, we can design new colloid-colloid binding rules. Here, we present two types of amorphous gels: Two inter-percolating but independent colloidal gels which we call bigels (Figure), and a single colloidal gel subsequently coated with a single layer of a different type of colloid. Later we call coaxially coated colloidal gels. [2]

I will discuss both the structural analysis and the mechanical properties of such systems. [3]

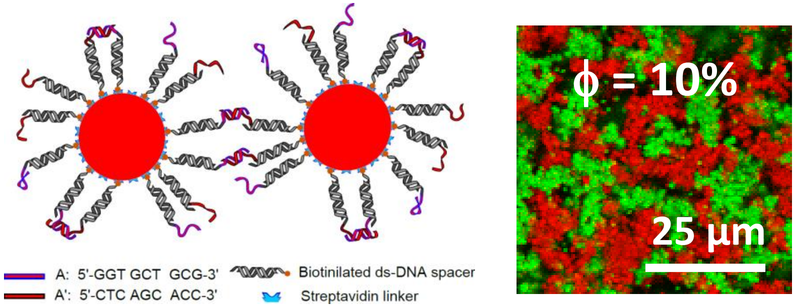

Figure: (Left) Carton of the typical colloid surfaces bound with DNA. The double strands are used a spacers, and the sticky overhangs are designed such that A and A' cannot bind to B or B'. The polymer strands in between are used to tune strength of the intra-colloidal bonds. (Right) Snapshot from a demixed bigel.[1,2]

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P58. Hydrotropes as Supercritical Carbon Dioxide Viscosifiers

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The development of applications involving supercritical carbon dioxide ($scCO_2$) could contribute towards a significant and necessary movement towards green chemistry, offering potential replacements for volatile organic compounds. Unfortunately, the physico-chemical properties of $scCO_2$ are sub-optimal for applications, including low poor solubilizing power of ionic and polar species alongside a low viscosity. These are two key properties that must be addressed if $scCO_2$ is to fulfil its potential as a green solvent. Success in enhancing both solvency and viscosity of $scCO_2$ has been achieved through the intelligent design and use of CO_2-philic, self-assembling amphiphiles, where addition leads to an increase in internal structure of the system, and therefore an enhancement of viscosity. The development of viscosifying agents has thus far focused on building the system internal structure, through elongating reversed spherical micelles to form ellipsoid, rod-like and worm-like structures which then may cross-link to make networks[1].

Formation of organogels has been reported in Aerosol-OT (Dioctyl sodium sulfosuccinate, AOT) and oil systems through the addition of para-substituted phenols[2], however the gels ‘dissolve’ with addition of water to the systems. Viscosity enhancement, paired with the formation of reverse rod-like and worm-like structures has also been reported with the inclusion of hydrotropic salts in both water-in-oil (w/o) and water-in-carbon dioxide (w/c) systems[3,4], though viscosity increases within w/c systems were significantly less pronounced than those in w/o systems[4] .

Here we report the results from novel combinations of para-substituted phenols and hydrotropic salts at a range of concentrations, ratios and water levels, and the impacts these combinations have on phase behaviour and viscosity of water-in-oil and water-in-carbon dioxide systems.

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P59. Structure and Growth Properties of Mesoporous Silica Anti-Reflective Coatings

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Here we report some of the early work and background for a 3 year project investigating the structure and growth properties of a proxy system for a commercial anti-reflective (AR) coating. When glass meets air, around 4 % of normal incident light is reflected, and this increases abruptly with incidence angle. Reflective losses from glass substrates can be eliminated by applying AR coatings.[1,2] To optimize transmission into solar cell modules reflective loses must be minimized; hence AR coatings are industrially, economically and environmentally important. Porous silica films, prepared via sol-gel routes, provide low and tuneable refractive indices, representing an approach for making AR coatings.[3-5] The commercial product uses a novel core-latex-template to fabricate a unique closed pore silica AR coating: offering advantages of greater performance and longer life-time, relative to traditional open pore coatings.

Despite the practical success of this AR coating, understanding of the structure and growth properties, necessary for optimising films properties, is lacking. Industrial formulations are complex and multicomponent. Initial work has been centred on preparing simple, model binary/ternary systems, comprising of the silicon alkoxide tetraethyl orthosilicate, a polymer latex particle and a surfactant. Some initial results from these model systems will be discussed, including the physical properties (e.g. phase behaviour, wettability on glass) and small-angle neutron scattering studies.

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P60. The behaviour of protein fibrils in complex system

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There is an on-going interest in the development of new functional structures in pharmaceutical, food and material science fields. Proteins are an important source of biomacromolecules for designing functional structures due to their ability to form different morphologies on a nano-scale. For example, protein fibrils are rod-like assemblies with a width of a few nanometers, whereas their length can be up to several micrometers long. Numerous proteins have shown the ability to aggregate into fibrils, such as, ovalbumin, soy proteins and whey proteins. Fibrils have received considerable attention from a variety of directions, reaching from physics to biology and the medical field. It has been found that the presence of fibrils leads to an increase in zero shear viscosity and that they show shear thinning behaviour, these properties make them also interesting as food ingredients. Fibrils are also surface active and were used to increase the strength of capsules in the production of microcapsules. For a wider application of fibrils, it is important to study the properties of fibrils also in more complex systems with the aim to better understand the interaction between fibrils and other components. Here we studied the interaction between protein fibrils and mono-disperse colloidal particles. Although the fibrils are efficient depletion agents at relatively low concentrations, thereby flocculating the dispersion, at higher concentration they stabilize the dispersion again.

Acknowledgement: This research is financially supported by NanoNextNL (consortium of Dutch government and 130 other partners).

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P61. Surface Contamination of Clays: Asphaltene Adsorption and Hydration

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Asphaltenes are a self-associating and surface active petroleum fraction. Clays, such as kaolinite and illite, can adsorb asphaltenes on their surface due to their structure and cation exchange capacity. Asphaltene adsorption alters clay surface properties such as surface composition, surface energy, and surface charge, and hence alters clay behavior during oil production, particularly near well bores, and at oil water interfaces in surface facilities. A detailed understanding of the behavior of “coated” clays is crucial to understanding the roles of clays in hydrocarbon resource exploitation. In this study, the effect of asphaltene adsorption and clay hydration on the association behavior of kaolinite and illite particles in diverse solvents (e.g. toluene, heptane, and pyridine) is investigated at 60°C and atmospheric pressure. A precision solution calorimeter was used to measure the enthalpy of solution of clays and clays coated with asphaltenes in solvents. Thermogravimetric analysis (TGA) was also used to measure the hydration capacity of clays and clays coated with asphaltenes. Asphaltene adsorption on illite has negligible effect on the enthalpy of solution of clay + solvent mixtures but a significant change in the enthalpy of solution is observed for kaolinite + solvent mixtures. Both calorimetric and TGA measurements show that kaolinite has a higher water saturation capacity and more sites for asphaltene adsorption than illite. Kaolinite contamination with asphaltenes would appear to play a more important role than illite in altering the production performance of hydrocarbon reservoirs.

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P62. Enhanced Electrogenerated Chemiluminescence in Responsive Microgels

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Stimuli-responsive hydrogels, and especially bioresponsive ones, have already demonstrated their interest in biosensing applications using various transduction methods, including luminescence as an easy readout. These highly swollen networks undergo volume phase transition upon stimulus application, which modifies many of their physical properties. Among them, various hydrogels or microgels have been designed to perform a change in fluorescence upon network expansion or contraction.

Another way to generate luminescence is electrogenerated chemiluminescence (ECL). ECL is the process of light emission by the excited state of a luminophore that results from an initial electrochemical reaction at the electrode surface. It is a remarkably versatile and ultrasensitive method that has emerged in various research fields[1] and it has already proved its performances in immunoassays and multiplexed arrays[2].

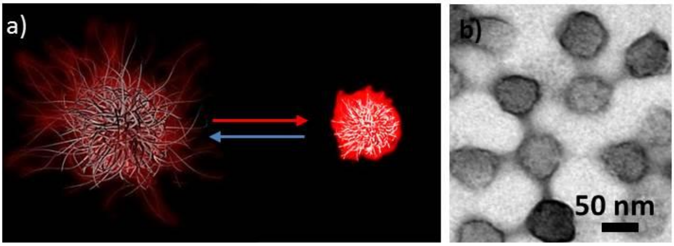

Figure. a) Concept of luminescence enhancement upon microgel collapse at the swell-collapse transition; b) Image of Transmission electron microscopy of microgels.

In the present work, we have synthesized microgels based on poly(N-isopropylacrylamide) (pNIPAM) copolymerized with a Ruthenium ($Ru(bpy)_3^{2+}$ monomer) complex. The electrochemistry, photoluminescence and electrogenerated chemiluminescence (ECL) of these thermoresponsive redox microgels has been investigated. For the first time, reversible ECL enhancement is demonstrated in stimuli-responsive 100-nm microgel particles[3]. Such an unexpected amplification reaches 2 orders of magnitude and it is intrinsically correlated with the collapse of the microgel particles. The swell-collapse transition decreases the average distance between adjacent redox sites and favors the electron-transfer processes in the microgels resulting in the enhanced ECL emission. This study opens new perspectives towards applications in ultrasensitive bioassays.

