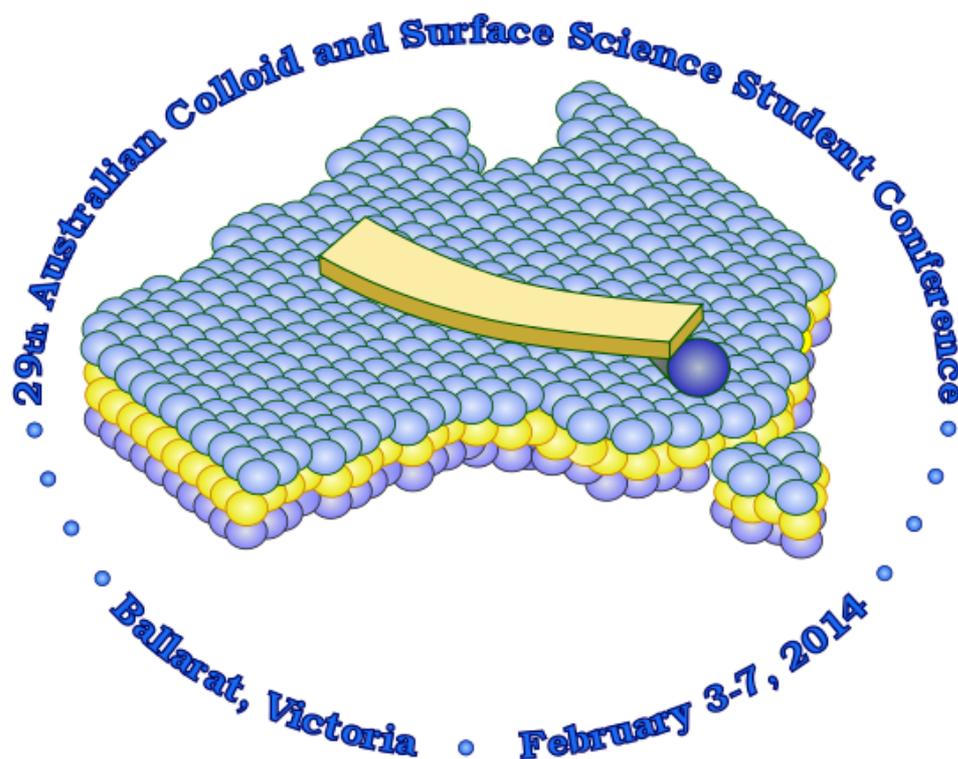


29th ACSSSC

ACIS

Australian Colloid and Interface Society



Program and Abstracts





In 1967 Bob Hunter and Tom Healy started the tradition of the Australian Colloid and Surface Science Student Conference. These conferences have provided postgraduate students of colloid and surface science with an opportunity to present and discuss their research in an informal, supportive and friendly atmosphere.

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Foreword

By Professor Russell Crawford, President of the Australian Council of Deans of Science.

Welcome to the 2014 Australian Colloid and Surface Science Student Conference, the 29th of its kind since they began in 1968.

Like many of the supervisors and students who have attended in the past, I have been looking forward to it for some time. We not only get to hear about the current research being undertaken by our talented, energetic and enthusiastic postgraduate students, but the ACSSSC also gives us the opportunity to catch up with our friends and colleagues who may have come from interstate, overseas, or just from over the other side of our own city, but for some reason we haven't had time to catch up with them since we saw them at the last conference we attended.

Students attending the ACSSSC for the first time may understandably be nervous about having to present their work to their peers and supervisors, and be feeling uneasy about the questions that may be asked. Even worse, some students may be concerned that even though they believe their project is 'nearing completion', somebody might point out a whole new section of work that really needs to be completed before writing your thesis! ACSSSC presenters are in the fortunate position of having the opportunity to gain the valuable experience that this conference offers to each of its presenters; the chance to show your work to a group of genuinely interested scientists in an extremely supportive environment, and it has been that way since 1968, thanks to the original vision for this conference, devised by two remarkable gentlemen, Professors Tom Healy and Bob Hunter.

Please rest assured that any comments, criticisms or suggestions that are made to you in the course of this conference will be made only with a view to helping you successfully complete your research. Who knows, one or more of the examiners of your future thesis may even be in the audience!

In 2008, the surface and colloid science community celebrated the 40th Anniversary of this conference. In four short years, the Golden Anniversary will be upon us. This is truly a noteworthy achievement, and many of us are already looking forward to the celebrations that will no doubt take place to mark this significant milestone.

Many photographs of past student conferences are posted on the *Australian Colloid and Surface Science Student Conference Facebook* site. We would encourage you to share your 2014 ACSSSC pictures and thoughts through this site, if you would like to do so.

As I have previously stated, the ACSSS conference was my equivalent of receiving a scientific vitamin shot when I was a postgraduate student. I returned from each conference with a renewed enthusiasm for my research, re-focused on completing my PhD studies. I hope that your experience at this ACSSSC will leave you feeling the same way.

Russell

Preface

The Australian Colloid and Surface Science Conference has grown and excelled in the more than 46 years since its inception by Bob Hunter and Tom Healy. On every occasion it introduces a new set of students to the Australian colloid community and renews lifelong connections between researchers across Australia. This conference continues to have international attendance and has even inspired similar colloids student conferences in Europe. The ACS SSC provides an invaluable forum for “young” researchers to present their work for review by their peers and the broader community.

The 29th Australian Colloid and Surface Science Student Conference, hosted by the University of Melbourne, is for the first time run under the auspices of the Australian Colloid and Interface Society (ACIS), a newly established society that brings together researchers from a diverse range of backgrounds into one membership. The organising committee would like to welcome the 70 students attending the conference, in particular those attending from overseas (Sweden, Germany, and Japan); we hope you enjoy both the academic and social activities planned. We would also like to thank Dr. Srinivas Mettu from the University of Melbourne for presenting the plenary talk. We would also like to thank the 27 staff members representing various Universities and CSIRO for attending.

Finally, we must also acknowledge the sponsors of this conference, without your generous support it would not be possible to keep this conference affordable for students. Thank you also to the students who have helped in the organisation of the conference: Christopher Bolton, Christine Browne and Christopher Fewkes.

In 2014, we have introduced several new activities. This year marks an inaugural poster and mini-presentation competition for a student studying at an Australian institution to have an opportunity to attend the annual meeting of the European Colloid & Interface Society (ECIS). The second new activity is motivated by the changing demands placed on PhD students, recognising that in addition to scientific discovery, communication of results and the completion of a thesis, there are increasingly formal expectations of professional development within the few short years students have to do their PhD. In order to take full advantage of the conference location here in Ballarat at the newly renamed Federation University (FU, formerly Ballarat University), we have arranged for several plant tours to local industry sites related to minerals processing and water treatment, as interfacial phenomena are critical to these industries. This conference has always had strong ties to industry and it is important to acknowledge the generosity of those companies that have donated the time and energy of their highly trained scientists and engineers to show us around these facilities.

We do hope that you enjoy the 29th Australian Colloid and Surface Science Student Conference and take full advantage of the FU facilities at our disposal. We hope that upon returning to your home institutions you will speak highly of the conference and share your FU experience with others. Have a great time, get involved in all the activities and enjoy the science and please remember the most important rule of the student conference — *you have to attend every talk!*

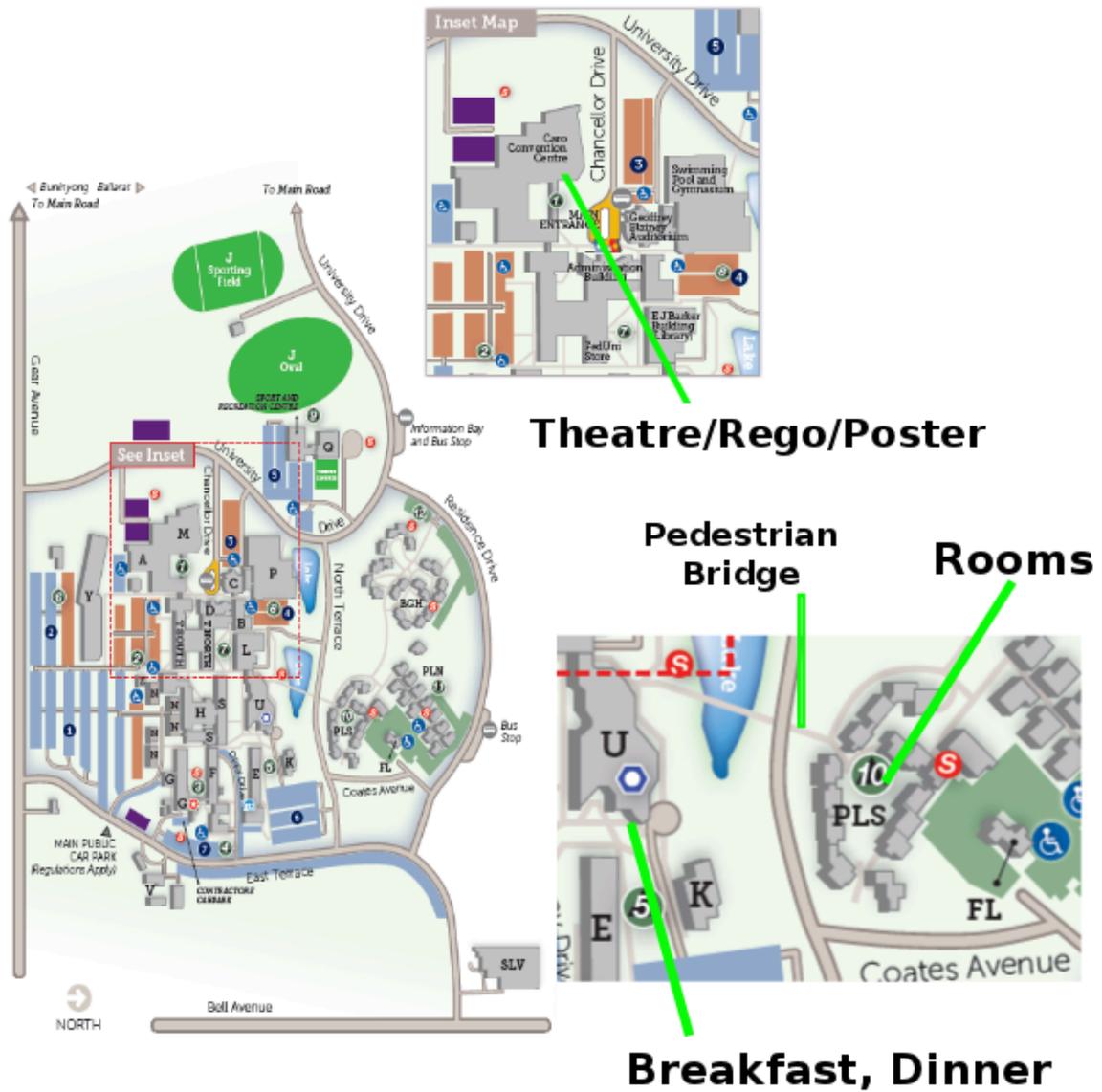
Ray Dagastine and Anthony Stickland

Conference Co-Chairs, 29th ACS SSC

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Map & Info



Warnings:

1. The rooms are fitted with extremely sensitive thermal fire alarms – smoking, incense, candles, etc can all trigger the alarm. In case of negligence, the charge of response to trigger alarms will be passed on those who trigger the alarm.
2. Do not lose your keys. If you do so, the cost of replacement will be passed on to you.
3. The cost of repair to any damage caused to rooms or facilities will be incurred by those responsible.

Accommodation and Check Out Procedures:

1. Kitchen / Lounge / Dining Area / Bathrooms

Each unit contains one kitchen/lounge/dining area and up to two communal bathrooms. The group will have full use of these facilities, however it is expected that all units are to be left by your group as you found them upon arrival. For Kitchen's this means all dishes, utensils, crockery and cutlery, pots and pans are to be washed, dried and put away. Stove-tops, ovens, refrigerators, benches and tables are to be left free of foodstuffs, clean and tidy. Floors should be vacuumed throughout units and mopped (kitchen and bathrooms). A supply of cleaning materials, including washcloths and tea towels will be provided.

2. Check-Out

Check-out on the day of departure is 10:00 am. **IT IS IMPORTANT** that you check out at time due to returning University students and other groups checking in later this day.

This means:

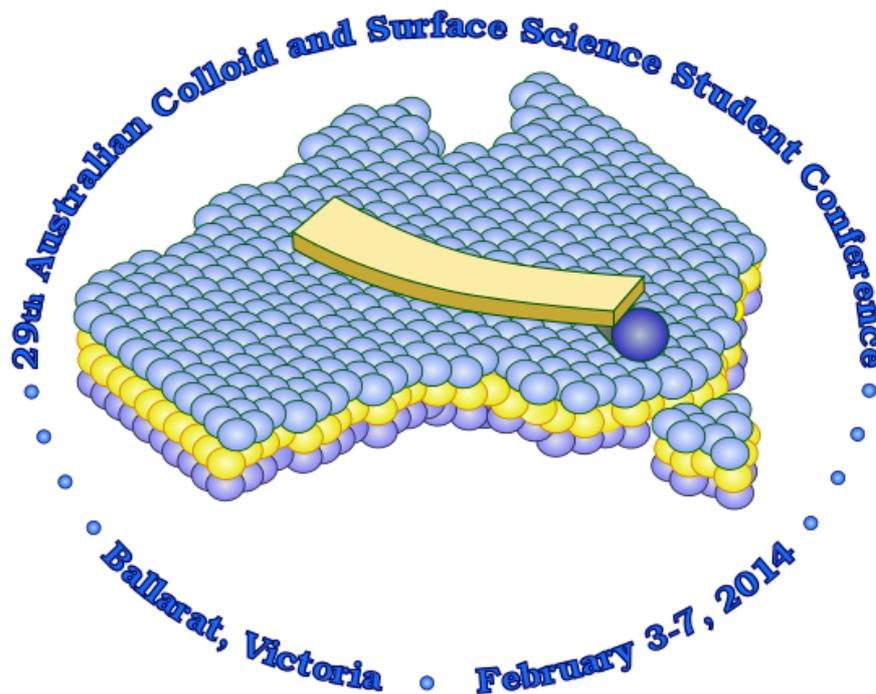
- All rooms and Units are to be left in a clean and tidy state
- All linen must be removed from beds and placed into the linen bags provided (excluding bedding i.e. pillows and doonas)
- All Swipe Cards must be returned to the conference committee between 9:30 and 10:00 am on Friday.
- All rubbish must be removed from the unit and placed in the outside bins / enclosures

3. Smoking

All buildings within residence, including the common room, are smoke free zones. If you smoke, only do so outside in designated areas.