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P63. Responsive Hyaluronic Acid Nanogels for Drug Delivery

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Nanogels are an attractive class of delivery systems. These soft particles, made of highly swollen polymer network, can physically entrap a drug and release it at a rate depending on its diffusion though the network. Therefore, any change in the swelling degree can trigger the release kinetics. In this work, we develop new nanogels made of hyaluronic acid which can swell or shrink in response to pH. These biocompatible and degradable matrices can encapsulate a drug and release it according to these stimuli.

Hyaluronic acid (HA) is a linear polysaccharide with acknowledged biocompatibility. It is functionalized with polymerizable methacrylate functions to be processed as network [1]. This linear precursor is confined in aqueous nanoreactors to be further cross-linked. To this end, monodisperse water-in-oil nanoemulsions are used as template and yield well-defined nanogels. Cross-linking is achieved via photopolymerization, which allows a fine control of the polymerization conversion rate. As a consequence, their swelling properties in different environments are modulated [2]. Thanks to their confirmed biocompatibility, these matrices displayed interesting drug delivery properties. Model macromolecules with different molecular weights have been encapsulated and can be released upon enzymatic degradation of the matrix. We show how the release kinetics can be triggered by nanogel structural parameters. Moreover, we show that release can also be triggered by nanogel responsie to an external stimulus like pH (Figure).

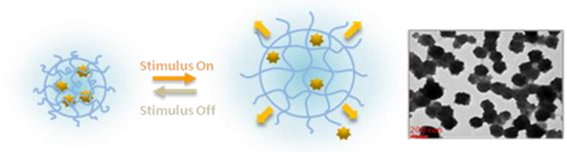

Figure. Stimulus-triggered drug release and TEM image of HA-based nanogels.

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P64. Pickering foams with long-term stability embedded in hydrogel

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Pickering foams are the gas in liquid or solid systems stabilized by particles.[1] These systems are highly relevant for applications in food science and industry.[2] The nanoparticles used in these systems are required to have suitable surface properties to form highly stable foams. Therefore, providing a proper formulation for surface modification of nanoparticles to reach a controlled contact angle and stability at the interface is a key challenge.

We have recently described a surface modification for hydrophilic silica nanoparticles (~18 nm) by adsorption of oleic acid.[3] Such modification leads to surface hydrophobization of nanoparticles and at the same time maintains their stability. The properties of Pickering emulsions formulated with those modified particles have been studied previously.[3, 4]

Our very recent findings reveal that the oleic acid modified silica nanoparticles can also be successfully applied to create surfactant free Pickering foams. In this contribution we will report about the stability of such foams. Furthermore, we will present how these Pickering foams can reach the long-term stability after getting embedded in a proper hydrogel.

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P65. Investigation of dispersion stability of modified glucan microcapsules for combined imaging and drug delivery

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Saccharomyces cerevisiae (baker’s yeast) can be processed by a simple chemical purification to glucan particles. They are hollow, porous 2–5 µm microspheres and typically consist of 85 % 1,3-D-glucan polymers. They can be used as drug carriers for the macrophage drug delivery. In the present work, glucan microparticles have been isolated from yeast and purified. Subsequently, the stability and agglomeration kinetics of glucan microparticles were measured in isotonic buffers. The release kinetics of a model substance (vitamin B12) loaded into the microparticles was investigated at temperatures systematically ranging from 10°C to 60°C. The release rate was found to be a non-linear function of temperature and this behaviour was explained by a glass transition of β-glucan, measured by DSC and supplemented by temperature-dependent FT-IR. The temperature-dependent diffusion coefficients of vitamin B12 across the glucan wall were calculated from the experimental data using a mathematical model. The glucan microcapsules were fluorescently labeled to enable not only drug release but to also act as an imaging moiety.

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P66. Chemical Mapping and Characterisation of Drying Colloidal Films

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The drying of colloidal films forms the basis for numerous technologies that are industrially important – such as; paints, industrial coatings and inkjet printing. Studying the drying of these films has been an area of research for a number of years now with a keen interest being shown in different methods of both characterising the drying process and the chemical mapping of the dried films.[1]

Most commercially available colloidal films are composed of a number of chemical components. For this reason, upon drying these systems have a tendency to undergo phase separation. The phase behaviour of these systems is largely dependent upon both the interactions between the different chemical components; and the drying time of the film these are both affected by factors such as humidity and temperature. For this reason finding methods for chemically mapping the dried films and understanding the phase separation is of great importance. This study will look at a number of ways that this can be achieved with techniques that include; Confocal Raman Microscopy, Fluorescent Microscopy and X-Ray Scattering. However, in order to make sense of how the phase structure of the film relates to drying time - ways to quantify the drying rate of colloidal films need to be established.

Laser speckle imaging has been used in the field of biology to study the flow of blood in animals in *in vivo* since the work carried out by Briers and Fercher in 1981.[2] Recently this same technique has been used to measure the rate of particle diffusion within a drying colloidal film, hence providing the potential for a new way to quantify the drying rate.[3]

In the second half of the study, this technique will be compared to more established ways of quantify the drying of colloidal films, with the hope to explore the validity of using this technique either alongside or as a stand-alone to the pre-existing methods.

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P67. Microemulsions containing essential oils

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Formulation and characterization of microemulsions (MEs) containing different types of essential oils (lemon, cinnamon, clove and thyme) were studied as well as their antibacterial activity against the growth of selected gram-positive (Micrococcus luteus, Staphylococcus aureus subsp. Aureus) and gram-negative (Pseudomonas aeruginosa, Escherichia coli) bacteria. The phase behaviour of microemulsions was
determined via pseudo-ternary phase diagrams in order to determine the miscibility areas of all components used and reveal the effect of solubilizing agent (propylene glycol) on the size of microemulsion region. The obtained microemulsions were characterized by visual observation and by measuring their particle sizes using photon correlation spectroscopy (PCS). The results showed that the presence of the solubilizing agent positively influences the oil solubilisation and increases the size of stable, single-phase microemulsion region. Prepared MEs were transparent in appearance, stable during the storage period and their particle sizes were in the
range of 9-14 nm. All prepared MEs showed the best antibacterial activity against both bacterial types at the highest used concentration of 9500 μm/ml, which always caused more than 50 % decrease in bacterial growth. Furthermore, in the presence of lemon, cinnamon and thyme MEs, the total growth inhibition of bacteria Staphylococcus aureus, was found at the same concentration. Generally, MEs containing cinnamon and thyme oil were evaluated as the most effective against the growth of the studied bacterial strains.

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P68. Preparation of Hydroxyapatite Nanoparticles with Functional Polymer Coatings for Medical Applications

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Current challenges involved in the design and preparation of functional nanoparticles include the difficulty of overcoming nanoparticle aggregation. The formation of aggregates is thermodynamically favourable; however it prevents the full functionality of nanoparticles from being expressed. If the nanoparticles could be made to disperse, this would increase their functionality and make them applicable to medicine and dentistry. The project aims to encapsulate nanoparticles of hydroxyapatite (HA) with functional polymer coatings to demonstrate an enabling technology with the possibility of opening new opportunities in medicine, dentistry and other non-health sectors.

Highly branched homopolymers of poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA) and poly(2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) have been synthesised independently by RAFT polymerisation. The effectiveness of two different RAFT agents, 4-vinylbenzyl-pyrrolecarbodithioate (1) and 4-vinylbenzyldithiobenzoate (2), was investigated to optimise the production of these polymers. (1)(2)

The PAA and PMAA polymerisations were successful using both RAFT agents, but the AMPS monomer was found to be incompatible with (2) as the monomer degraded the RAFT agent. Nano and microparticles of hydroxyapatite (HA) were then included in the polymer reaction mixtures to investigate whether they could be coated in situ. Optical microscopy showed the presence of particles in every solution regardless of polymer, RAFT agent and size of HA. However, the size of the particles did change between solutions. Particle sizing and zeta potential studies were conducted on pure HA nano and microparticles, then on the resultant polymer solution from the in situ reactions. It was found that the size of the particles changed when subjected to polymer treatment.

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P69. Which key factors determine Cal B activity in bicontinuous microemulsions?

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Enzyme catalysed biotransformations offer great potential due to high substrate specificity and high enantioselectivity, e.g. as observed for lipases. However, many processes lack the right reaction conditions to benefit from all the enzyme's advantages as special requirements are needed to achieve optimum enzyme activity and stability. We propose a bicontinuous microemulsion for lipase catalysed hydrolysis reactions. The large connected interface between oil and water domain consists of a surfactant monolayer, where the lipase adsorbs and converts substrates from the oil phase of the microemulsion. In the present contribution, a basic microemulsion consisting of buffer-n-octane-nonionic surfactant CiEj was used to investigate the key factors that determine a successful hydrolysis reaction catalysed by the lipase B from Candida antarctica. In a model reaction, p-nitrophenyl palmitate, -laurate and -caprylate were used as substrates, yielding the respective fatty acid and p-nitrophenol as products. The kinetics of the reaction was then monitored by UV/Vis detecting the formation of p-nitrophenol as a function of time. The phase behaviour of the microemulsions containing the reactants was studied, and their partitioning between the phases determined. Special focus was set on clarifying the behaviour of p-nitrophenol in the microemulsion and the effect of the reaction media on the spectral properties of the product. Temperature, ionic strength and substrate polarity was varied to determine the optimum values for Cal B based on the obtained second order rate constants k_2. The Cal B activity was found to be linearly dependent on both enzyme and substrate concentration, as expected. Surface tension measurements of diluted Cal B solutions were carried out and correlated with the performed activity measurements The impact of the composition of the interfacial film on the Cal B activity was measured using two different co-surfactants, the phospholipid 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) and the sugar surfactant decyl β-D-glucopyranoside (β-$C_{10}G_1$).

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P70. Self-Assembly of Aqueous Surfactants on Patterned Surfaces: Insights from Coarse-Grained Simulations

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The adsorption and self-assembly of surfactants are ubiquitous processes in several technological applications. From a fundamental point of view, understanding such processes is also important because it can have profound implications in the manufacture of nano-structured materials using bottom-up strategies. Although a lot is known about the adsorption of surfactants on homogeneous flat surfaces, limited information is available, in quantifiable terms, regarding the adsorption of surfactants on heterogeneous surfaces. We will present dissipative particle dynamics simulation results for the adsorption of model surfactants on
patterned flat surfaces. The results show that the surface pattern can be used to direct the morphology of the self-
assembled aggregates (flat monolayers, hemi-cylinders, hemi-spheres, hollow hemi-cylinders, and irregular structures have all been observed using the same surfactant but different surface patterns). We will discuss how our predictions could be tested experimentally, and how, if reliable, they could be used for the design of new materials.

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P71. Magnetic-Plasmonic Heterostructured Nanoparticles as a Novel Cellular Probe for Bioapplications

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Magnetic nanoparticles (NPs) have been used for cell/protein separation. Recently they also have been used for subcellular vesicles separation, because this technique has advantages in terms of purification compared to conventional technique including ultracentrifugation and density gradient centrifugation. This magnetic separation technique provides important knowledge to the biological field and also to the pathology field. So far, magnetic separation was operated for stable vesicles which can exist for long time in a cell. However most subcellular events are transient processes including transformation of the vesicle membrane. Therefore it is important to observe subcellular events to trace what happened in a cell. Usually, fluorescent probes (dye molecules or quantum dots) have been used for bioimaging, but it has drawbacks in terms of color failure. On the other hand metal nanoparticles, for example Au NPs and Ag NPs, have attracted much attention as an alternative to fluorescent probes because they scatter light semipermanently through localized surface plasmon resonance. In this study, we synthesized magnetic core plasmonic shell FeCo@Ag and FeCo@AgAu NPs as novel probes which have plasmonic
imaging and magnetic separation capabilities at the same time. These two types of NPs were characterized by TEM, EDS, XRD, UV-vis and the magnetic properties of the NPs were investigated by SQUID. Because as synthesized NPs were capped with hydrophobic organic molecules, these NPs were made water soluble by ligand exchange with poly L-lysine with lactose and thiol moieties as a watersoluble bio-
compatible capping ligand (PLL-Lac-SH) and FITC modified PLL-Lac-SH (FITC-PLL-Lac-SH). Furthermore, to assess the capability of magnetic separation of subcellular vesicles, magnetic separation of W/O emulsion which mimics vesicles was conducted under confocal laser scanning microscope.

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P72. Phase-Separated Structures of Mixed LB Films of Long-Chain Carboxylic Acid and Long-Chain Amine

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We have studied the phase-separated structures of mixed LB films of long-chain fatty acid and hybrid carboxylic acid having both perfloroalkyl and alkyl portions in the hydrophobic part [1]. The phase-separated structures are controlled by adjusting the intermolecular interactions. In this study, we
investigate the phase-separated structures of mixed LB films of long-chain carboxylic acid and long-chain amine. In this combination, line tension should be small due to the strong coulombic interaction between carboxylic and amino groups. To facilitate the occurrence of phase separation, we use
perfluorocarboxylic acid as a carboxylic acid.

Solutions of perfluorotetradecanoic acid ($CF_3(CF_2)_{12}COOH$: FTDA) and octadecylamine ($CH_3(CH_2)_{17}NH_2$: ODA) at a concentration of 1mM each were mixed at specific molar ratios and spread on pure water. Surface pressure-area isotherms of FTDA, ODA and their mixtures were measured at 298K. When the average area per molecule was plotted against x_{F13A}, molar fraction of FTDA, two linear portions were observed in the regions of $0 \le x_{F13A} \le 0.5$ and $0.5 < x_{F13A} \le 1.0$. This suggests the salt formation of FTDA and ODA:$ODA^+ \cdot FTDA^-$. AFM observations revealed the phase-separated structures in the regions of $0 \le x_{F13A} \le 0.5$. The area fraction of the domains increased with an increase in x_{F13A} in this region. This shows that the domains consist of $ODA^+ \cdot FTDA^-$ salt and that the other region consists of ODA. On the other hand, domains were absent in the region of $0.5 < x_{F13A} \le 1.0$.

[1] H. Kimura et al., *J. Phys. Chem. B*, 2008, 112, 15313-15319.

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P73. Controlled Release of Highly Reactive Water Soluble Active by Microencapsulation

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Encapsulates are particles which can have different structures, including core-shell and multiple cores embedded in a matrix. Encapsulates have found more and more applications in different products, especially in printing and imaging, chemical and agrochemical, food and feed, cosmetic and household, and pharmaceutical/ biomedical, where they are used not only to allow stabilization of active ingredients but also to achieve their controlled release and targeted delivery. However, to design and produce encapsulates loaded with hydrophilic and water soluble active ingredients such as carbamide peroxide (CP) in order to achieve a sustained release of hydrogen peroxide (HP) is currently recognised to be very challenging.

We have constructed CP-loaded encapsulates and achieved a sustained release of HP by spray cooling paraffin wax containing solid CP. The release profile of HP was temperature dependent and was tuned to achieve fast or slow release using release rate modifiers including solid polyethylene glycol and inorganic particles such as silica nanoparticles. Along with the long-term stability, these encapsulates now offer the potential to be used in the formulations of tooth whitening products which can realise hydrogen peroxide in a controlled and sustained manner.

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P74. Structures of Langmuir-Blodgett-Gibbs films

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Layers of water-soluble surfactants form Gibbs films at the air-solution interface while layers of water-insoluble amphiphiles form Langmuir films at the air-water interface. The phenomena that water-soluble surfactants in the solutions adsorb to the Langmuir films are known as monolayer penetration. Recently we have fabricated Langmuir films in contact with Gibbs films using deuterated arachidic acid (D19A) as a Langmuir-film-forming material, and sodium dodecyl sulfate (SDS) and octaethylene glycol monododecyl ether as Gibbs-film-forming materials(1). We have concluded multilayer formation and termed these films Langmuir-Gibbs (LG) films. In this study, we transferred the LG films onto hydrophobic substrates and investigated the structures of the films. We termed the films on the solid substrates Langmuir-
Blodgett-Gibbs (LBG) films.

Langmuir films were prepared by spreading 1 mM hexane solution of D19A at 20°C on purified water. A given amount of SDS aqueous solution was injected into the subphase 30 min after the preparation of the Langmuir film. The LG films were
transferred onto hydrophobized Si wafers using the horizontal lifting method 24 h after the injection of SDS into the subphase. The structures of the LBG films were characterized using IR and AFM. IR measurements revealed the presence of both D19A and SDS in the LBG films. AFM observations showed that the LBG films consist of bilayers as a structural unit. These results are consistent with the structures of the LG films in that multilayers are formed in both the LG and LBG films.

1) K. Oka et al., J. Oleo Sci., 62, 681 (2013)

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P75. Controlled release and reaction kinetics in magnetic liposome microgels stable under isotonic conditions

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Many biochemical processes in living cells are regulated by internal structuring of cells, i.e. compartmentalisation. Enzymes and reactants are separated by semi-permeable membranes. In order to mimic this feature we present internally structured alginate gel micro-particles containing thermo-responsive liposomes (filled with reactants) and colloidal iron oxide allowing remote heating of micro-particles by radiofrequency field.

Utilizing these particles we controlled the progress of the oxidation of ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)) catalysed by the enzyme laccase. The substrate was encapsulated inside the immobilized liposomes and the enzyme was dispersed within the alginate hydrogel. We were able to dose the substrate by short RF pulses and the product of the reaction was stepwise released out of the gel micro-particles.

However, alginate gel particles are not very stable in isotonic buffers and are dissolved in few hours. Rigidity of such particles is necessary for further bio-adhesive study; therefore, a method of their stabilization in concentrated solutions was developed. The modification utilizes polycationic polysaccharide chitosan as a co-cross-linker of alginate gel. Such particles remain stable and rigid in an isotonic PBS buffer for more than a month.