4. Study Environment

The halls of residence are specifically designed and designated as University student accommodation. They are not motels. Therefore during school months, priority is given to maintaining an environment conducive to study at all times in all living/study areas of the halls of residence. Your respect for maintaining a “quiet time” after 10.30pm each night is expected.



The 29th Australian Colloid and Surface Science Student Conference is proudly hosted by



Co-chairs: Raymond Dagastine and Anthony Stickland

Organising Committee Members:

Christopher Bolton
Christine Browne
Christopher Fewkes

Previous Conferences

Year	Location	Total number of participants
1967	Melbourne	-
1968	Sydney	-
1970	Melbourne	14
1972	Sydney	-
1973	Melbourne/Blackwood	30
1974	Sydney/Woy Woy	39
1976	Canberra	33
1977	Melbourne/Blackwood	34
1978	Yarrowood	-
1980	Kioloa	50
1982	Mt. Eliza	75
1983	Yarrowood	51
1985	Roseworthy	49
1987	Kioloa	55
1988	Albury	107
1990	Camden	-
1991	Roseworthy	118
1993	Deakin University	144
1995	Fairy Meadow	185
1996	Murramarang	118
1998	Hahndorf	141
1999	Morpeth	143
2001	Bendigo	110
2002	Lake Hume	114
2004	Sunset Cove	116
2006	Beechwood	135
2008	Warrnambool	126
2010	Roseworthy	127
2012	Riverwood Downs	105
2014	Ballarat	97

List of Participants

University of Melbourne

Christopher Bolton
Emma Brisson
Christine Browne
Wilhelm Burger
Adam Crust
Raymond Dagastine
Mina Dokouhaki
Chris Fewkes
George Franks
Katelyn Gause
Irvianti Hadiputra
Terence Hartnett
Lauren Hyde
Tiara Kusuma
Srinivas Mettu
Michael Neeson
Marta Redrado Notivoli
Sayuri Rubasingha
Peter Scales
Sam Skinner
Anthony Stickland
Cathy Sutton
Carolina Tallon
Hui-En Teo
Brant Walkley
Chu Wu

Swinburne University

Martina Abrigo
Hannah Askew
Russell Crawford
Peter Koegler
Sally McArthur
Rohan Shah

Tokyo U. Science and MANA

Masaaki Akamatsu

University of Sydney

Saffron Bryant
Stephan Burger
Andrew Dolan
Paul FitzGerald
Manuel Ghezzi
Hahui Joy Jiang
Thu Lam
Chiara Neto
Greg Warr

Australian National University

Hongjie An
Timothy Duignan
Namsoon Eom
Virginia Mazzini

CSIRO

Patrick Hartley
Yali Li
Leonie van 't Hag
Yuriy Veytskin
Emmy Wijaya

Monash University

Ben Boyd
Joanne Du
Thomas McCoy
Stephanie Phan
Matthew Pottage
Rico Tabor

Deakin University

Wren Greene
Ninghui Han
Roger Horn
Tingting Hou

UniSA

Jonas	Addai-Mensah
Eric	Agorhom
Samuel	Asare-Asher
Bellson	Awatey
David	Beattie
Jason	Connor
Lorena	Del Castillo
Iliana	Delcheva
Shadrack	Fosu
Catherine	Fung
Paul	Joyce
Mohammed	Kor
John	Linden
Andrew	Lo
Jennifer	Maccarthy
Magnus	Nyden
Muireann	O'Loughlin
Clement	Owusu
Ishmael	Quaicoe
John	Ralston
Rossen	Sedev
Bill	Skinner
Catherine	Whitby

University of Queensland

Grace	Dolan
Nichola	Selway

University of Newcastle

Aaron	Elbourne
James	Sweeney
Erica	Wanless
Grant	Webber
Joshua	Willott
Ross	Wood

Max Planck Inst. Polymers

Victor	Bergmann
--------	----------

KTH

Nicklas	Hjalmarsson
---------	-------------

Johannes Gutenberg University

Florian	Mathias
---------	---------

University of Freiburg

Jochen	Schneider
--------	-----------

Stockholm University

Christina	Schütz
-----------	--------

Trivia & Talent Groups

Group 1

Christopher Bolton
Terence Hartnett
Chu Wu
Jochen Schneider
Andrew Dolan
Yali Li
Ninghui Han
Paul Joyce
Aaron Elbourne
Paul FitzGerald
Raymond Dagastine
David Beattie

Group 2

Christine Browne
Tiara Kusuma
Victor Bergmann
Christina Schütz
Manuel Ghezzi
Leonie van 't Hag
Tingting Hou
Mohammed Kor
James Sweeney
Chiara Neto
Russell Crawford
Jason Connor

Group 3

Chris Fewkes
Michael Neeson
Emma Brisson
Grace Dolan
Thu Lam
Yuriy Veytskin
Eric Agorhom
John Linden
Joshua Willott
Greg Warr
Sally McArthur
Rossen Sedev

Group 4

Mina Dokouhaki
Sayuri Rubasingha
Rohan Shah
Nichola Selway
Hahui Joy Jiang
Emmy Wijaya
Samuel Asare-Asher
Andrew Lo
Ross Wood
George Franks
Rico Tabor
Lorena Del Castillo

Group 5

Wilhelm Burger
Sam Skinner
Masaaki Akamatsu
Saffron Bryant
Hongjie An
Joanne Du
Bellson Awatey
Jennifer Maccarthy
Marta Redrado Notivoli
Peter Scales
Ben Boyd
Bill Skinner

Group 6

Adam Crust
Cathy Sutton
Peter Koegler
Stephan Burger
Timothy Duignan
Thomas McCoy
Iliana Delcheva
Muireann O'Loughlin
Lauren Hyde
Anthony Stickland
Wren Greene
Catherine Whitby

Group 7

Katelyn Gause
Hui-En Teo
Martina Abrigo
Nicklas Hjalmarsson
Namsoon Eom
Stephanie Phan
Shadrack Fosu
Clement Owusu
Srinivas Mettu
Patrick Hartley
Jonas Addai-Mensah
Erica Wanless

Group 8

Irviandi Hadiputra
Brant Walkley
Hannah Askew
Florian Mathias
Virginia Mazzini
Matthew Pottage
Catherine Fung
Ishmael Quaicoo
Carolina Tallon
Roger Horn
Grant Webber
Magnus Nyden

Scientific Program

Time	Monday 03/02/13	Tuesday 04/02/13	Wednesday 05/02/13	Thursday 06/02/13	Friday 06/02/13
		07:00 - 08:30 Breakfast	07:00 - 08:30 Breakfast	07:00 - 08:30 Breakfast	08:00 - 09:30 Breakfast
09:00	Registration (09:00 – 13:00)	9 am Dr. Srinivas Mettu Plenary Lecture sponsored by the MMI	Talent Night Preparation	Chair: G. Webber	Return Keys by 10:00 am and depart
09:20				O25 Akamatsu	
09:40				O26 Hou	
10:00	O27 Schutz				
	10:00 - 10:30 Morning Tea	10:00 - 10:30 Morning Tea	10:20 - 10:50 Morning Tea	10:20 - 10:50 Morning Tea	
	Chair: J. Connor	Chair: D. Beattie	Chair: R. Tabor		
10:30	Registration (09:00 – 13:00)	O10 Bolton	O20 Linden	O29 Van't Hag	
10:50		O11 Hjalmarsson	O21 Askew	O30 Hartnett	
11:10		O12 Teo	O22 Koegler	O31 Asare-Asher	
11:30		O13 Dolan	O23 Ghezzi	O32 Neeson	
11:50		O14 Sweeny	O24 Joyce	12:10 – 13:30	
12:10	12:30 – 13:30 Lunch	Lunch	12:30 – 13:30 Lunch	Lunch	
	Chair: C. Whitby	Chair: R. Sedev	Staff-Student Cricket Match	Chair: M. Nyden	
13:40	Welcome	O15 Wu		O33 Elbourne	
13:50	O01 Kor	O16 Wood		O34 Sutton	
14:00		O17 Selway		O35 McCoy	
14:10	O02 Browne	O18 Schneider		O36 Phan	
14:20		O19 Fewkes		O37 Willott	
14:30	O03 Han			15:20 – 16:00 Afternoon Tea	
14:40				Chair: R. Crawford	
14:50	O04 Duignan			O38 Gause	
15:00				O39 Abrigo	
15:10	15:10 – 15:40 Afternoon Tea	15:20 – 16:00 Afternoon Tea	O40 Shah		
15:20	Chair: P. Scales		O41 Poster Comp.		
15:40	O05 Bellson				
16:00	O06 Owusu	(16:00 - 18:00) Poster Session Sponsored by ANSTO			
16:20	O07 Walkey				
16:40	O08 Agorhom				
17:00	O09 MacCarthy				
18:00	Free Time	Free Time	Free Time	Free Time/ ACIS AGM	
19:00	19:00 – 20:30 Dinner	19:00 – 20:30 Dinner	19:00 – 20:30 Dinner	19:00 – Late Conference Dinner Sponsored by MERIT	
20:30 - Late	Mixer	Trivia Night	Talent Night		

Conference Awards



Healy-Hunter Award – the most outstanding oral presentation will be awarded the Healy-Hunter Award. This award consists of a commemorative medal and a contribution (\$1500) towards the travel costs of attending an international conference. Students enrolled at an Australian university are eligible candidates for this award. All staff members attending the student conference are eligible to vote. Supervisors may vote for their own PhD students if so desired.

Best Poster Award – the most outstanding poster presentation will be awarded the Best Poster Award. This award is a prize of \$250 gift voucher with CSIRO Publishing and is voted by eligible staff.

ACIS-ECIS Poster Award – the most outstanding poster presentation and four minute mini-presentation will be awarded the ACIS-ECIS Award. This award provides free conference registration at the next ECIS conference in Europe and is voted by eligible staff where the student's supervisor must commit to supporting the additional travel expenses. Students enrolled at an Australian university are eligible candidates for this award.

The Most Probing Question and the Most Memorable Moment Awards – as a part of the tradition, there will be a presentation of specially designed trophies for both the Most Probing Question and the Most Memorable Moment witnessed at the conference. To be eligible, the event is nominated and a winner decided by a carefully chosen panel of judges. The prize – embarrassment and notoriety!

Plenary Lecturer

Sponsored by the Melbourne
Materials Institute



MATERIALS
Research Institute

Motion of Liquid Drops on Surfaces Induced by Vibration: Role of Contact Angle Hysteresis

Dr. Srinivas Mettu

the Particulate Fluids Processing Centre

Department of Chemical and Biomolecular Engineering,

University of Melbourne, Parkville, AU.

srinivas.mettu@unimelb.edu.au

In this talk we explore the fundamental role played by contact angle hysteresis on contact line pinning and movement on various surfaces. The research work shown in the first part of the talk is motivated by challenges associated with inkjet printing onto polymeric materials especially for commercial label printing. Ink jetted image pattern de-wets resulting in defective image on polymeric material due to low surface energy and low contact angle hysteresis. Hence, pinning of contact line of jetted ink drops at desired position is crucial for better image quality. In order to overcome this problem, we explored the use of structured rough surfaces. We made rough surfaces with $3\mu\text{m}$ diameter hemispherical protrusions (bumps) and pits (cavities) using standard photolithography and polymer casting. The distance between the bumps and cavities on the surface is systematically varied from $4.5\mu\text{m}$ to $96\mu\text{m}$. We measured static, advancing and receding water contact angles on these surfaces to study wetting properties. We found that smaller is the distance between the bumps and cavities higher are the static and advancing water contact angles hence better contact line pinning. We found that on the surfaces with hemispherical bumps, the contact angle hysteresis has an optimum high value for a spacing of $12\mu\text{m}$ whereas for the cavities surface, the optimum high value is at the lowest spacing of $4.5\mu\text{m}$. We also explored the use of recently developed modified Wenzel equation which is based on the contact line region as opposed to classical Wenzel equation which is based on the area under the drop. We found that the modified Wenzel equation accurately predicts static water contact angle measured in the experiments.

In the second part of the talk, we explore the role of contact angle hysteresis on asymmetric vibration induced movement of liquid drops on surfaces. The contact angle hysteresis which is like Coulombic friction generally prevents the movement of liquid drops on surfaces. However, we show a counter intuitive example where hysteresis enables the movement of drop without which the drop cannot move on the surface. We use non-linear contact angle hysteresis model to explain the result. Using this model we accurately predict the detailed contact line movement and direction of 1 and 4 μL which move in opposite directions when subjected to same asymmetric vibration.



Dr. Srinivas Mettu completed his PhD in the department of Chemical Engineering at the Lehigh University, Bethlehem, Pennsylvania in 2012. He then completed 18 months of postdoctoral studies at the Xerox Research Center in Webster, NY, prior to joining the Department of Chemical and Biomolecular Engineering and the Particulate Fluids Processing Centre as a research fellow in 2013. Dr. Mettu's research is within the broad area of colloid and interfacial science. Dr. Mettu already has 9 well-cited peer reviewed publications and four patents from his postdoctoral work. Dr. Mettu's work has focused on several areas including the fundamental interactions of complex liquids (colloidal suspensions) with solids in the context of inkjet and offset printing technologies as well as the effects of contact angle hysteresis during movement of small drops on solid surfaces. Dr. Mettu's most recent position is focused on soft matter (drops and bubble interactions) in food processing and formulation.

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Bubble-Surface Collisions of Polymer-Treated Talc and Molybdenite

Mohammad Kor¹, Piotr M. Korczyk^{1,2}, Jonas Addai-Mensah¹, David A. Beattie¹

1. Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes, SA 5095
2. Institute of Fundamental Technological Research, Polish Academy of Sciences, Warsaw, Poland

mohammad.kor@mymail.unisa.edu.au

Flotation is a physico-chemical separation process that relies on the differences in wettability of the solid phases [1]. In complex flotation systems, such as flotation of metal sulfide ores, selective separation of minerals does not take place without the aid of added reagents into the mineral suspension. Water-soluble polymers are employed in flotation system to alter particle/bubble interactions. One of the most important steps for successful flotation is the replacement of water at the mineral surface by an air bubble which has been traditionally quantified by static contact angle values of mineral surface in water. Consequently, there have been several studies correlating and comparing measured static contact angles with the effect of polymers on mineral flotation [2, 3, 4]. Although static contact angles measurements can give an indication of what will happen when bubbles collide with mineral particles, they are unable to describe the dynamics of the bubble–particle attachment of flotation (thin liquid films, dewetting, etc.). Therefore, the collision of a rising air bubble with a freshly cleaved and polymer coated mineral surfaces of molybdenite as a valuable mineral in the sulfide ore and talc as an unwanted waste mineral in sulphide ore were examined using high speed video capture of the bubble-surface collisions. The recorded images from high speed camera then are used for a quantification of the film drainage time and three phase contact line movement as well as dynamic receding contact angle. We report on the effect of polysaccharide-based polymers including normal dextrin as well as hydrophobically modified dextrans Capsul and Capsul TA on bubble-surface interactions for talc and two carboxymethyl cellulose polymers with specific variation in functional group degree of substitution and distribution of substitution on molybdenite. The bubble-surface collision data reveal that both bare molybdenite and bare talc surfaces have short thin film drainage times and rapid dewetting speed and that the presence of an adsorbed polymer layer significantly increases thin film rupture times and retards dewetting rates to varying degrees depending on the adsorbed different polymer layer. The information gained from this study may offer better understanding into the dynamics of the bubble–particle attachment of flotation in presence of adsorbed polymer layer to improve flotation performance and significant cost savings.

1. Wills, B. and T. Napier-Munn, *Mineral Processing Technology: An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery*. 7 ed2006: Butterworth-Heinemann. 444.
2. Beattie, D.A., et al., Influence of adsorbed polysaccharides and polyacrylamides on talc flotation. *International Journal of Mineral Processing*, 2006. 78: p. 238-249.
3. Mierczynska-Vasilev, A. and D.A. Beattie, Adsorption of tailored carboxymethyl cellulose polymers on talc and chalcopyrite: Correlation between coverage, wettability, and flotation. *Minerals Engineering*, 2010. 23(11-13): p. 985-993.
4. Crawford, R. and J. Ralston, The influence of particle size and contact angle in mineral flotation. *International Journal of Mineral Processing*, 1988. 23(1-2): p. 1-24.

Depletion and Structural Forces in Foams: Interactions between Bubbles in the Presence of Polyelectrolytes

Christine Browne¹, Rico Tabor², Derek Chan¹, Franz Grieser¹, Raymond Dagastine^{1,3}

1. Particulate Fluids Processing Centre
The University of Melbourne, Parkville VIC 3010 Australia

2. School of Chemistry
Monash University, Clayton VIC 3268 Australia

3. Melbourne Centre for Nanofabrication
Clayton VIC 3268 Australia

browneci@student.unimelb.edu.au

The interactions between bubbles are important in a number of commercial applications. For example the stability of food products containing foams, separation processes such as flotation and personal care products. As the forces between bubbles in aqueous solutions containing solutes in general and polyelectrolytes in particular are not fully understood further understanding of these interactions could lead to improvements in many consumer and industrial products.

The aim of this work was to investigate the forces between bubbles in aqueous solutions containing the polyelectrolyte sodium poly(styrene sulfonate). The technique of Atomic Force Microscopy (AFM) was used to measure the forces between bubbles and rigid systems. The differences between deformable and rigid surfaces have been investigated using deformable surfaces because the latter are more sensitivity to the presences of polyelectrolytes in solution. Other focuses of this work include effects of varying bubble collision velocity, polyelectrolyte concentration and molecular weight. Influences due to molecular weight were investigated further to understand the effect that increasing polydispersity has on these interactions. The observations undertaken on structural forces under varying conditions such as the collision speed of bubbles and polydispersity of the polyelectrolyte have been made.

A new angle on the coalescence of drops

Ninghui Han, Wren Greene, Roger Horn

Institute for Frontier Materials.
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Drops and bubbles are everywhere in the world and play a major role in the exchange of mass and heat between the oceans and the atmosphere, and also in many industrial processes where drops or bubbles interact with another solid surface. These areas include agricultural spraying, inkjet printing, spray coating, fuel injection in internal combustion engines, drug formulation, aerosol drug delivery, multiphase flow and others. Agricultural spraying wants the pesticide drops to stay with plants as long as possible, inkjet printing requires ink drops to absorb to paper quickly and uniformly, multiphase flows frequently want phases to remain dispersed by avoiding drop or bubble coalescence. All these phenomena require basic study of drop (bubble) and surface collisions. However, currently the vast majority of investigations into drop and bubble collisions have considered only head-on collisions between drops (bubbles) or perpendicular approach of drops (bubbles) to surfaces. These investigations are only the first step toward helping industry to develop a better system because drops (bubbles) in our real world are overwhelmingly more likely to collide with each other or with surfaces at random angles, and there are very few detailed investigations into the effects that non-perpendicular approach angles will have.

Our main aim is to address this lack of knowledge by conducting experiments with a single air bubble in a liquid environment rising to a glass slide tilted at various angles to the horizontal. The optical system also has to be tilted so that the optical path remains normal to the solid surface. A schematic diagram of our experimental set-up can be seen in Fig. 1 (a). Newton’s rings can be viewed during the bubble sliding process (shown in Fig. 1 b). These asymmetric fringes demonstrate a complex thin film shape between a sliding bubble and the glass surface that has not been reported before. We would like to describe the shape as ‘tobogganing bubble’ because it has two ‘rails’ at the edge and a channel in the middle with a small dimple shape at the back. We also found the bubble could be rolling instead of sliding along the surface during the experiments.

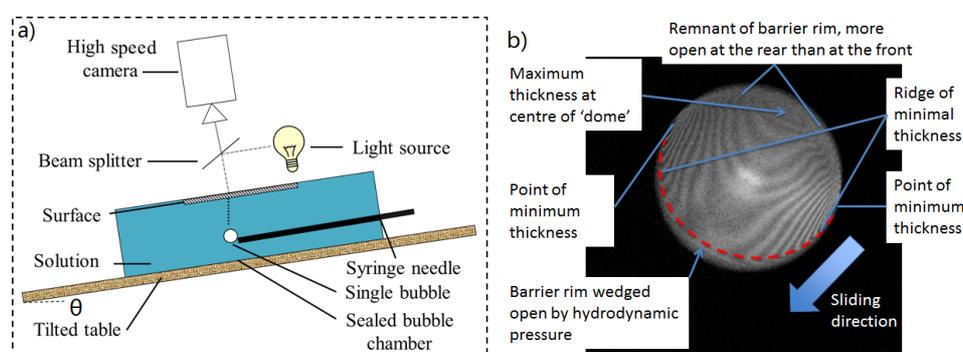


Figure 1. a. Schematic diagram of experimental set-up of this project. b. Newton’s rings observed of a sliding bubble with glass slide.

A Successful Continuum Solvent Model of Ionic Interactions with the Air Water Interface

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Explanation and prediction of the interfacial tensions of ions with the air-water and oil-water interface has been a central challenge for Hofmeister effects in physical chemistry for over a century. Renewed focus on this problem in recent years has been driven by the surprising observation that large halide anions adsorb to the air-water interface.¹

In essence the problem amounts to calculating the change in the solvation energy of an ion as it approaches the interface. We have recently developed a satisfactory continuum solvent model of ionic solvation energies in the bulk.² Here, we generalize this model to calculate the free energy change as an ion approaches the air-water interface. The change in the Born energy as well as the polarization response of the ion are included by using the COSMO software package, which treats the ions quantum mechanically. Approximate expressions for the dispersion repulsion, cavity attraction and surface potential contributions are also included. This model reproduces the ion specific behaviour of the surface tensions of electrolyte solutions, and is in agreement with approximate *ab initio* molecular dynamic simulation of the iodide anion at the interface.³ The model provides a straightforward physical explanation of iodide's adsorption. Unlike alternative models,⁴ no ion specific fitted parameters are necessary and all of the important contributions to the interactions are included.

Solving this problem is directly important for atmospheric chemistry and understanding the properties and interactions of bubbles and nanobubbles. In addition to this, the model is also important as a prerequisite to understanding the more complex interactions of ions with protein and mineral surfaces. Our model is conceptually simple and has low computational demand. This facilitates further extensions to these systems that are important in biology, medicine and industry.

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Effect of Superficial Gas and Water Flow Rates, Bed-level and Contact Angle on Fluidized-bed Flotation of Ultra-coarse Sphalerite Particles

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This work investigates the effect of hydrodynamic parameters (gas and water flow rates and bed-level) and particle hydrophobicity (contact angle) on the flotation recovery of ultra-coarse sphalerite particles in a fluidized-bed separator (HydroFloat). Each of the hydrodynamic parameters was varied independently until an optimum was determined. Particles contact angle was varied by altering the conditioning process before flotation. Contact angle values were determined by using the Environmental Scanning Electron Microscope (ESEM) technique. The bed-level was denoted as the position of the top of the fluidized bed, whereas the superficial flow rates were defined by dividing the volumetric flow rate of the gas or water by the cross sectional area of the flotation cell used. Each of the hydrodynamic parameters was found to have an optimum limit which gives maximum recovery, below or above which recovery begun to dwindle. In the case of the contact angle, the experimental results indicated that recovery increased with increasing contact angle up to approximately 85°. At similar contact angle, finer particles have a better chance of being recovered compared to coarser particles.

Influence of aeration on chalcopyrite and pyrite flotation

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This work investigates the effect of aeration on the flotation kinetics of chalcopyrite and selectivity versus pyrite in a chalcopyrite/pyrite mixed mineral system of varying pyrite content (20-80 wt. % pyrite) after fine grinding. Surface species responsible for the flotation behaviour of the minerals were identified and quantified using X-ray photoelectron spectroscopy (XPS). Laboratory batch flotation tests showed that pulp aeration has a significant impact on chalcopyrite recovery, grade and selectivity. The flotation kinetics and recovery of chalcopyrite increased with aeration until reaching a maximum after which further aeration of the pulp resulted in a decrease in chalcopyrite flotation recovery. Pyrite recovery on the other hand decreased continuously upon aeration. XPS results indicated that the continuous decrease in pyrite recovery observed with increasing aeration time was due to the formation of iron oxy/hydroxide on its surfaces, the same species accounting for the decrease in chalcopyrite recovery after prolonged aeration.

Synthesis of Stoichiometrically Controlled Reactive Aluminosilicate Powders as a High-Purity Geopolymer Precursor

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Geopolymers are formed by mixing solid aluminosilicate precursors such as fly ash (FA), granulated blast furnace slag (GBFS) or metakaolin with an alkali activating solution, forming a solid binder with similar properties to Ordinary Portland Cement (OPC), with low-cost refractory and construction applications. Geopolymers offer an 80% reduction in CO₂ emissions compared to OPC binders, and also provide an avenue for utilisation of industrial waste materials such as FA or GBFS. Geopolymer use in industry is not yet widespread due to significant difficulties controlling reproducibility in performance and stoichiometry of phases formed in these systems. This is in part restricted by the current incomplete understanding of the fundamental fluid-particle reactions involved in geopolymerisation, and which parameters predominantly influence these processes. In order to better understand the complex relationships between the initial compositions of the aluminosilicate precursors, the thermodynamics and reaction kinetics governing the final structure and therefore physical properties of those binders, the stoichiometry of the aluminosilicate precursor and alkali activator must be strictly controlled. This study develops a robust method for synthesis of stoichiometrically controlled reactive aluminosilicate powders via an organic steric entrapment method. Polyvinyl alcohol is used to hinder movement of precursor cations within the gel, enabling the synthesis of homogeneous single phase reactive aluminosilicate powders, which are subsequently reacted with sodium silicate solution to form geopolymeric binders. The reactive aluminosilicate powders and geopolymeric binders are characterised by thermogravimetric analysis, X-ray fluorescence, X-ray diffraction, scanning electron microscopy and solid state nuclear magnetic resonance spectroscopy.