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P76. Direct Impact of Non-Equilibrium Aggregates on the Structure and Morphology of Pdadmac/SDS Layers at the Air/Water Interface

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The exploitation of non-equilibrium effects in oppositely charged polyelectrolyte / surfactant (P/S) mixtures is attracting more and more attention. Here we discuss various different mechanisms to explain the non-equilibrium properties of P/S mixtures at the air/water interface in terms of adsorption vs. trapping or spreading of particles delivered by convection[1] or deposition under gravity.[2]

Poly(diallyldimethylammonium chloride)/sodium dodecyl sulfate (Pdadmac/SDS) samples have been examined with respect to the bulk composition, changes in the bulk phase behavior and sample history using ellipsometry, neutron reflectometry and Brewster angle microscopy (BAM). Aggregate penetration into the adsorption layer is observed from kinetically-trapped particles at the edge of the phase separation region for fresh-mixed samples. For the supernatant of well-equilibrated aged-settled samples, penetration of aggregates occurs only when the particles are positively charged, which is attributed to their interaction with the negatively charged headgroups of the surfactant monolayer. Through the application of a light mechanical stress to the sediment, the surface properties of aged-redispersed samples are significantly modified. Trapping of particles at the interface occurs for samples where the surface is not subjected to cleaning by aspiration, and the process is most prevalent at compositions close to charge neutralization (0.82 mM). This work begins to outline the complexity how non-equilibrium P/S aggregates can dramatically impact the interfacial properties directly. The implications of our findings are discussed in terms of applications.

[1] Angus-Smyth, A.; Bain C. D.; Varga, I.; Campbell, R. A. Effects of bulk aggregation on PEI–SDS monolayers at the dynamic air–liquid interface: depletion due to precipitation versus enrichment by a convection/spreading mechanism. Soft Matter, 2013, 26, 6103;
[2] Campbell, R. A.; Arteta, M. Y.; Angus-Smyth, A.; Nylander, T.;Varga, I. Multilayers at Interfaces of an oppositely charged polyelectrolyte/surfactant system resulting from the transport of bulk aggregates under gravity. J. Phys. Chem. B 2012, 16, 7981.

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P77. Particularities of electrical properties of water colloids and possibility of a new mechanism of communications in biological systems

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Our experimental studies of the behavior of water suspensions of inorganic and organic particles in electric fields revealed several anomalous properties, providing us to offer a new mechanism of communications between bio-systems based on low-frequency resonant oscillations of these suspensions.

First, we studied aqueous suspension of submicron grains of pollen, which demonstrated a high electric and electro-optical activity. Grains of pollen have a size of about 1-1,5 micron. Being placed inside the electrical capacitor this suspension demonstrated active movement of the grains towards the positive electrode and simultaneous creation of the optical anisotropy. In addition, when the electric field inside the capacitor was modulated spatially using local field concentrators the seeds were redistributed as well creating the corresponding modulation of the refractive index of the suspension and inducing modulation of the profile of the suspension surface.

It has been experimentally established that positive and negative charges of grains in water suspension cannot connect, as it should happen in a normal environment under the action of the Coulomb attraction, because the dielectric permittivities inside the grains are much smaller compared with water and therefore the external electrical field induce negative dielectric polarization inside the grains leading to their pushing away from the strong field region. In result, the competition between the Coulomb attraction and dipole repulsion results in an equilibrium distance between the clusters, where these forces compensate each other. Thus, these clusters create sustainable “macromolecules” with the equilibrium distance determined by the electrical charges and the geometrical dimensions of the clusters. On the other hand, the grains in these “macromolecules” can be oscillating around as usual molecules around their equilibrium state.

Our estimations of the equilibrium distances between the components of these molecules (charged grains or clusters) gave the values of several micrometers whereas the resonance frequencies of their oscillations can vary between several Hz and hundreds of Hz being dependent on the charges and dimensions of the constituents. Therefore, these resonators can serve as the basis of emitters and receptors of low-frequency electromagnetic waves in various biological systems (either plants or living organisms). Since low frequency fields can pass easily through organic environment, these “macromolecules” and resonators are able to provide a new mechanism of communications between Bio-systems. For example, it is well known that electromagnetic fields in the frequency range from 10 to 50 Hz affect rather severely the behavior of bees. However, microbiological studies of bees have not found any receptors which can be responsible for sensitivity of bees to this radiation. Our studies show that the receptors of this kind can be based on bound resonant states of clusters with charges of opposite signs, located in the aquatic environment.

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P78.Numerical simulation of nanoparticle formation in a co-flow capillary device

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The purpose of this study was to simulate the flow and concentration fields in a co-flow glass capillary device during formation of poly-ε-caprolactone (PCL) and polylactide (PLA) nanoparticles by nanoprecipitation ("diffusion-stranding" process). A numerical simulation using computational fluid dynamics (CFD) has been done by coupling Navier-Stokes and convection-diffusion equations for laminar flow.

The organic phase (0.1 % (w/w) polymer in tetrahydrofuran (THF)) was injected through the inner capillary tube with a tapered cross section culminated in a circular orifice. The water phase was delivered co-currently through the outer square capillary. The inner diameter of the orifice was 60 μm and the water phase flow rate was 5 ml h^{-1}. The flow rate ratio of the water to organic phase was varied from 1.5 to 10 by varying the organic phase flow rate between 0.5 and 3.3 ml h^{-1}.

Both THF and the polymer diffused to the water phase causing a decrease in the concentration of THF and the polymer downstream from the orifice in both the longitudinal and perpendicular direction. Nanoprecipitation of PCL and PLA occurred when the mass fraction of THF decreased to 0.82 and 0.66, respectively. The mixing time was found to reduce from 1.26 to 0.29 s when the aqueous-to-organic-phase flow rate ratio increased from 1.5 to 10. We observed a vortex formation in the vicinity of the orifice as a result of the high shear rate at the interface between the organic and water phase. The maximum vortex was formed at the organic phase flow rate of 3.3 ml h^{-1}, creating a shear rate between the two phases at the orifice of 1.8×10^4 s^{-1}. Due to local vortex formation, the polymer was mainly transferred by convection near the orifice and by molecular diffusion farther downstream.

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P79. Encapsulation of Drugs in Microparticles Produced in Flow Focussing Glass Microcapillary Devices

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Encapsulation of drugs in biodegradable poly(lactic acid) (PLA) and poly(lactic-co-glycolic acid) (PLGA) particles was achieved by emulsification using axisymmetric flow focusing glass capillary devices and subsequent solvent evaporation. Due to the circular cross section of the orifice of the collection capillary, the dispersed phase was symmetrically surrounded by the continuous phase resulted in the generation of monodispersed droplets without wetting. By varying the orifice size and manipulating the flow rates of the dispersed and continuous phase, size-tuneable droplets were generated that have been transformed into monodispersed particles after droplet evaporation (Vladisavljević et al., 2014).

In this work, flow focusing glass capillary devices were exploited to produce drug loaded biodegradable particles. The dispersed phase was a mixture of drug and polymer dissolved in a volatile organic solvent (ethyl acetate or dichloromethane) and the continuous phase was 5% (w/w) aqueous poly(vinyl alcohol) solution. As a result of the presence of nanoclay nanoparticles or a phase change material (2-methyl pentane) in the dispersed phase, nanoclay embedded particles or golf ball-like particles (Kim, Lee, Park, & Cho, 2010) were respectively produced. Their microstructural differences were investigated to ascertain its effect on drug encapsulation and in-vitro drug release profile. Although glass capillary devices cannot easily be replicated as microfluidic devices made from mouldable polymers such as polydimethylsiloxane (PDMS), glass is chemically and mechanically more robust and offer superior optical properties compared to PDMS.

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Vladisavljević, G. T., Shahmohamadi, H., Das, D. B., Ekanem, E. E., Tauanov, Z., & Sharma, L. (2014). Glass capillary microfluidics for production of monodispersed poly (dl-lactic acid) and polycaprolactone microparticles: Experiments and numerical simulations. Journal of Colloid and Interface Science, 418, 163–70

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P80. Alternate Soaking Technique for the Direct Fabrication of Hydroxyapatite films on Wettability-Patterned Substrates

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We report a hydrogel-free alternate soaking technique for the direct fabrication of hydroxylapatite (HAp) films on wettability-patterned substrates. Hexamethyldisilazane (HMDS) monolayers were formed on glass plates and were removed selectively by UV/Ozone treatments through a metal mask, resulting in the formation of wettability-patterned substrates.[1] The wettability-patterned substrates were soaked alternately in methanol solution of $CaCl_2$ and aqueous solution of Na_2HPO_4, leading to the formation of calcium phosphates (CP) which served as scaffolds for the growth of HAp in HAp precursor solution (Figure 1a). The HAp films were grown selectively on the CP films on the wettability-patterned substrates when immersed in the precursor solution containing calcium acetate, ammonium hydrogenphosphate, and ammonium acetate. Optical microscopy, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy showed that the CP films were formed selectively on the hydrophilic regions of the wettability-patterned substrates. Figure 1b shows an SEM image of the HAp films on a wettability-patterned substrate after immersion in the HAp precursor solution for 48 h. HAp films were grown selectively on the CP films and their thickness was about 20 μm. These results demonstrate that HAp films can be fabricated selectively from the CP films on the wettability-patterned substrates.