Selective depression of pyrite and its implications on gold flotation in a porphyry copper-gold ore

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In porphyry copper-gold flotation, gold and chalcopyrite are the main valuable mineral phases with pyrite being the major gold host and associated gangue mineral. Their economic extraction requires selective depression of pyrite. During copper sulphide flotation, copper adsorbs on pyrite via superficial oxidation of the copper sulphide minerals (e.g. chalcopyrite) and this promotes pyrite flotation in the presence of collector. This ‘inadvertant’ pyrite activation and flotation adversely affects concentrate grades. The present study makes use of X-ray photoelectron spectroscopy (XPS) and ethyle diaminetetraacetic acid (EDTA) extraction analysis to examine the selective depression of pyrite in a porphyry copper-gold ore using diethylenetriamine (DETA) and aeration, after regrinding ($d_{80} = 38$ and $8 \mu\text{m}$ grind sizes). The flotation results show that pyrite depression increases after aeration and with decreasing grind size. The surface analysis (XPS and EDTA extraction) revealed that the improved depression of pyrite at the finer grind size after aeration was due to the increased amount of iron oxy-hydroxide (Fe-O/OH), sulphate species and increased liberation of mineral phases (QEMSCAN analysis), whilst the poorer pyrite depression at coarser grind size was due to insufficient liberation of the mineral phases (QEMSCAN analysis) and persistence of activating Cu species. The addition of DETA increased pyrite depression at the coarser grind size ($d_{80} = 38 \mu\text{m}$) due to a significant reduction in Cu(I)S and increased Cu(II)-O species, correlating with the flotation results of pyrite under this test condition. The effect of changes in the pulp chemistry on gold flotation using N-butoxycarbonyl-nbutyl thionocarbamate collector (XD5002) is also examined and discussed. Pyrite cleaning flotation at $8 \mu\text{m}$ grind size in air, followed by leaching of the flotation tailings is suggested as the secondary strategy to recover gold in this ore.

Mechanisms and kinetics of saprolitic nickel laterite leaching by sulphuric acid at atmospheric pressure

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Aqueous processing of complex, low grade (< 1.5 wt.% values) saprolitic nickel (Ni) laterite ores faces intractable challenges which underpin Ni and pay metal cobalt (Co) recovery rates and yield, lixiviant consumption and pulp handleability. Whilst our generic knowledge and understanding of acid leaching behaviour of lateritic ores are advanced, there is a dearth of fundamental knowledge needed to optimize and improve the stirred tank leaching process. In this study, atmospheric, stirred tank leaching behaviour of Western Australian saprolitic Ni laterite ore was investigated under isothermal, batch conditions at pH 1 using sulphuric acid. The influence of agitation rate (600-1000 rpm) and temperature (70 and 95 °C) on the leaching mechanisms and kinetics over 4 h was established for -2 mm, 40 wt.% solid dispersions.

The leaching behaviour was distinctly incongruent and reflected strong temperature-dependent Ni/Co recovery/yield, acid consumption and the proliferation of gangue minerals' constituent elements (e.g., Mg, Al, Fe). The overall analyses showed that the leaching process followed a chemical reaction-controlled, shrinking core mechanism which reflected activation energies of 80.6 ± 1.2 and 78.3 ± 1.0 kJ/mol, respectively, for the release of Ni and Co. This was accompanied by low 22/18 % and high 90/78 Ni/Co recoveries and high H₂SO₄ consumption of 177 and 644 kg/t bone dry ore, respectively, for leaching at 70 and 95 °C over 4 h. The level of agitation had no noticeable impact on the Ni and Co leaching rates, consistent with insignificance of volume diffusion limitation. Temporal behaviour of leached dispersion's non-Newtonian rheology in tandem with solid mineralogy and solution speciation analyses indicated the formation of a viscous gel-like structure whose silica mineral content increased and crystallinity decreased with time. The findings suggest that for saprolitic ores, to process at higher solid loading and have higher throughput there is the need to reduce pulp viscosity, yield stress and acid consumption.

Experimental & Theoretical Basis for Frustrated Evanescent Wave Particle Sizing

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Microscopy techniques such as TIRM or SNOM rely on light scattering behaviour that is described analytically by a generalisation of Lorentz-Mie theory (G-LMT) developed to include the case where an incident field is evanescent. Our work with TIRM has led to the observation that dielectric particles immersed in an evanescent field produce a strong scattering hotspot at their leading-edge in the direction of wave propagation, and a weaker backscattering hotspot at their trailing-edge. Comparing results against a standard radiation pressure method for measuring particle radius during a TIRM experiment, we have shown that radii can be reliably determined via CCD imaging by finding the distance between the centroid of a particle and the hotspot at its leading-edge. In order to establish a theoretical basis for this frustrated evanescent wave single-particle sizing (FEWPS) method, we applied G-LMT to directly compute theoretical scattering profiles along principle planes; solid-angle sections of these profiles were then mapped to image space via a Debye-Wolf integral transform (i.e. a vectorial diffraction model) in order to determine the theoretical location of scattering hotspots relative to a given particle radius. We also adopted a numerical approach to compute scattering directly from Maxwell's equations using finite-element analysis in COMSOL, and found the predicted location of scattering hotspots to be consistent with G-LMT. With these models, we have been able to quantify the range of conditions for which scattering hotspots are effectively localised to the periphery of a particle and the FEWPS method can be expected to furnish a valid measure of particle radius.

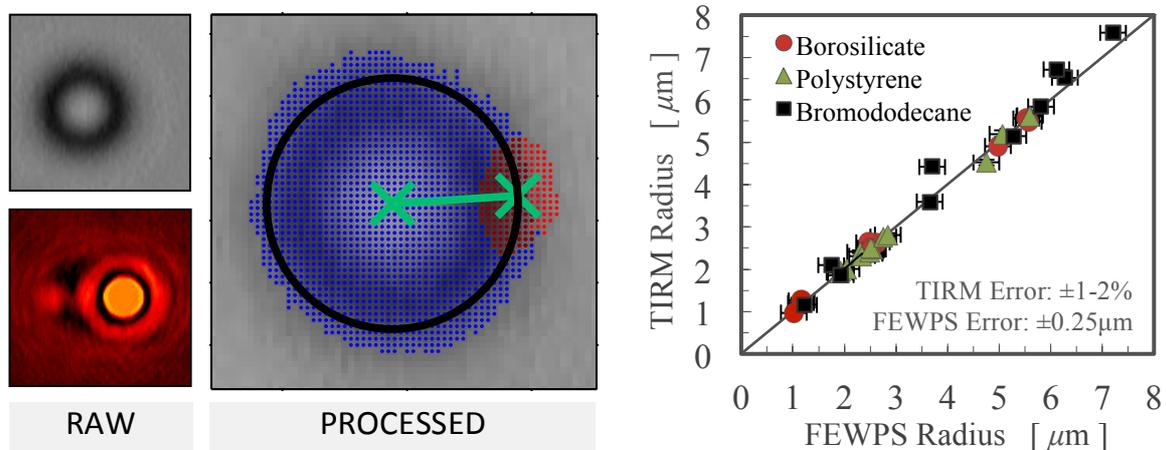


Figure 1. Hough transform edge-finding routines identify regions enclosing unique scattering particles, and trainable centroid-finding routines are used to compute FEWPS radii from raw pairs of CCD images [left]; One-to-one comparison of radii obtained by a standard radiation pressure method for measuring particle radius during a TIRM experiment against FEWPS values for the same particles [right].

Layering in a confined ionic liquid: Effect of temperature and rheology on lubrication capabilities

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Ionic liquids (ILs) present a potential answer to the need for new and more tuneable lubricants. They are defined as salts existing in their liquid form below 100 °C and are generally thermally and electrochemically very stable, have high viscosities, high conductivities, and low vapour pressures. There are potentially up to 10^{18} different ILs, so the possibility of tuning to a specific task is high. In this study ethylammonium nitrate was used to investigate how the layering, frictional properties, and interfacial viscosity changes with temperature. This is done using the Colloidal Probe – Atomic Force Microscopy (CP – AFM) with EAN confined between a silica probe and mica surface. The temperature was increased from room temperature up to 120 °C. In total, 25 force curves were obtained per speed and temperature and a method for averaging force curves was used to investigate how accurate the obtained force curves were. The curves show that steps, previously seen for EAN only at and around room temperature and very low speeds, could be distinguished independent of speed at much higher speeds and temperatures (Figure 1a); it was also shown that the interfacial viscosity is much lower than the bulk value. Friction loops, obtained at different temperatures (Figure 1b) and velocities (not shown here) display different regions of friction and that the difference between regions diminishes as the temperature increases friction at higher temperatures not shown here for clarity). This indicates that the boundary layer lubrication decreases with temperature. However, there are no changes to the friction coefficient at higher loads. This can have important consequences for lubricant formulation.

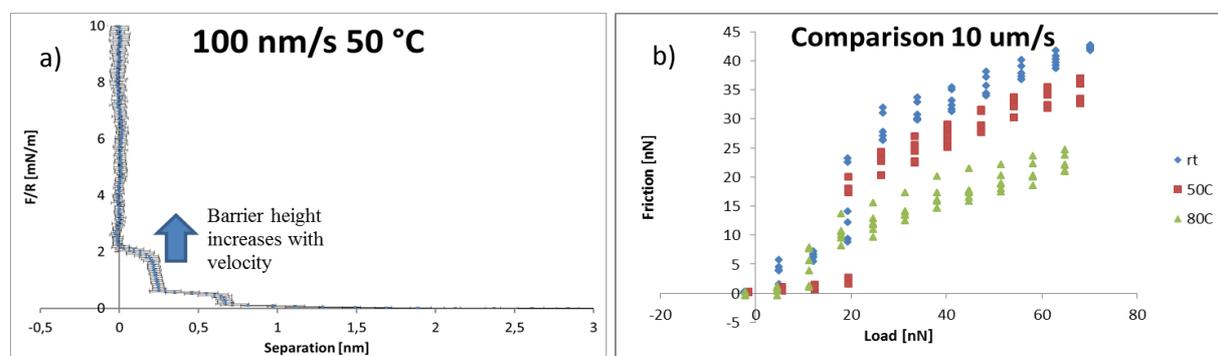


Figure 1. a) shows an averaged force curve and b) displays friction, at three different temperatures, as a function of load.

What happens when a sheared suspension is loaded compressively?

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The investigation of particulate fluid behaviour under deformation and flow conditions is essential for the optimisation of industrial suspension processing. To that end, suspension rheology research has resulted in the characterisation of yield behaviour through two key material properties: the shear and compressive yield stress, σ_y and p_y . These parameters give a viscoplastic description of yielding in concentrated suspensions above the gel point. As p_y is typically an order or two greater than σ_y , the effect of one on the other can be ignored in predominantly one-dimensional settings. However, great difficulty is faced when attempting their application into multi-dimensional processes which are not properly understood rheologically. Such combined loading operations, like roll compression, raked thickening and belt filtration, occur in many industrial dewatering processes.

As a first step towards discerning multi-dimensional processes, the constitutive behaviour of suspensions under combined shear and compression is sought. Rigorous requirements for the factual determination of σ_y and p_y are the avoidance of wall slip in shear and the application of differential pressure in compression. Taking these into account, the experimental method employs an ARES strain controlled rheometer loaded with a sintered disc and dead weights. Exploration of the effect of compression on material shear properties was conducted on a model inorganic calcite suspension. From rate controlled stress relaxation data, the shear modulus $G(\gamma_0, t)$ and strain softening function $h(\gamma_0)$ were extracted and compared. The sub-yield behaviour from constant rate tests was also fitted to a standard linear solid (SLS) model. It was observed that under both types of rheometry, shearing under minor compression resulted in higher peak stresses past a critical strain, γ_c , of 0.1. Quicker stress dissipation was also detected in stress relaxation conditions below γ_c . The development of transient force chains within the suspension is postulated to affect the stress behaviour of the sheared material. These findings point to significant interaction between shear and compressive loadings in suspensions and will guide constitutive rheological modelling into the multi-dimensional era.

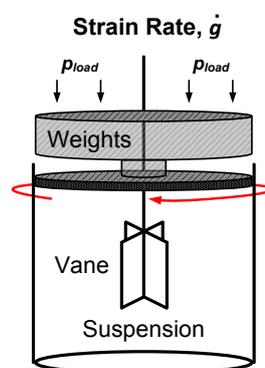


Figure 1. Schematic of a modified ARES rheometer set up for compression in shear.

Investigating the Lubricating Role of Non-cellulosic Polysaccharides between Model Plant Cell Walls

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Coordinated expansion of adjoining cell walls is important during plant growth. The adhesive layer that resists sliding of cell walls under large strains is referred to as the middle lamella and is rich in pectic polysaccharides¹. It has been previously shown that pectin in aqueous solution is highly lubricating due to strong adsorption of the polymer to model hydrophobic surfaces². Therefore it is hypothesised that the pectin in the middle lamella lubricates the contact between neighbouring cell walls. We attempt to characterise the lubricating role of pectin solutions using bacterial cellulose pellicles as model cell wall surfaces. We will further determine the effect of incorporating other non-cellulosic plant polysaccharides into the model system. The development of a novel approach for mimicking cell-cell friction like in growing plant tissue utilises a rotational rheometer. Plant polysaccharides are found to have an effect on the friction and adhesion behaviour when incorporated into bacterial cellulose composites or present in aqueous solution at the interface.

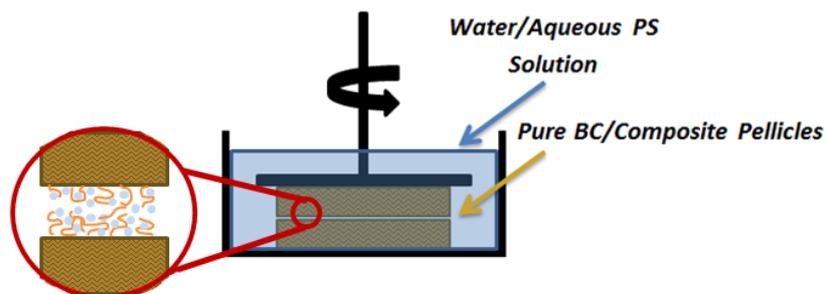


Figure 1. Experimental technique for measuring friction between model plant cell wall surfaces.

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Effect of Molecular Structure on Friction in Protic Ionic Liquids

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Ionic liquids (ILs) have generated considerable interest recently as lubricants on account of their useful properties; ILs have low vapour pressures and high thermal stabilities and conductivities. Friction Force Microscopy has been used to probe the lubricity of six protic ionic liquids (ILs) confined between an atomic force microscope colloid probe tip and a mica surface. The ILs investigated are ethylammonium formate (EAF), ethylammonium nitrate (EAN), propylammonium formate (PAF), propylammonium nitrate (PAN), dimethylethylammonium formate (DMEAF), and ethanolanionium nitrate (EtAN). Comparison of results for these liquids reveals the effect of cation alkyl chain length, anion type, charge group steric hindrance and extent of hydrogen bonding. For IL lubricants, energy is dissipated via friction in two main ways. Firstly, the structure of the ions, and their concentration at the interface, determines the roughness of the IL boundary layer. More energy is required to move the tip over a rougher surface resulting in energy dissipation and friction. Secondly, at higher loads, it can be more energetically favourable for the composition of the boundary layer (the cation:anion ratio) to change to produce a smoother sliding plane. This change in composition also has an energetic cost, which also results in energy dissipation. The measured friction force is the sum of these two dissipation mechanisms.

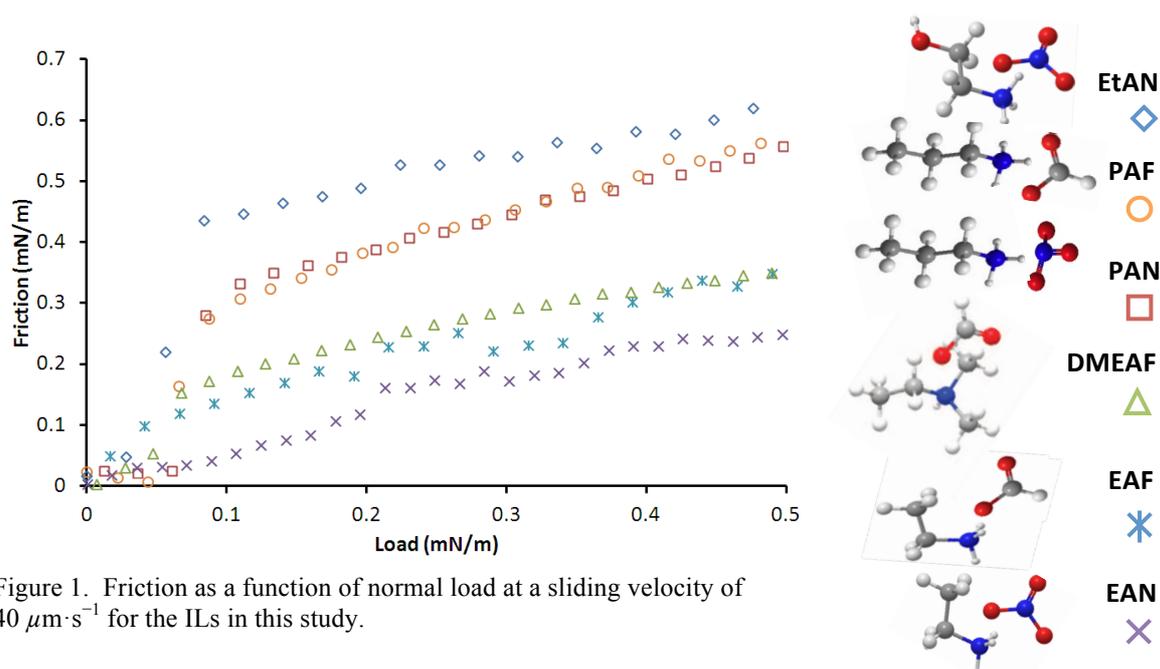


Figure 1. Friction as a function of normal load at a sliding velocity of $40 \mu\text{m}\cdot\text{s}^{-1}$ for the ILs in this study.

Drop – Drop Behaviour for Periodic Drive Profiles

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Interactions of bubbles and drops are very difficult to predict due to the complicated relationship between film drainage and drop deformation. When two surfaces separated by a thin film are pushed together they experience hydrodynamic pressure from film drainage and disjoining pressure due to surface chemistry. This causes the deformable surface to undergo shape changes which in turn influences film drainage. A series of atomic force microscope (AFM) experiments were conducted in air-water-air and PFO-water-PFO systems at various linear variable differential transformer (LVDT) drive profiles, with the aim of determining the role that retraction velocity has on coalescence. These experimental studies have been supplemented with modeling results obtained through the Stokes Reynolds Young Laplace (SRYL) model which combined provide greater insight into coalescence behavior of deformable surfaces.

Switching Off Friction with an Ionic Liquid Lubricant

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Friction can literally be “switched” on and off when an ionic liquid (IL) is used to lubricate the silica-graphite interface. ILs are pure salts with melting points less than 100 °C. As ILs are composed solely of cations and anions, *lubricity can be externally controlled in situ by application of a potential to the graphite surface*; as the potential is varied, the ion composition of the boundary layer responds, and this alters lubricity. The outermost layer of the graphite surface is a single layer of graphene, so the use of a silica AFM tip models a nano-electromechanical systems (NEMS) interface. The IL is an excellent lubricant at all potentials. It binds strongly to the graphite surface and resists squeeze out. However, at positive potentials the anion rich boundary layer is “superlubricating” and friction falls to immeasurable levels, (*cf.* Fig. 1).

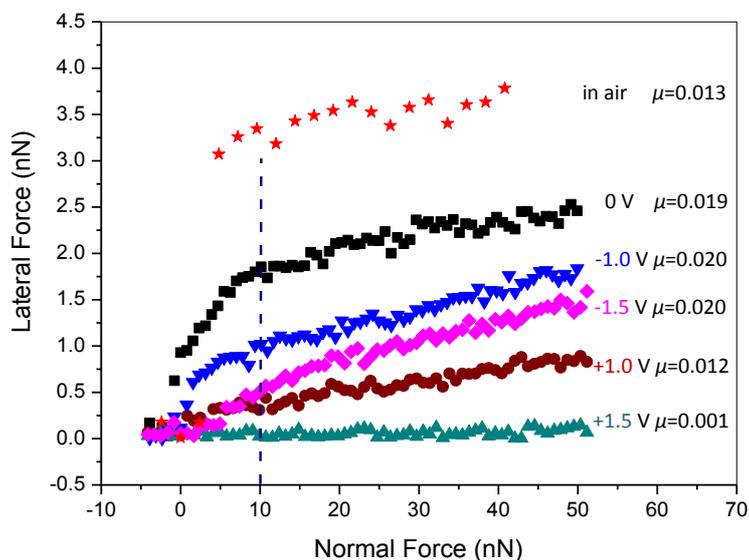


Figure 1. Lateral force versus normal load in air and in IL as a function of applied potential for a sharp AFM tip ($r \approx 5$ nm) sliding on a HOPG surface over 100 nm at $6 \mu\text{m}\cdot\text{s}^{-1}$. The friction coefficient, μ , is extracted from the gradient of the plot when the normal force is higher than 10 nN.

Aqueous biopolymer lubrication as a function of solvent quality

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The lubricating capacity of biopolymers in aqueous systems is an important parameter in industrial applications and at bio-interfaces within natural and biomimetic systems. The lubricity of these solutions has been directly correlated to the properties of the adsorbed film they form on PDMS substrates¹. We investigate the effect of solvent quality (kosmotropic/chaotropic strength) on the tribological properties of aqueous polysaccharide solutions, as well as salivary proteins in human whole saliva (HWS), using soft-tribological measurement. Adsorbed film kinetics and mechanics (thickness and viscoelasticity) are also quantified as a function of solvent quality using quartz crystal microbalance with dissipation monitoring (QCM-D). The variation in boundary film formation and structural integrity observed for different solvents provides insight into the mechanisms that govern transient and dynamic lubrication of aqueous biopolymer systems.

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Colloidal stabilization by unattached homopolymers – when does depletion repulsion play a role

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Dealing with colloidal dispersions, one of the most important tasks is to prevent particle aggregation due to van-der-Waals forces. Nowadays the stabilisation is mainly controlled by electrostatic and/or sterical interactions. Colloidal dispersions may also be stabilised by addition of a certain amount of free non-adsorbing polymer. While the first two mechanisms are well understood the latter one – named depletion stabilisation – still raises many questions. The established theoretical models describing this polymer-induced stabilisation are over-simplified and are not able to predict the dependence of the polymer-induced interactions on solution parameters quantitatively.

To improve the understanding of PI stabilisation a new theoretical model was proposed. Based on self-consistent field theory numerical calculations were performed for the thermodynamic potential as a function of the distance between colloidal surfaces. It could be shown that, under certain conditions of the polymer solution, there is a repulsive barrier of interaction between two solid surfaces [1].

These theoretical studies could verify that the repulsive barrier depends strongly on the size of the particles and the polymer. In the case of hard sphere particles (HS) and non-adsorbing polymer an influence of the repulsion on the thermodynamic behaviour of a colloid-polymer mixture is predicted to be only relevant in the case of large particles ($R \geq 500\text{nm}$) and much smaller polymers ($R_g < 25\text{nm}$), but these predictions have not yet been tested experimentally.

To gain experimental access to the influence of polymer-induced interactions on the thermodynamic behaviour of HS turbidimetry represents a reliable tool [2]. Turbidimetry provides access to the osmotic compressibility of the system, which allows estimations of the interaction potential. So far it was not possible to find valid experimental proof for depletion repulsion in a HS-system, but such experiments were carried out on rather small particles ($R \approx 50\text{nm}$) [2,3]. Therefore we are extending the method towards larger particle sizes to check whether the polymer-induced stabilisation described in [1] is able to give a more satisfying description of the data than the classic depletion theories.

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Droplet collisions in spherical and rod-like micelle systems and their impact on structural and depletion forces

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Surfactant systems are commonly used in colloidal dispersions and emulsions in the formulation of complex fluids for a range of applications including personal care products, foods, lubricants and in pharmaceuticals. At higher surfactant concentrations, surfactant aggregates often transition from smaller aggregate structures (*e.g.* spheres, ellipsoids, etc) to larger structures including worm like micelles, sponge phases and lamella phases.

It has been shown in literature that when in sufficient concentrations in a thin film, different particles can create unique pressure profiles due to their packing structure and entropic differences from the bulk solution. This manifests as oscillatory structural forces in the case of spherical particles and depletion forces for long rod particles. These phenomena are also present in soft particles such as micelles, polyelectrolytes and polymers among others. This study hopes to investigate the transition between these two pressure profiles by examining the effect of spherical, short-rod, and long-rod micelles on droplet collisions.

Measurements were taken using atomic force microscopy (AFM) to investigate the interactions between rigid (particle-plate) and deformable (drop-drop) systems. Solutions of hexadecyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal) were used to generate micelles of varying profiles. The influence of the micelle shape on both static and dynamic interactions with a particular focus on structural forces was investigated. It was found for both rigid and deformable systems that a sudden transition from long range structural to short range depletion forces occurs as the aspect ratio of the micelles increase. This loss of long range forces is theorised to occur due to increased packing flexibility of rods at large separations.

Ultra-thin polyethyleneimine coatings for copper scavenging

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Scavenging of metal ions from trace concentrations is relevant to a wide range of applications¹. Examples of areas of interest include water purification, extraction of precious metals etc. We also note a new application area, namely marine antifouling through absorption and external stimulus for release of copper ions.

We report on ultra-thin crosslinked polyethyleneimine coatings with excellent copper binding performance. The thickness of the coatings is in the range of tens of nanometers and the coatings are stable after immersion in aqueous solutions. Even more interesting, the coatings effectively accumulate copper from model solutions with 200 ppb but also from real seawater with even lower copper content. As determined by the copper to nitrogen ratio acquired from x-ray photoelectron spectroscopy, these coatings can accumulate as much as about 10 wt% of copper relative to polyethyleneimine in less than 3 hours from a 200 ppb model solution. In artificial seawater with 12 different seawater relevant metal ions, the material has metal ion selectivity in the order Cu(II) > Zn(II) > Cd(II).

The copper binding capacity, metal ion selectivity and stability of the material suggest the coatings to be interesting for a wide range of applications. We note the possibility for a new application area, namely marine antifouling through absorption and external stimulus for release of copper ions

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Lipid Interactions with Plasma Polymers and Gold: Nontraditional Surfaces for the Development of Complex Supported Lipid Bilayer Systems

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The cell membrane encases and protects cellular components and plays an important role in transport, signalling and disease. Studying membrane behaviour is a challenging task due to the complexity and scale on which these processes occur. Supported lipid bilayers (SLBs) have provided researchers with stable and reproducible platforms to recreate cell membrane environments. The planar structure of the model means a variety of patterning techniques can be employed to recreate membrane architecture on both a micro and nanoscale. In particular pre-patterned substrates are of great interest as they eliminate complications associated with preserving membrane integrity during patterning. To date not all surfaces have proved suitable for SLB formation. Results on gold for example, a conductive material desirable for sensing applications, have been varied. Plasma polymerisation provides a versatile, one step, dry method of creating thin films of different chemistries on almost any substrate. Successful bilayer formation on such coatings would be beneficial for promoting specific organisation in complex SLB systems using patterned surface chemistries. In this work we explored the use of collapse parameters such as pH and buffer chemistry to control vesicle-substrate interactions. Lipid structures formed on gold and commonly used plasma polymers such as allylamine (ppAAm), acrylic acid (ppAAc) and allyl alcohol (ppAAlc) were characterised using quartz crystal microbalance with dissipation (QCM-D) and fluorescence recovery after photobleaching (FRAP). It was shown that by carefully controlling the conditions for vesicle collapse, bilayer formation is possible on unmodified gold and ppAAc. On both surfaces, an increase in pH following vesicle adsorption was required to induce SLB formation. Systems on gold surfaces also required the removal of NaCl, a known inhibitor of SLB formation on gold due to the presence of chloride ions. This work demonstrates a new pathway for bilayer formation on gold, eliminating the need for a tethered system. Plasma polymers provide novel surfaces whose lipid interactions can be controlled by pH alone. Together these surfaces can be combined to produce patterned systems for the development of increasingly complex SLB systems.