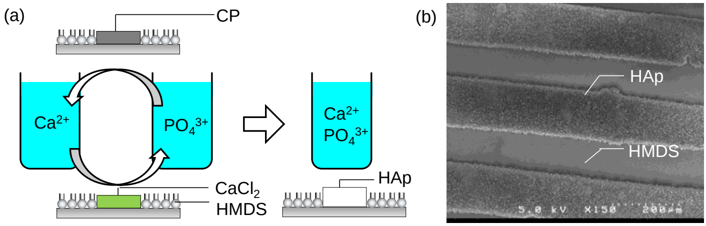

Figure 1 (a) Experimental scheme and (b) SEM image of HAp film on a wettability-patterned substrate.

[1] S. Watanabe et al., *Langmuir* **2013**, 29, 7743−7748.

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P81. Preparation of Double Emulsions using Hybrid Polymer/Silica Particles: New Pickering Emulsifiers with Adjustable Surface Wettability

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A facile route for the preparation of water-in-oil-in-water (w/o/w) double emulsions is described for three model oils, namely n-dodecane, isopropyl myristate and isononyl isononanoate, using fumed silica particles coated with poly(ethylene imine) (PEI). The surface wettability of such hybrid PEI/silica particles can be systematically adjusted by (i) increasing the adsorbed amount of PEI and (ii) addition of 1-undecanal to the oil phase prior to homogenization. In the absence of this long-chain aldehyde, PEI/silica hybrid particles (1.0 wt % fumed silica, PEI/silica mass ratio = 0.50) produce o/w Pickering emulsions in all cases.

On addition of sufficient 1-undecanal, this reagent reacts with the primary amine groups on the PEI chains, which renders the PEI/silica hybrid particles sufficiently hydrophobic to stabilize w/o Pickering emulsions at 20ºC. ^{1}H NMR, gas chromatography and x-ray photoelectron spectroscopy provide compelling experimental evidence for this in situ Schiff base surface chemistry, while a significant increase in water contact angle indicates markedly greater surface hydrophobic character for the PEI/silica hybrid particles.

However, when PEI/silica hybrid particles are prepared using a relatively low adsorbed amount of PEI (1.0 % w/w fumed silica, PEI/silica mass ratio = 0.075), the extent of surface modification achieved using this Schiff base chemistry is insufficient, and only o/w Pickering emulsions can be obtained. Fluorescence microscopy and laser diffraction studies confirm that highly stable w/o/w double emulsions can be achieved for all three model oils. Dye release studies from the internal aqueous cores into the aqueous continuous phase indicate some immediate loss of dye (12-18 %) during the high speed homogenization required for double emulsion formation, but no further dye release is observed at 20 °C for at least 15 days thereafter.

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P82. Electrochemical Study on the Effect of Polyethylene Glycol on the Interfacial Behaviour of the Water/Trifluorotoluene (TFT) interface

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The electrochemical potential across the oil-water interface within *water-oil-surfactant* emulsions or microemulsions is typically not considered. Their electrochemistry can however, be studied at oil-water interfaces in a similar way as with solid electrodes with the primary difference being that the ions can also carry the current across the oil/water interface.

By using a conventional four electrode cell, (Fig 1a) experiments were performed to determine the impact of a water soluble polymer, polyethylene glycol (PEG), on the electrochemical behaviour at a polarised water|trifluorotoluene interface. PEG concentration within an aqueous solution (containing for example H^+ or Li^+) was varied to determine the resultant effect on the interface ion transfer.

The results demonstrate that additions of PEG to the aqueous phase can cause a marked reduction in the potential window of more than 30% (Fig 1b). This appears to result from the facilitation by PEG of the transfer of positively charged ions from the aqueous to the oil phase. This type of knowledge can help further the understanding of the microemulsion interfacial characteristics.

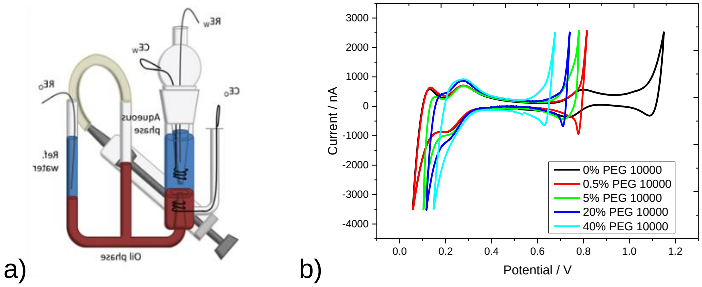

Figure 1a: Four electrode cell for oil-water electrochemistry; (b) Change in the potential window of a 5mM HCl|TFT interface with increasing PEG (M_w 10000) concentration

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P83. A SANS study of water in supercritical CO2 microemulsions with spherical core-shell structures

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Being a non-flammable, green, and abundant compound, supercritical CO_2 has been considered as a promising alternative for volatile organic solvents, however, in fact
CO_2 is a poor solvent especially towards polar solutes, and this remains a significant barrier to applications. Employing effective surfactants which generate stable dispersions and water/CO_2 (w/c) microemulsions is accepted as one way to improve the physico-chemical properties of CO_2.

In this paper, a Small-Angle Neutron Scattering (SANS) study on w/c microemulsions is described with contrast variation, which successfully shows clear evidence for spherical core-shell structures for the microemulsion droplets. These results extend our understanding of w/c microemulsions since SANS studies on such systems in the past are fully based on the
structures of water core droplets, whereas here detailed structural parameters, such as surfactant film thickness and film bending energy, could only be extracted from the core-shell SANS profiles. Furthermore, with reduced pressure, elongated ellipsoidal droplet structures have been observed, which is uncommon for CO_2 microemulsions/emulsions. The implications of the presence of ellipsoidal droplets for applications of CO_2, and viscosity enhancements will be discussed.

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P84. Efficient Synthesis of oly(methacrylic acid)-block-Poly(styrene-alt-N-phenylmaleimide) Diblock Copolymer Lamellae Using RAFT Dispersion Polymerization

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RAFT dispersion polymerization is used to prepare diblock copolymer nano-objects via polymerization-induced self-assembly (PISA) using a poly(methacrylic acid) macromolecular chain transfer agent (PMAA macro-CTA) as the steric stabilizer and AIBN initiator at 70 °C. The core-forming block is a 1:1 alternating copolymer comprising styrene (St) and *N*-phenylmaleimide (NMI), and the continuous phase is a 50:50 ethanol/1,4-dioxane mixture. The 1,4-dioxane co-solvent is essential for this formulation, because it aids solubilization of the NMI comonomer within the growing diblock copolymer micelles. Even so, kinetic studies reveal a significant retardation effect once micellar nucleation has occurred. More importantly, the relatively high glass transition temperature of the P(St-alt-NMI) core-forming block (T_g = 219°C) has an interesting influence on the evolution of the copolymer morphology with conversion. At the polymerization temperature of 70°C, this alternating copolymer is so stiff and inflexible that 2D lamellae are formed, rather than the vesicular phase that is commonly observed for other RAFT dispersion polymerization formulations.

Small angle X-ray scattering studies confirmed the gradual evolution in copolymer morphology from spheres to worms to lamellae when targeting more asymmetric diblock compositions. A detailed phase diagram is reported for a series of $PMAA_{79}$-$P(St\text{-}alt\text{-}NMI)_x$ diblock copolymers, which enables the *reproducible* synthesis of pure spheres, worms, and the lamellar phase. It is also noteworthy that the worm phase region is unusually broad compared to previous PISA formulations. The worms are relatively short and stiff but form free-standing gels above 9% w/w solids. Increasing the mean degree of polymerization of the core-forming block (x) leads to stronger, more brittle gels. On transferring the diblock copolymer nano-objects into water via dialysis, highly negative zeta potentials are observed above the pK_a of the PMAA stabilizer chains, regardless of the copolymer morphology. Thermogravimetric analyses indicate that these diblock copolymer nano-objects have relatively high thermal stabilities, with little or no mass loss being observed on heating in air up to around 350°C.

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P85. The effects of key factors to precise measurement of zeta potential

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Zeta potential is one of the important indicators to address the dispersion stability in micro- or nano- colloidal systems. Being widely used in fundamental research and industries, the way to evaluate the accuracy and precision of the measurement method are however rarely discussed. Due to the increasing
importance in EHS (Environment, Health and Safety) related issues, there is an urgent need to build a standardized measuring system which provides reliable zeta potential values with appropriate traceability. This paper describes an architectural way to examine the effect of several key factors to precise zeta potential measurements utilizing a commercial zeta potential analyzer manufactured by Malvern Instruments. The measurements are carried out with the electrophoretic light scattering technique according to “ISO 13099-2 Colloidal systems - methods for zeta potential determination, Part 2: optical methods” and the evaluation of uncertainties of modulator frequency, frequency shift, electrode voltage, and laser wavelength are demonstrated following the guidance of “ISO/IEC Guide 98-3 : 2008”. The long-term stability of the measuring system is monitored with polystyrene nanoparticles.

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P86. Nano-structures mediated assembly of small molecules and polymers

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The effect of embedded nano-structures on the self-organization and ordering of a *host media* of self-assembling molecules has been demonstrated in a few systems. Observations accumulated over the last two decades indicate that embedded nano-structures may affect the phase diagram of the host material, shift the onset of micellization, the liquid-liquid phase transition, induce polymer crystallization and more. Rationalization of the observed behaviors indicates that the relevant mechanisms are fundamentally different from those predicted by classical colloidal theories. In my talk I will describe experimental studies of a few examples investigated by us over the last years, where nano-structures induce self-assembly in a surfactant phase, modify the phase diagram of an amphiphilic polymer in an aqueous media, and nucleate the crystallization of conjugated polymers.