Controlling biointerfacial interactions using colloidal assemblies and advanced surface modification strategies

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Controlling biointerfacial interactions is of great importance to *in vivo* and *in vitro* biomedical applications such as implantable devices, biosensors, and tissue engineering scaffolds. Prevention of non-specific protein adsorption and the associated effective reduction in cell attachment whilst presenting specific biological cues such as peptides represents a promising route to gain superior control over cellular responses. The density with which these biological signals are displayed as well as the spacing between them has been proven to greatly influence the cellular response. In the current study we have utilised polymeric colloidal particles in the range from 200 nm to a few micrometers with different surface functionalities to generate surfaces with highly spatially resolved surface chemistry. In addition, subsequent chemical surface modification of the particles was carried out to investigate the influence of different signal spacing towards the cellular response. Scanning electron microscopy (SEM) was used to evaluate the cell morphology and to verify the colloidal assembly pattern. Furthermore, uniform plasma polymer coatings were applied to the colloidal assemblies to evaluate the cellular response towards micro- and nanotopography and isolate chemistry from topography effects. We believe that the results from this study can be utilised in a wide range of biomedical applications where superior control over the cellular response is required.

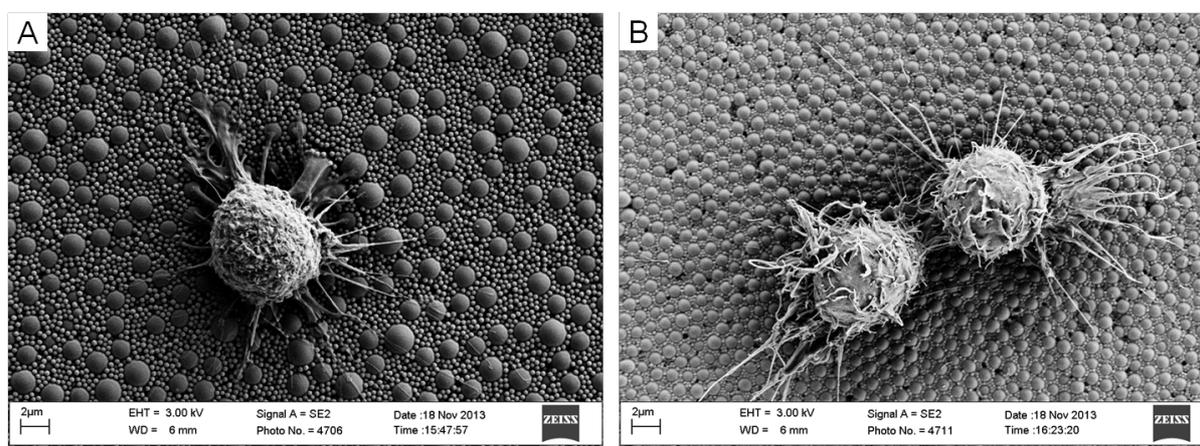


Figure 1. Cellular response towards different assemblies (A) 2 μm carboxylated polystyrene (PS-COOH) particles and 0.4 μm poly(methyl methacrylate) (PMMA) particles, (B) 1.1 μm PMMA and 0.2 μm PS-COOH particles.

PEG Grafting on Dewetted PLGA Films: Biocompatible and Degradation-Resistant Surfaces for Protein Micro-Patterning

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The ability to control protein adsorption on solid substrates is crucial for many applications including cell patterning (e.g. cell co-cultures), as the interaction of cells with their environment can be mediated by the presence of extracellular proteins.^{1,2} In the present work we report the grafting of PEG chains onto micro-patterned thin films of biodegradable poly(D,L-lactide-*co*-glycolide) (PLGA) for protein micro-patterning (Figure 1). The dewetting of PLGA thin films on polystyrene (PS) was combined with the grafting of protein-repellent poly(ethylene glycol) (PEG) on the dewetted PLGA surface, in order to form topographical and chemical surface micro-patterns consisting in protein-adhesive PS domains surrounded by protein-repellent PEG-grafted PLGA (PEG-g-PLGA) films.³ PEG-g-PLGA films showed higher resistance to bio-degradation than plain PLGA films, due to passivation by the thin PEG coating. The combination of protein-repellence and coating-tunable degradation makes PEG-g-PLGA films a promising platform for biological applications involving controlled positioning of proteins and cells (e.g. single cell studies and tissue engineering). For applications involving the adsorption of proteins and cells in an ordered fashion, surface patterns with topographical order can be fabricated by dewetting the polymer film on micro-contact printed substrates.⁴

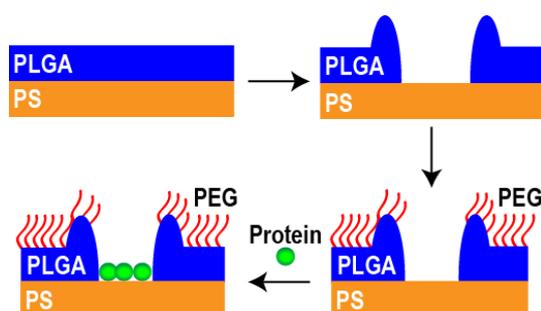


Figure 1. Schematic of the patterning and functionalization of PLGA/PS bilayers for biological applications.

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The Role of Porous Nanostructure in Controlling Lipase-Mediated Digestion in Silica Particles

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Understanding the enzymatic hydrolysis of lipids is of great importance for the rational design of lipid-based drug formulations. Lipid hydrolysis is controlled by the ability for pancreatic lipase to access the lipid interface [1]. In this investigation, we demonstrate the ability to control lipase-mediated digestion by adsorbing lipid within the pores of silica particles with different nanostructures and surface chemistries. The rate and extent of lipid digestion was significantly enhanced when a partial monolayer of lipid was loaded in porous hydrophilic silica particles compared to a submicron lipid-in-water emulsion. Lipase action was inhibited for lipid loaded in hydrophobic silica, due to the interaction between the lipase active site and the methylated silica surface. Thus, hydrophilic silica promotes enhanced digestion kinetics, whereas hydrophobic silica exerts an inhibitory effect on lipase action.

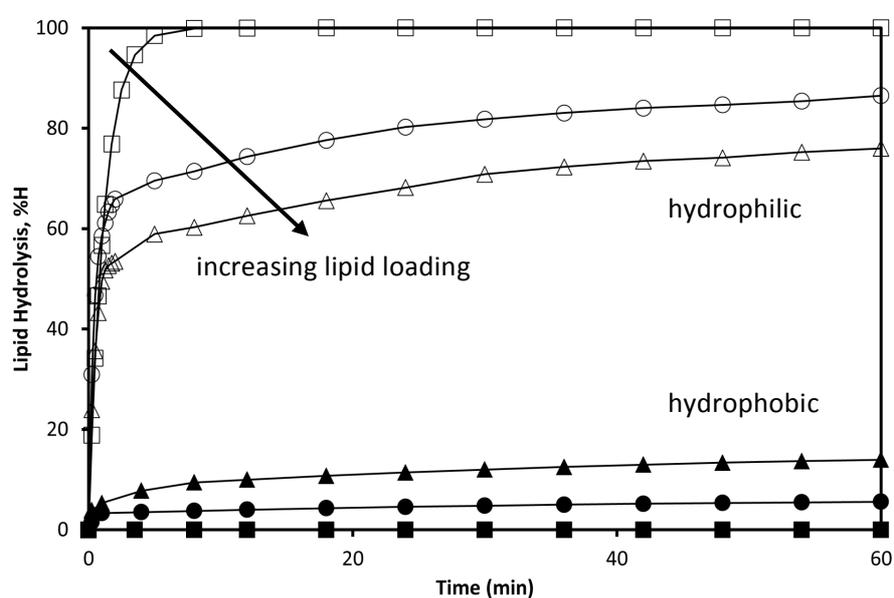


Figure 1. Lipase-mediated digestion for medium-chain triglycerides loaded in hydrophilic and hydrophobic porous silica particles at 10, 20 and 30 wt% lipid loading, under simulated fasted intestinal conditions.

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Development of a Chemical Temporary Access Memory with a Phenol Fluorophore

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A temporary access memory, whose information can be read out for only a limited time is expected to be useful for information security system. Moreover, storing of multistep information is favorable for technologies to code information. Memory devices consisting of organic components have a potential to realize these functionalities because of their responsivity to external stimuli through chemical reaction, e.g. temporal changes with addition of volatile reagents and continuous variations of their states using chemical equilibrium.

Here, we have demonstrated a chemical temporary access memory is capable of storing information using fluorescence color variation of phenol fluorophores (Fig. 1a) by treatment with base (Tetra-*n*-butylammonium fluoride: TBAF) and/or acid (water). The memory operates in temporary access mode because of the volatility of the protic solvent used for writing. Thus, the use of increasingly non-volatile solvents can be used to vary temporal access to information. Additionally, this system can be used to store a variety of information as individual fluorescent colors, which are derived from the bulk gradual deprotonation of phenol to a known hydrogen bonded species then to the phenoxide. (Fig. 1b) With application of a solution of the phenol fluorophore onto filter papers, both temporary and non-temporary access memory functions are fulfilled even on substrates. These systems where information is only temporarily available permit highly secure information transmission, by way of secret code keys or single use passwords.

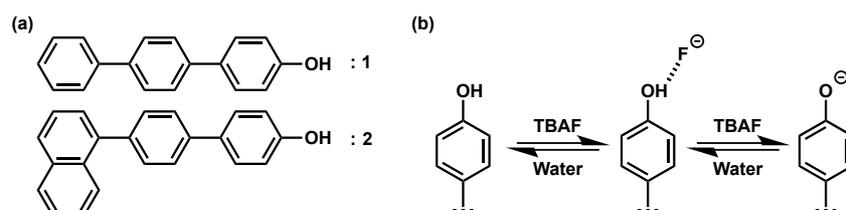


Figure 1 (a) Structures of phenol fluorophores, (b) Structural changes by addition of TBAF and water.

Sensors based on optical interferometry

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Fringes of equal chromatic order (FECO) is a sensitive optical interferometric technique that has been widely applied to study surface topography with imaging¹. This project aims to develop FECO to be a new inexpensive sensing technique based on monitoring fringe pattern shifts induced by chemical or biochemical interactions. To realize that purpose, a simple but reliable interferometer was set up by using thermal silicon oxide wafers as a substrate which is further modified by PVD metallic films or metallic nanoparticles. Due to the special layered substrate, multiple reflections from the top and underneath interfaces can form an interference pattern which is detectable in a spectrograph as intensity variations with wavelength. Any chemical or biological materials accumulated on the top surface will lead to a change in the optical thickness and a shift of the interference pattern. To minimize the method errors such as local variations in the oxide layer thickness or small differences in the incident angle, a surface patterning technique was introduced for building an inbuilt reference system. This patterning enables the measurement of the region of interest and reference simultaneously. Therefore the local thickness variations and angle differences can be largely cancelled out. To demonstrate the feasibility of this sensing technique, PVD Au and Au nanoparticle films were analysed and the results highlight the insufficient knowledge of the sign and magnitude of optical phase change at the interface between silica and the ultrathin metallic layer. Further Hg vapour adsorption on these metallic films demonstrates that FECO could provide a new means for measuring the interaction of Hg vapour and metallic layer.

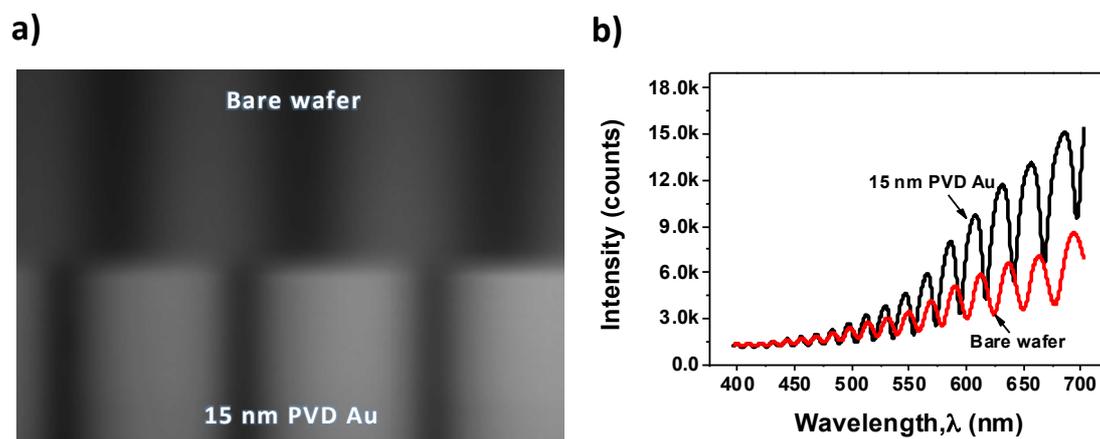


Figure 1. (a) is the FECO image of half-half patterned substrate with an area of Au film prepared via e-beam evaporation of gold target. The actual FECO images are coloured, showing a small portion of optical spectrum with wavelength increasing along the horizontal axis. (b) is the corresponding reflectance spectrum in visible range.