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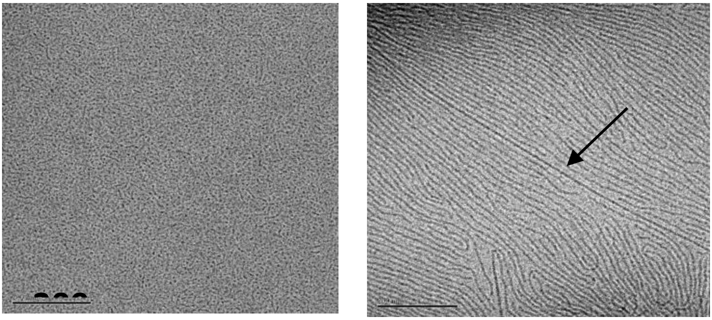

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P87. Preparation of well-dispersed iron-deposited graphene oxides and evaluation of their effect on the electromagnetic wave absorption of polymer composites

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GHz electromagnetic (EM) waves are increasingly applied in various applications due to the saturation at lower frequency bands and simultaneously, electronic devices are getting smaller and thinner. One of recent issues for such high frequency EM waves is a noise generation resulting in malfunctions of the devices. In order to suppress the noise, polymer composites containing magnetic fillers have been utilized as EM wave absorbers. In this work, Iron (Fe)-deposited graphene oxide (GO) particles which could be well dispersed were fabricated by wet process. They were analysed using TEM, SEM, and VSM to optimize the ratios of GO to Fe and the fabrication conditions with respect to proper magnetization and improved dispersion. The Fe-deposited GOs were used as secondary filler to assist the primary hollow magnetic fibers for the improvement of near-field electromagnetic absorption property. We prepared composite film absorbers with 50 wt% primary hollow fibers and 2 wt% of
several kinds of secondary fillers: Fe-deposited GO, GO, and Fe nanoparticles. The power losses of the absorbers measured by a microstrip line method showed that the incorporation of a small amount of Fe-deposited GO into the film alongside the hollow fibers could lead to a dramatic increase in the power loss compared to the other secondary fillers. According to the experimental results, it is expected that this increase was due to the fact that Fe-deposited GOs,
which were aligned tin the in-plane direction and placed among the hollow fibers throughout the film, played a role
in connecting the hollow fibers and spreading the electric and magnetic fields originated from the signal.

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P88. Bayesian Sphere Sizing using NMR and X-ray □CT for Food Systems Research

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The bubble or droplet size distribution (B/DSD) is an important structural characteristic for a wide range of food colloidal systems. It is thus necessary for the scientists working in the food industry to have a non-invasive, rapid measurement technique for the B/DSD. Currently there are a wide range of available techniques but they all suffer from various limitations. Sphere sizing using standard Bayesian probability theory combined with nuclear magnetic resonance (NMR) data has been developed recently [1]. The main advantage of this method is the short experimental time required. The basis of the method is a statistical model which is constructed through numerical simulations. This model ultimately generates likelihood functions, which describe statistically the intensity of the NMR k-space signal for a range of sphere sizes. By performing an NMR experiment on the sample of interest a single line in k-space

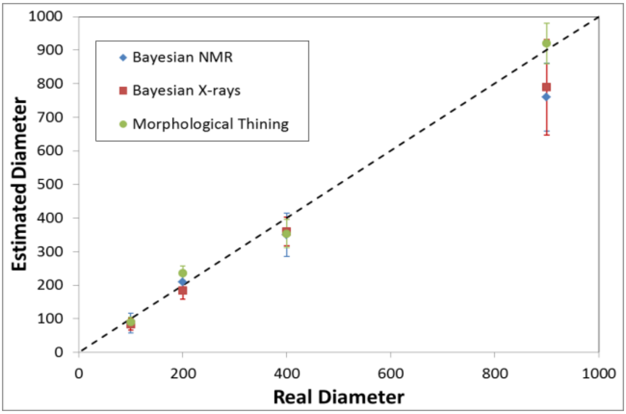

Figure 5 – Estimated glass sphere diameter from three different methods.

can be acquired. The acquired data are compared to the statistical model and a probability estimation for the size distribution is subsequently calculated. In this paper different types of samples are described. Initially, a model system was used. Glass spheres were dispersed in both Xanthan gum gels (used as a model system) and milk chocolate to mimic aerated food products. Different samples with a range of sphere diameters between 1.7 mm down to 100 µm were tested. A Bruker Biospin DMX-300 MHz spectrometer was used to acquire 1D-NMR k-space data and a Bruker Skyscan 1172 was used to acquire X-ray data. Figure 1 shows a summary of the results from the Bayesian/NMR and the Bayesian/X-ray experiments along with a third reference method (morphological thinning analysis). All three methods show a good agreement. Future work will focus on studying commercial food products.

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P89. Encapsulation of actives with hydrophobic property into polyhydroxybutyrate (PHB) nanoparticles

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Polymer-based colloids have been used to produce diverse types of particles for many applications with emphasis on biomedical areas. The class of the polyhydroxyalkanoates, synthesized by a variety of microorganisms, has attracted great interest because of its biocompatibility with animal tissue. Researches have been focused on the polyhydroxybutyrate (PHB) and the copolymer polyhydroxybutyrate-co-hidroxivalerato (PHBV). Recently it was demonstrated that short poly[(R,S)-3-hydroxybutyrate] is very efficiently internalized by living cells. In this work, the preparation of polymer particles PHB was performed by the methods of emulsion and solvent displacement in the presence of the Tween 80 surfactant. Encapsulation of actives with hydrophobic property, like magnetic nanoparticles (Fe3O4), CdSe quantum dots, and dexamethasone (Sigma) were performed. The morphology and structure of the polymer particles were characterized by scanning (SEM) and transmission (TEM) electron microscopy. Release assays of dexamethasone were performed in PBS at pH 7.4. By control of viscosity and interfacial tension of the initial compositions was possible to get PHB particles with different sizes. Systems with high water content yielded the preparation of microparticles, whereas high levels of 2-propanol resulted in the formation of polymeric nanoparticles (100-400 nm). The release of dexamethasone presented an initial burst, with 50% release around the first 4 hours and complete release in 48 horas. The release profile followed the Weibull equation, indicating that the mechanism of drug transport through the matrix was according to Fick's diffusion. The used methods showed to be appropriate not only for the preparation of polymer particles, but also suggested that the drugs encapsulation in polymeric matrices by this system is possible, as well as, inorganic nanoparticles, like quantum dots, gold or iron oxide nanoparticles, thereby, demonstrating high versatility for many other studies.

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P90. High pressure synthesis of FePt nanoparticles with controlled morphology and Fe content

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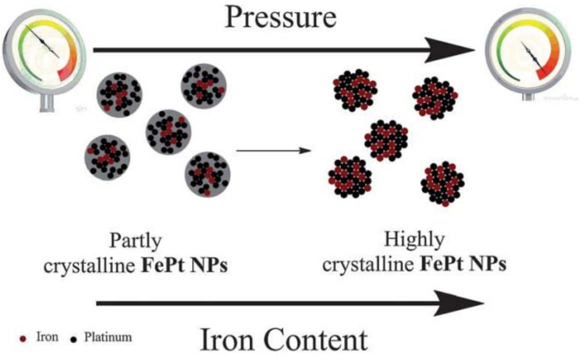
Magnetic nanoparticles (MNPs) are intensively researched due to their large potential in biomedicine, catalysis, and high density information storage. FePt NPs could be an alternative for commonly used magnetite NPs and the synthesis of FePt NPs is an active area of research. The challenge is to increase the Fe content and saturation magnetisation of FePt NPs so that they can be used in many practical applications. Fine tuning of synthetic methods is required in order to achieve the enhanced magnetic properties of FePt nanoparticles and novel methods are being sought. Here, use of an autoclave is shown to increase the Fe content, crystallinity and the subsequent magnetic properties of FePt pseudo cube nanoparticles compared to those synthesised under atmospheric pressure. Decreasing amount of oleic acid is also shown to increase the iron content and can lead to elongated FePt nanoparticles under normal pressure. Further application of nanoparticles synthesised in organic media often requires functionalisation or exchange of stabiliser chemicals. Greater demand for control over such functionalisation requires more information about nanoparticle-stabiliser chemical interactions. Infra-red studies indicate mono and bi dentate coordination with oleic acid, however shifts of spectra show that the strength of the bi-dentate interactions weaken with increasing oleic acid amount



Ref: L. A. W. Green and **N. T. K. Thanh*** (2014) High pressure synthesis of FePt nanoparticles with controlled morphology and Fe content. RSC Advances. 4: 1168-1173

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P91. Multicore magnetic FePt nanoparticles: controlled formation and properties

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Research in magnetic nanoparticles (NPs) has become one of the most active and exciting fields in materials science. The challenge is to produce magnetic NPs with high magnetic saturation without exceeding the super-paramagnetic limit so that they may be used as non-permanent magnets in biomedicine and catalysis. FePt offers enhanced saturation magnetisation properties compared to iron oxide, however synthetic methods require fine-tuning to achieve these superior properties. Multicore FePt NPs up to 44 nm in diameter and composed of Pt rich FePt nanocrystals within an iron rich FePt matrix not previously seen in the literature are presented here. The results indicate that coordination of Fe and Pt intermediates with oleic acid and oleylamine respectively hinders deposition of each respective metal in the growth of discrete and multicore NPs.

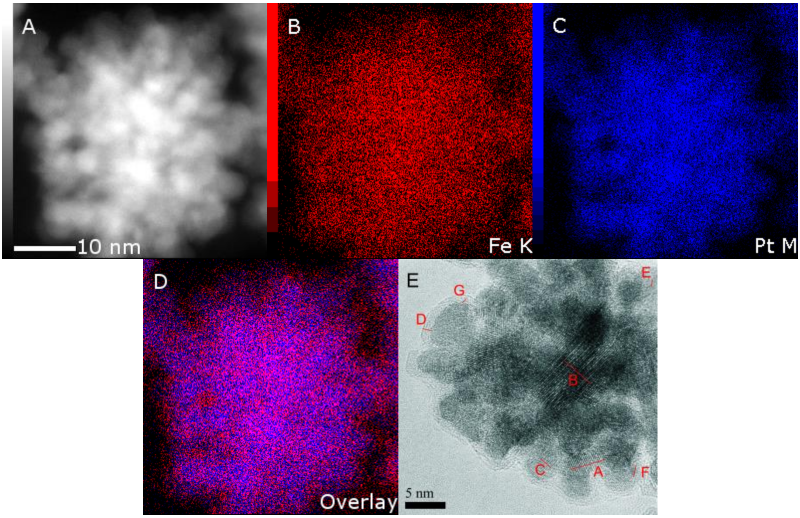

Fig. 1, STEM-HAADF images and elemental mapping of sample mcNPs prepared in dioctyl ether with 4.5 mmol (17 %) OA and tSf equal to 31.5.

Ref: Green, L.A.W., Thuy, T.T., Mott D., Maenosono, S., **Thanh, N.T.K.***, (2014). Multicore magnetic FePt nanoparticles: controlled formation and properties. RSC Advances. 4: 1039 - 1044

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P92. Pathogen detection using protein A conjugated iron oxide nanoparticles

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Pathogen detection plays a key role in the control and prevention of infectious diseases. For the first time protein A conjugated iron oxide nanoparticles were used for a convenient and quick detection of Vibrio cholerae O1 bacteria at the detection limit of 10 cfu mL-1 within 15 min of incubation.

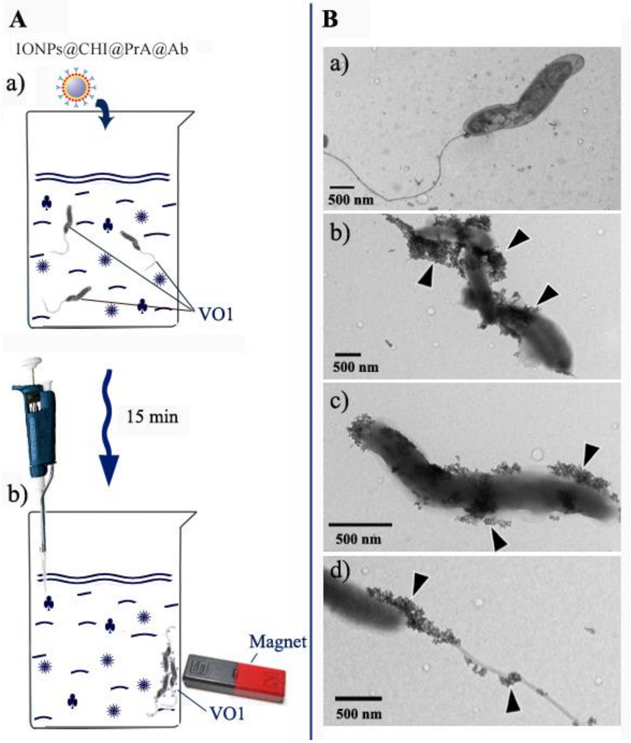

Fig. 1. A) Separation of bacterial cells from liquid samples: (a) adding the complex of IONPs@CHI@PrA@Ab to the sample, and (b) attracting bacterial cells by a magnet. B) TEM images of V. cholerae bacteria (a) before interaction with the complex of IONPs@CHI@PrA@Ab, (b) aggregated and bound by IONPs, (c) IONPs bound to the cell wall, and (d) IONPs bound to the bacterial flagellum.

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P93. Production of polymer beads by membrane emulsification

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Highly uniform droplets are firstly produced by membrane emulsification using a hydrophilic ringed membrane of 10 μm pore size with an array of uniform pores under the paddle blade stirrer. A mixture of methyl methacrylate (MMA) and specific grade of polyvinyl alcohol (PVA) were used as monomer and stabiliser respectively. The various process parameters which affect the size and uniformity of the droplet (i.e. shear stress, stabiliser concentration, flow rate, and process type) are investigated. The second stage of the process is the polymerisation of the emulsion by conventional method. Before polymerisation takes place; however, wide ranges of the reactor's impeller speeds were covered to study the optimum condition to prevent break-up or coalesces and obtain a define particle size with narrow size distribution.

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P94. Tailoring the properties of P3HT particles by varying the emulsion processing parameters

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Two polymeric macrosurfactants based on the same hydrophobic component (*n*-butyl methacrylate, BuMA) and two different hydrophilic components, 2-(dimethylamino) ethyl methacrylate, DMAEMA and poly(ethylene glycol) methyl methacrylate, PEGMA were used to fabricate poly(3-hexyl thiophene), P3HT particles via emulsion templating. Four parameters were varied during the emulsion processing. Specifically, the i) type of macrosurfactant, ii) processing temperature, iii) homogenization technique, iv) organic solvent in the oil phase and v) phase in which the macrosurfactant was dissolved were varied and we investigated how these parameters affect the size and optical properties of the P3HT particles.

Excitingly, both the size and optical properties of the P3HT particles were affected by these four parameters. Specifically, the size of the particles depended mostly on the droplet size, which was affected by the macrosurfactants' ability to stabilise the emulsion as well as the evaporation rate of the solvent. On the other hand, the optical properties of the particles, i.e. the colour and UV-Vis absorption depend on aggregation of the P3HT chains within the particle. So the optical properties were affected when the P3HT aggregation was affected and interestingly the latter was influenced by all four parameters.

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P95. Synthesis and characterisation of semiconducting polymer nanoparticles as photostable imaging agents

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Background. Semiconducting polymer nanoparticles (SPN) have attracted wide attention for potential applications in bio-imaging due to their strong fluorescence and excellent photo-stability. This study investigates the impact of two different SPN compositions on physicochemical properties and cellular uptake versus green fluorescent polystyrene beads.

Methods. Poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT) SPNs were synthesised using mini-emulsion technique utilising sodium dodecyl sulphate or pegylated 12-hydroxystearate as stabilizer. Zeta-potential and hydrophilic interaction chromatography (HIC) were used to study protein corona formation. The size of particles incubated with water/CCM was assessed by DLS. *In vitro* assays using J774A.1 cell line were performed to evaluate cytotoxicity (MTT) and cellular uptake.

Results. Colloidally stable SPNs coated with ionic and non-ionic surfactants were obtained. The size (CCM/10%FCS) of F8BT-PEG, F8BT-SDS and polystyrene was approximately 152nm, 137.5nm and 247nm, respectively. F8BT-SDS and polystyrene nanoparticles demonstrated evidence of protein corona formation due to zeta potential change (-32.3mV to -15mV and -23.9mV to -18.6mV, respectively) after incubation in CCM/10%FCS. The HIC assay showed that all the surfactants were displaced by serum proteins after incubation and the protein corona formation reduced the hydrophobicity of the nanoparticles surface. The nanoparticles demonstrated cell internalisation both in presence and absence of serum, however cell association of F8BT-PEG was lower. SPNs tested at 90µg/mL showed cell viability of approximately 90% for polystyrene, 84% for F8BT-SDS and 3% for F8BT-PEG.

Conclusion. This study showed that protein corona formation and composition is driven by the nature of the stabilizer and hydrophobicity of the nanoparticle core. However, nanoparticle internalization by macrophages was observed to be related primarily

to surface chemistry. This study demonstrates the importance of nanoparticle surface characteristics on the biological responses and highlights the need for studying the surface physiochemistry of particles in biological medium for accurate interpretation of results derived from particle-cell interaction studies.