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Nanocellulose-based materials: from hard and transparent TiO₂ nanoparticle hybrids to liquid crystalline self-assembly of cellulose nanocrystals

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Novel nanomaterials based on renewable resources for structural and functional applications are attracting a rapidly growing interest. Not only does the utilization of nature-based nanomaterials offer ecological advantages, but the extraordinary performance of biological composites like bone, nacre, wood, and butterfly wings is also an important inspiration for the development of new multifunctional materials. However, full utilization of the intrinsic properties of the nanosized starting materials requires the development of robust and versatile synthesis and processing routes to control assembly at several length scales [1]. Cellulose, one of the most versatile and richly available biopolymers in nature, has been used by mankind for millennia. Recently, the possibility to isolate and utilize novel forms of cellulose that have at least one dimension in the nanosized range has generated a significant research interest. Nanocellulose features an attractive combination of properties of interest in applications such as composites, and stiff, rodlike cellulose nanocrystals (CNC) can also form a stable chiral nematic liquid crystalline phase [2].

Here, we will give examples on recent research on the fabrication of hybrids of nanocellulose and calcium carbonate [3] and titania [4]. The hybrids may be prepared as a foam or as a flexible transparent film due to the small size and low degree of light scattering of the nanostructured components. The influence of the formation mechanism and processing conditions on the mechanical and optical properties will be discussed. Examples will also be given on how the optical properties of films of cellulose nanocrystals (CNC), can be tuned by controlling the formation and arrest of the chiral nematic liquid crystalline phase [2]. In the fluid state, the pitch of this helical arrangement is in the range of tens of micrometers, but upon drying it frequently reduces to submicron values, resulting in Bragg reflection of visible light from dried films.

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A Fundamental Study on Plasma Polymer Film Growth and Interfacial Mixing

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Plasma polymerisation has gained increasing attention over the past decade as a tool to selectively modify material surfaces with a wide range of properties and chemical functionalities. It is commonly accepted that plasma polymerisation is a substrate independent method meaning that films deposited on different substrates are the same physically and chemically. However, a growing body of research investigating plasma polymer film growth is revealing that the deposition process and the chemistry of the resulting plasma polymer films are affected by the underlying material substrates. In this work, we have investigated the interfacial structure of plasma polymerised hexamethyldisiloxane (HMDSO), allylamine (AA), and di(ethylene glycol) dimethyl ether (DG) films that were used as a ‘substrate’ for the deposition of a deuterated plasma polymer film on top. The resultant multilayer films were examined with X-ray photoelectron spectroscopy, atomic force microscopy, focused ion beam scanning electron microscopy, and neutron/ X-ray reflectometry to obtain a comprehensive understanding of the multilayer film chemistries, degree of chemical unsaturation, thickness, interfacial roughness and mass densities. For single layer DGpp films, their thicknesses are substantially influenced by the substrate material whilst the chemistry on the film-air side only has a subtle variation. For single layer HMDSO, AA and DG plasma polymer films, at higher deposition powers, the surfaces are rougher. When a second layer is deposited on top of these single layer coatings, the interfacial width between the two plasma polymer films is strongly dependent on the chemistry underlying plasma polymer substrate film.

***In meso* crystallisation of amphiphilic peptides**

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A novel *in meso* crystallization method has facilitated the structural determination of several biologically relevant integral membrane proteins (IMPs). However, the method remains poorly understood as IMPs are difficult to express and handle. In particular, the non-rigid hydrophilic loop associated with many human IMPs must be removed or modified before successful crystal growth. Analogous to solution based crystallisation, *in meso* crystallisation requires extensive screening of precipitant conditions. Bicontinuous cubic phases are the most commonly used lipid phases for *in meso* crystallisation. The self-assembled lipid structures of the three different experimentally observed cubic phases are shown schematically in Figure 2. The effect of the IMPs on the cubic phase and the compatibility of the crystallisation screen used with the cubic phase are important; if the underlying 3-D cubic nanostructure is destroyed, the screen or protein and lipid combination may not be suitable for *in meso* crystallisation experiments.

A peptide synthesiser was used to synthesise amphiphilic peptides which mimic integral membrane proteins. Peptides with varying hydrophilic loop sizes were synthesized and their effect on lipidic cubic phases was studied. The 3-D lipid nanostructure of several lipids upon incorporation of the synthetic peptides at different concentrations was determined by using Small Angle X-ray Scattering. An improved understanding of the effect of integral membrane peptides and proteins on the cubic mesophase can lead to an improved understanding of *in meso* crystallisation success rates of integral membrane proteins and facilitate the structural determination of more IMPs.

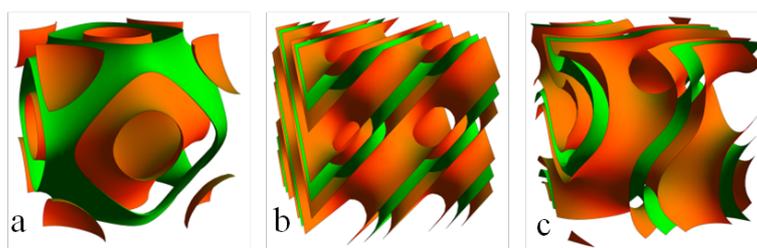


Figure 2. Schematic presentation of self-assembled lipid structures, (a) Primitive cubic phase, (b) Diamond cubic phase, (c) Gyroid cubic phase.

Controlling the architecture of cubosomes for the delivery of bioactive therapeutics

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The recent increase of commercially available bioactive therapeutics in the pharmaceutical industry has resulted in the necessary advancement of drug delivery vehicles for their specific encapsulation and release. A colloidal nanoparticle that has received attention in the field of drug delivery, due its ability to sustain the release of therapeutics, is the cubosome. Cubosomes are lyotropic liquid crystalline dispersions of a special group of amphiphiles, such as phytantriol and glycerol monoolein (GMO), that self-assemble to form a bicontinuous bilayer with an internal surface area of $400\text{m}^2\text{ g}^{-1}$ of lipid.¹ Due to the non-ionic nature of the cubic phase forming amphiphiles, cubosomes require stabilisation to prevent their flocculation following the dispersion of the bulk phase into nanoparticles. This is most commonly achieved using the surfactant Pluronic® F127.² Traditionally, the dispersion of cubosomes occurs via energy intensive methods. However, due to the likelihood that these methods will denature biotherapeutics, the use of cubosomes has been limited in this growing field of drug delivery.

Recently, there has been a new cubosome production method developed that uses phosphate buffered saline (PBS) to induce a lamellar to cubic phase transition in phytantriol based dispersions.³ It has been suggested that this method of cubosome production may be a solution to the problem cubosomes face for the encapsulation of biotherapeutics. We have further developed this method to use the anionic lipid 1-2 dipalmitoyl phosphatidyl serine (DPPS) and have shown that by controlling the concentration of DPPS and PBS we can regulate the curvature of the bicontinuous bilayer and in turn the size of the water channels within the cubosomes (Figure 1). Controlling the water channel size is important for the use of cubosomes as drug delivery vehicles as the water channel size will regulate the size of the hydrophilic biotherapeutics that can be encapsulated and their release rate.⁴ Additionally, we have found that we can control the size of the cubosomes by regulating the temperature of formation. This has been achieved by taking advantage of the critical micellisation temperature of the surfactants that are used to stabilise the cubosomes (Figure 2).



Figure 1 – Phosphate buffered saline (PBS) and 1, 2 – dipalmitoyl phosphatidyl serine were used to regulate the water channel size within the cubosomes

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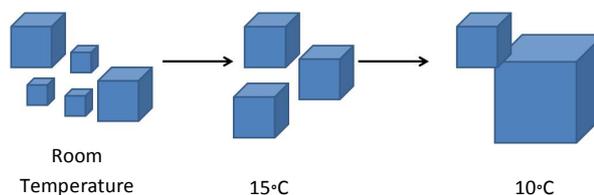


Figure 2 – The temperature of the dispersions was found to have a significant influence on the size and polydispersity of the cubosomes.

Wetting and Forced Wetting of Polymer Surfaces with Ionic Liquids

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Ionic liquids are important solvents because of their chemical diversity, low volatility, thermal stability, conductivity and tuneable properties (such as surface tension, density, viscosity and melting point) which make them good replacements for conventional solvents. However the effect of the ion composition of ionic liquids on their properties is still not well mapped. In this study, three groups of ionic liquids; (i) ionic liquids with the same anion but varying alkyl chain length of the imidazolium cation, (ii) ionic liquids with the same NTf_2 anion but varying cations and (iii) ionic liquids with the same Rmim cation but varying anions are used to characterise polar (polystyrene and polymethylmethacrylate) and non-polar (amorphous fluoropolymer) surfaces to assess the suitability of ionic liquids as probe liquids for surface characterisation. The composition (anions and cations) affects the surface tension of the ionic liquids and their wetting behaviour. The interfacial layering properties of ionic liquids is peculiar and affects the suitability of ionic liquids for surface characterisation especially on polar surfaces. The effect of polarity on ionic liquids wetting behaviour is further explored by electrowetting, i.e. forcibly wetting surface with the same ionic liquids. Reversibility of the polarity on the AF1600 surface showed a corresponding change in the electrowetting behaviour of the ionic liquids confirming the effect of changing solid surface polarity on wetting behaviour.

Investigating the 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 evaporative lithography to particle coalescence. By considering a capillary bridge between a spherical particle and a flat substrate, we investigate the how 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 Janus configuration to an axisymmetric collar configuration. Having established a theoretical model, a variety of key physical systems are presented. Fitting the theoretical model to experimental images provides important physical insights into the underlying dynamics of such systems.

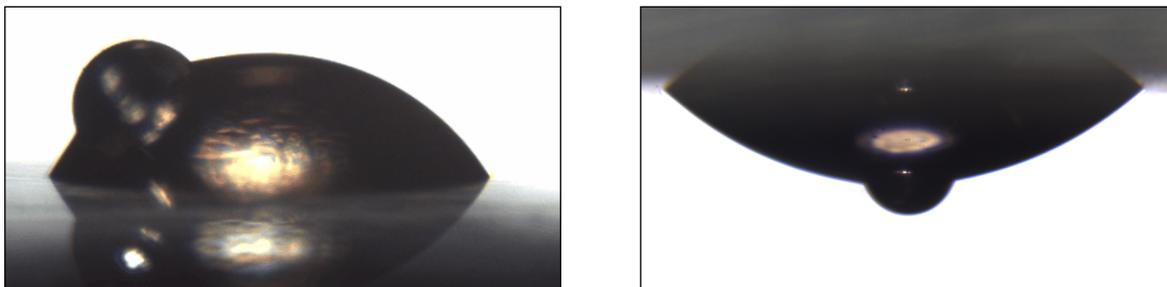


Figure 1. Example capillary bridge systems.

Nanostructure of Ionic Liquid-Mica Interfaces Revealed with High Resolution Using Amplitude Modulated-Atomic Force Microscopy

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Amplitude Modulation – Atomic Force Microscopy (AM-AFM) has been used to resolve the structure of Ionic Liquids (IL) at the mica interface with high resolution. The ILs investigated are propylammonium nitrate (PAN), ethylammonium nitrate (EAN), ethanolammonium nitrate (EtAN), ethylammonium formate (EAF) and dimethylethylammonium formate (DMEAF). Images of the IL ions in direct contact with, and near to, the mica surface have been obtained with unprecedented clarity; the lateral structure is much more pronounced than previously suspected. These results will impact upon a wide range of fields where surface - IL interactions play a role, which include charge storage devices, electrodeposition, dye solar cells, and lubrication, amongst others, because the physical arrangement of IL ions at the interface determines process efficiency.

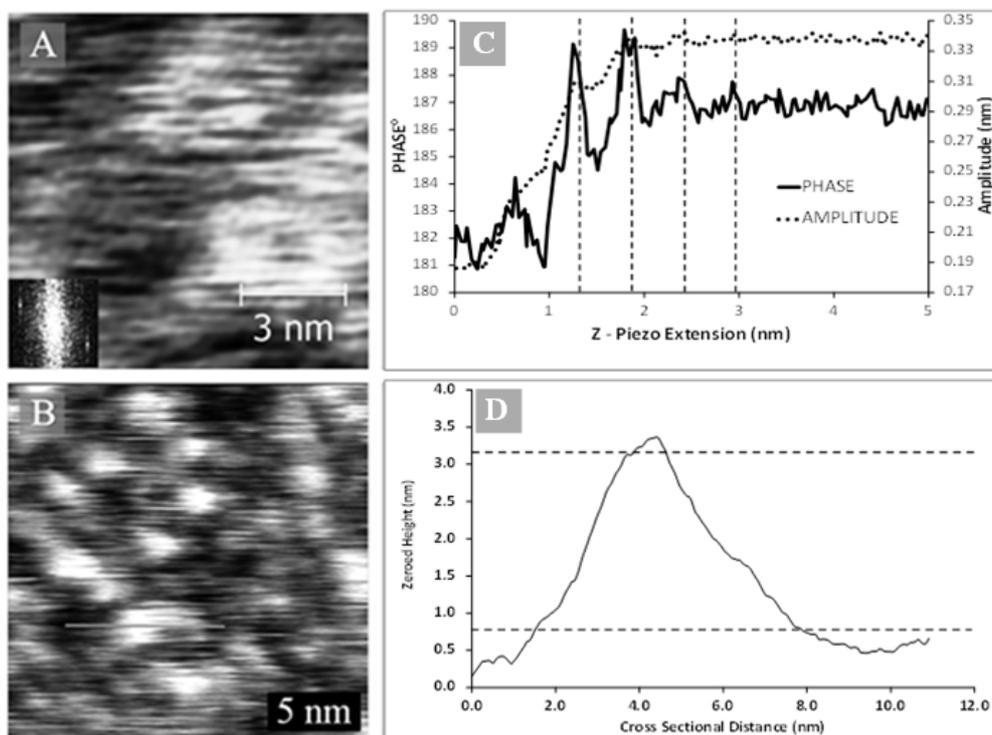


Figure 1. (A) Topographic AFM image of the PAN-mica interfacial innermost surface structure. The inset shows the 2D fast Fourier transform (B) Topographic AFM image of the near surface structure of the PAN-mica interface (C) Amplitude & phase vs. distance profile of the PAN-mica system normal to the interface. Distinct maxima have been marked in both the phase and amplitude data ~ 0.5 nm apart in agreement with the molecular dimension of PAN. (D) Section analysis taken across the blue line in Figure 1(B) showing the height of the near surface structure which is ~ 2.5 nm.