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P96. Copolymer nanoparticles via RAFT emulsion polymerization: synthesis, characterization and interfacial activity

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A poly(glycerol monomethacrylate) (PGMA) macromolecular chain transfer agent has been utilized to polymerize benzyl methacrylate (BzMA) via reversible addition-fragmentation chain transfer (RAFT)-mediated aqueous emulsion polymerization. This formulation leads to the efficient formation of spherical diblock copolymer nanoparticles at up to 50 % solids. The degree of polymerization (DP) of the core-forming PBzMA block has been systematically varied to control the mean particle diameter from 20 nm to 193 nm. Conversions of more than 99 % were achieved for PGMA51-PBzMA250 within 6 h at 70oC using macro-CTA/initiator molar ratios ranging from 3.0 to 10.0. DMF GPC analyses confirmed that relatively low polydispersities (Mw/Mn < 1.30) and high blocking efficiencies could be achieved. These spherical nanoparticles are stable to both freeze-thaw cycles and the presence of added salt (up to 0.25 M MgSO4). Three sets of PGMA51-PBzMAx spherical nanoparticles have been used to prepare stable Pickering emulsions at various copolymer concentrations in four model oils: sunflower oil, n-dodecane, n-hexane and isopropyl myristate. A reduction in mean droplet diameter was observed via laser diffraction on increasing the nanoparticle concentration. Finally, the cis diol functionality on the PGMA stabilizer chains has been exploited to demonstrate the selective adsorption of PGMA51-PBzMA100 nanoparticles onto a micro-patterned phenylboronic acid-functionalized planar surface. Formation of a cyclic boronate ester at pH 10 causes strong selective binding of the nanoparticles via the cis-diol groups in the PGMA stabilizer chains, as judged by AFM studies. Control experiments confirmed that minimal selective nanoparticle binding occurred at pH 4, or if the PGMA51 stabilizer block was replaced with a PEG113 stabilizer block.

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P97. Self-Assembly of Poly(Methacrylate-co-Acrylic Acid) Copolymers of Varying Architecture Synthesised by RAFT Polymerisation

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Polymers with segmented amphiphilic structure possess numerous supramolecular properties leading to interesting nano-scale structures.1 The study of this behaviour has largely been limited to linear block copolymers, but as the supramolecular organisation of the segments is expected to be controlled by architecture, consideration of other segmented architectures could lead to new and useful supramolecular and nanoscale structures. As a technique for producing segmented polymers of differing architectures, Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerisation2,3 is possibly the most versatile of the controlled radical polymerisation techniques.4

Amphiphilic block copolymers with constant chemistry but differing architectures have been shown by transmission electron microscopy (TEM) and small angle neutron scattering (SANS) to self-assemble into micellar structures in water. RAFT polymerisation has been used to synthesise poly(alkyl methacrylate-acrylic acid) copolymers in a range of different architectures: graft, highly branched block and linear block, in addition to random versions of each of these copolymers. This set of model materials has allowed us to investigate the effects of architecture and composition on the properties of the copolymers. Additionally the hydrophobicity of the methacrylate block has been varied to study its effect on solution conformation.

These materials were designed to improve the adhesion of hydrophilic materials to a hydrophobic substrate via deposition from a fluid. However due to the amphiphilic nature of the materials they show potential for further use as surface active polymers in a range of nano- and bio- technologies.

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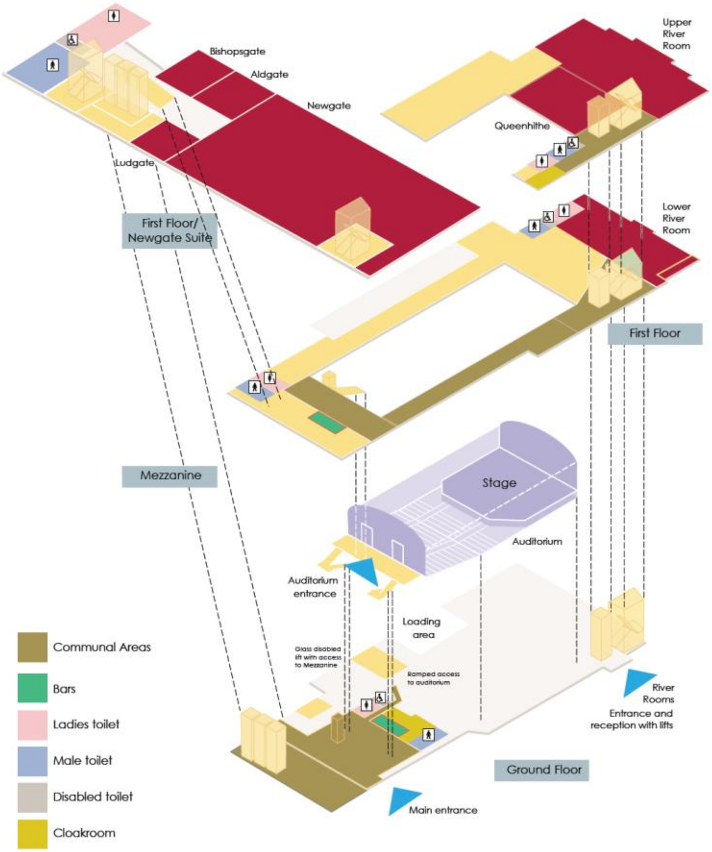

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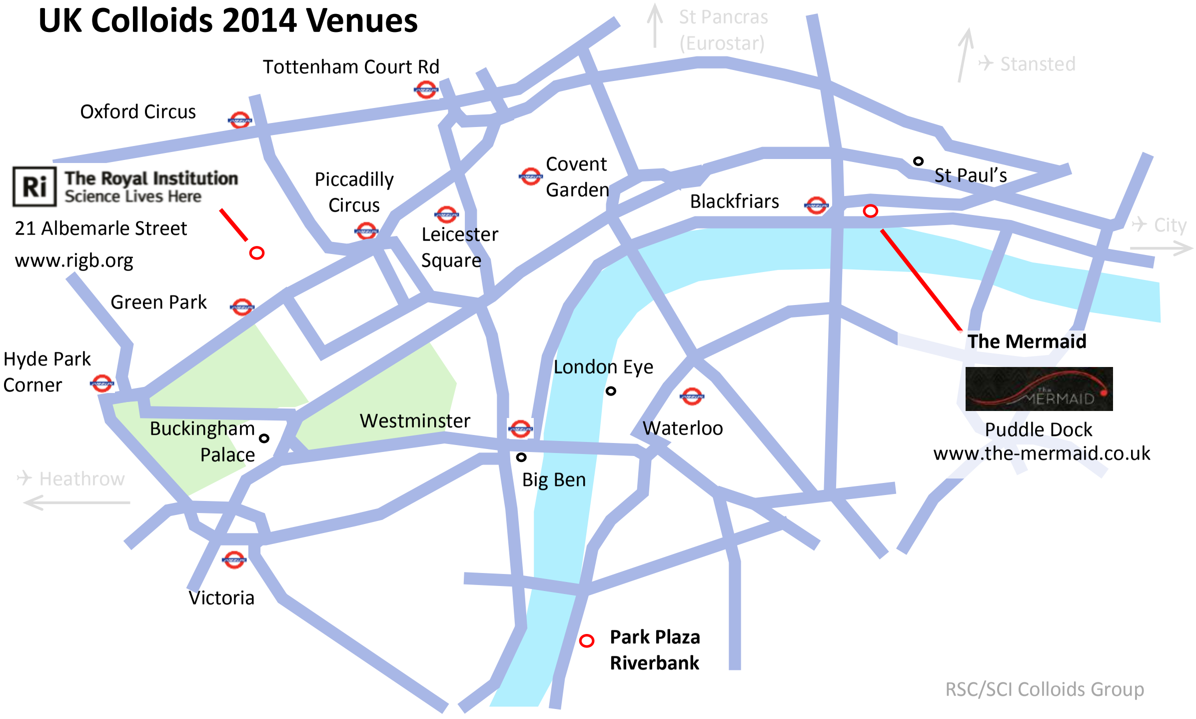

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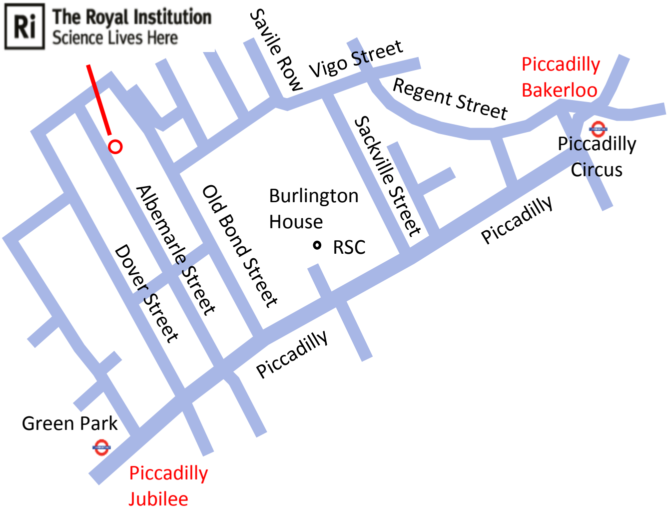

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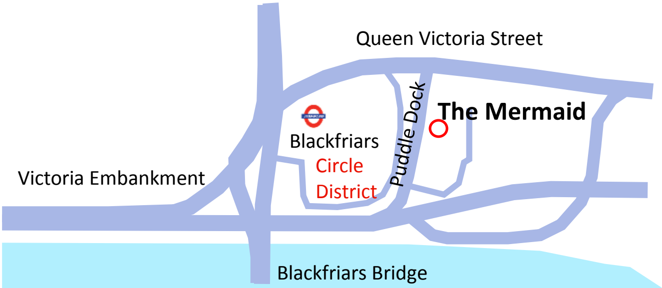

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