Theoretical Modelling of the Adsorption of Citrate onto Zinc Oxide Surfaces

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The carboxylate anion citrate has been seen experimentally to have an effect on the aspect ratio of zinc oxide (ZnO) particles (crystals) grown hydrothermally. Citrate slows the growth rate in the [0001] direction because it adsorbs specifically to the (0001) surface rather than to prismatic planes. It has been observed that when citrate is adsorbed onto the (0001) surface that there is a shift of the peak corresponding to the asymmetric vibrations in the characteristic infrared spectra of citrate. The change in IR spectra provides clues about the configuration of the molecule on the surface and binding mechanism. This work models ZnO and citrate with the ONIOM technique, employing high-level density functional theory calculations on citrate and surrounding ZnO atoms (at the M05-2X/cc-pVTZ level of theory) with the bulk ZnO crystal treated using an efficient molecular mechanics protocol. Calculations are performed in the gas phase as well as with the SMD solvent model. Citrate is seen to bond with the (0001) surface. Harmonic vibrational frequencies are calculated for citrate alone as well as for the citrate–ZnO system allowing for a comparison with the experimentally observed shifts. The modelling work reveals the binding configuration of carboxylates with zinc oxide and provides insight into the specific chemical interactions leading to strong bonding.

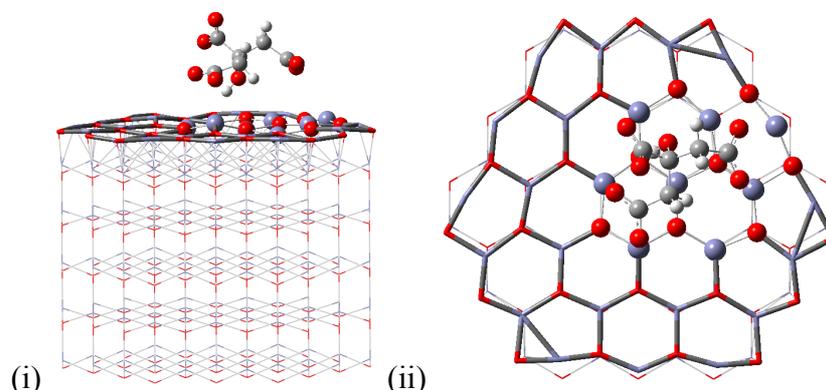


Figure 1. Citrate adsorbed onto the (0001) zinc oxide surface, viewed from (i) the side and (ii) above.

The Adsorption of Graphene Oxide at Hydrophobic Interfaces

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Two dimensional nanomaterials - especially graphene and the closely related graphene oxide - have attracted huge research momentum in the last decade due to their unique mechanical, thermal and electrical properties. Only recently however have their surface activity and adsorption properties come under scrutiny, leading to an array of new materials and applications.

In this work, we demonstrate the strong pH dependence of the ability of graphene oxide to stabilise the oil-water interface, and also to adsorb at other hydrophobic interfaces. Using formulation experiments, dynamic light scattering and atomic force microscopy, we explore the affinity of GO for various model interfaces, underlining the unique properties of this material. Due to its unique surface chemistry, the charging behaviour of GO is particularly unusual and provides opportunities for specific, tailored adsorption and assembly methods. It is seen that a complex interplay of charge, hydrophobicity and surface chemical interactions control the behaviour seen.

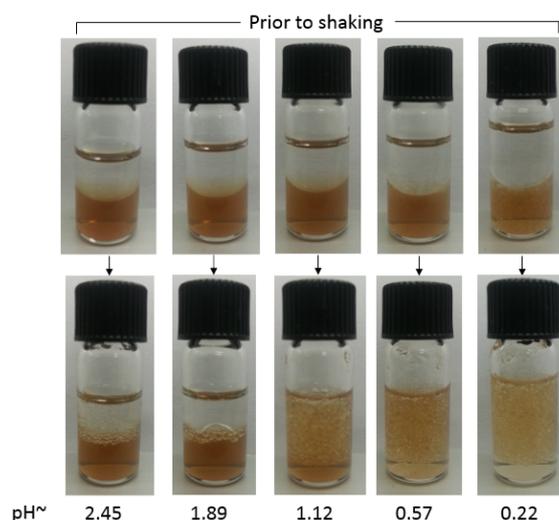
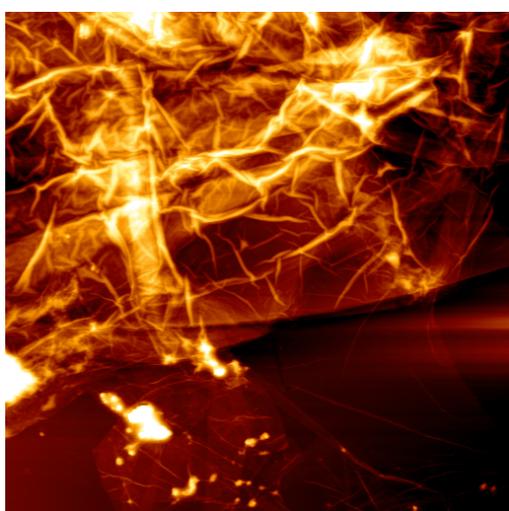


Figure 1. *Left*: Height image of strongly-adsorbed graphene oxide on a gold surface. *Right*: emulsions stabilised by aqueous graphene oxide dispersions at various, low pH values.

Structural investigation into the influence of lipolysis products on the structure of bile salt micelles

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During the digestion of triglycerides, fatty acids and monoglycerides are produced which combine with endogenous amphiphilic molecules to produce submicron colloidal species and liquid crystalline structures¹⁻³. These phases are important in digestion, as they transport lipids through the aqueous environment to the enterocyte membrane for uptake, and enable drug solubilisation, thus they are of relevance to the nutritional and drug delivery fields.

Biologically relevant equilibrium systems were prepared by adding monoglycerides and deuterated fatty acids in 1:2 mol ratio to bile salt/phospholipid micelles, simulating the gastrointestinal state on digestion of tricaprylin (C₈), trilaurin (C₁₂) and trimyristin (C₁₄). Small angle X-ray scattering (SAXS) and neutron scattering measurements were performed to characterize self-assembly into colloidal species. Size was determined by dynamic light scattering (DLS).

SAXS measurements demonstrated that the structures formed depend on composition, lipid chain length and pH. At low q , all systems exhibited an upturn which could indicate aggregation or the presence of larger assemblies. With increasing pH, there was a decrease in the forward scattering, indicative of the micelles decreasing in size or transforming from elongated to spherical. This decrease in size was confirmed using DLS. In the C₁₄ system, where the fatty acid was crystalline, Bragg peaks indicative of lamellar phase was observed at low pH which was abolished upon increasing pH.

The results provide insight into likely structure formation during lipid digestion. It was observed that the structures formed depend on composition, lipid chain length and pH.

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Smart pH- and Salt-Responsive Polymer Brush Coatings

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We have recently shown that activators regenerated by electron transfer radical polymerisation can be employed to prepare pH-responsive poly(2-(diethylamino)ethyl methacrylate) (PDEA) brushes from macroinitiator-modified silica particles.¹ Here we investigate the behaviour of PDEA brushes synthesised from planar oxidised silicon wafers.

PDEA is a weak polybasic, hydrophobic polymer and thus displays pH- and electrolyte-dependent solubility. Specifically, as the pH is decreased below the pK_a of the brush (~ 7.3 for the free polymer,² and similar for the brush), the solvated thickness of the brush dramatically increases due to protonation and osmotic swelling of the tethered polymer chains. While at high pH (pH 9), the brush collapses by expelling solvent as the polymer is deprotonated. It is clear that the kinetics of the pH-induced swelling of the brush is rapid (pH 9 \rightarrow 4) while the collapse process is much slower (pH 4 \rightarrow 9), Figure 1a. It is hypothesised that upon switching the pH from 4 to 9, a denser, more hydrophobic region of polymer located at the periphery of the brush is formed which hinders the egress of solvent and counterions from within the brush, hence slowing the collapse transition. Ionic strength also has a pronounced influence on the equilibrium state and swelling/collapse kinetics of the brush, Figure 1b. At higher ionic strength, the diffusion of ions out of the brush is osmotically hindered and hence the rate of brush collapse is slower.

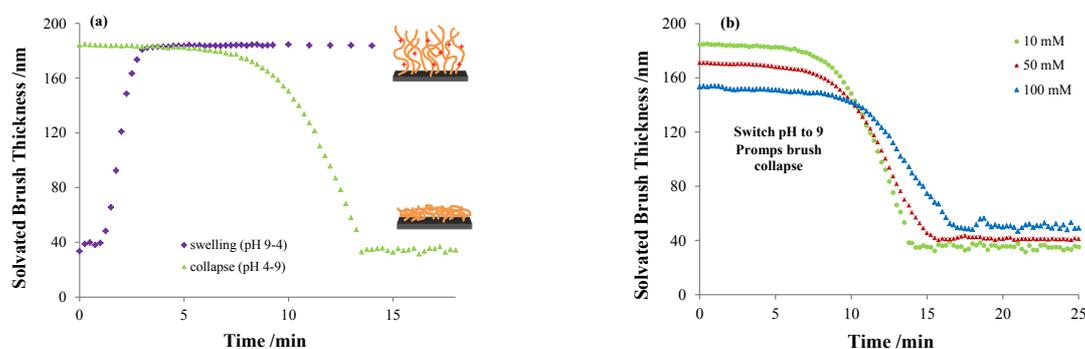


Figure 1. In situ ellipsometry (a) swelling and collapse kinetics of a PDEA brush at 10 mM ionic strength and (b) brush collapse transition kinetics as a function of solution ionic strength.

This research adds to our ever increasing understanding of the inherent physical and chemical properties of polyelectrolyte brushes at solid interfaces. Specifically, we are interested in being able to tune brush behaviour by changing environmental conditions in order to attain a desired macromolecular response, e.g. controlling wettability or adhesion.

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Differential Roles of the Protein Corona in the Cellular Uptake of Polymer Particles by Human Monocyte and Macrophage Cell Lines

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Particulate therapeutics are often introduced into protein-rich biological fluids such as the blood stream. These proteins adsorb onto the particle surface to form a dynamic protein corona with characteristics governed by the physiochemical properties of the particle. Surface-adsorbed proteins change the biological identity of the particle and can significantly affect its behaviour and subsequent interactions at the biological interface. In this work, we have characterized the protein corona formed by exposing nanoporous disulfide-stabilized poly(methacrylic acid) (PMA_{SH}) polymer particles to cell culture media containing heat inactivated fetal bovine serum (FBS). Moreover, we have investigated the effect of this protein corona on particle uptake in human monocytes and macrophages.

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Development of Nanofibrous Meshes as Smart Dressings for the Healing of Chronic Wounds

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Diabetic, pressure, venous and arterial ulcers are a large social, economic and healthcare burden. These chronic non-healing wounds show delayed and incomplete healing processes exposing patients to high risk of infection. Chronic wound care currently focuses on dressings capable of preventing microbial infiltration and keeping a balanced moisture and gas exchange environment. The design of dressings that combine the necessary morphological and physical requirements for wound healing with the value-added capability to address optimal cell responses and impair bacterial proliferation represents a major challenge in wound care.

Polymeric nanofibrous meshes are good candidates as wound dressings and cell scaffolds due to their high surface area, micro-porosity and non-woven structure. Electrospinning is used for the fabrication of these structures because it is a simple, cost-effective and reproducible process. Moreover, electrospinning enables fibres of synthetic and natural polymers to be combined as multifunctional dressings capable of addressing a range of wound challenges.

In this study, the parameters of the electrospinning process (such as spinning rate and electric field intensity) were optimized to fabricate nanofibrous membrane in Polystyrene (M.W. 250.000). The morphological properties of the electrospun meshes have been analysed by bright microscopy, three-dimensional optical profiler, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). As the first step to understand microbial infiltration and control in wound dressings, a number of microbiological assays (MTT, MTS and live/dead) have been completed using *E. Coli*, *P. Aeruginosa*, *S. Aureus* in an effort to understand how the morphological and structural properties of the electrospun meshes influence bacterial attachment, proliferation and growth.

Formulation and characterization of non-steroidal anti-inflammatory drug (NSAID)-loaded solid lipid nanoparticles (SLNs) by a novel microwave-based technique

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Solid lipid nanoparticles (SLNs) are colloidal carriers produced from solid lipids. These may provide an attractive alternative to existing traditional colloidal carriers (emulsions, liposomes and polymeric nanoparticles) for successful delivery of lipophilic compounds. The properties of SLNs are theorised to impart useful properties including controlled release of drug, biocompatibility and improved drug dissolution. The aim of this work was to prepare and characterise SLNs loaded with the non-steroidal anti-inflammatory drugs (NSAIDs), indomethacin, ketoprofen and nimesulide.

NSAID-loaded SLNs were prepared by a novel microwave-based technique developed in our laboratory using a microwave synthesizer. The particle size and zeta potential of the SLNs were measured by photon correlation spectroscopy and laser Doppler electrophoresis respectively, using a 90Plus Particle size analyser. Incorporation of NSAIDs into the SLNs was confirmed by differential scanning calorimetry and X-ray diffraction analyses. The crystalline structure of bulk lipid (stearic acid) and pure NSAIDs was assessed, along with changes in the lipid crystal lattices which occurred during SLN production and drug loading. The mean particle size of the prepared formulations on the production day was less than 200 nm with a polydispersity index of less than 0.15 for drug-free and drug-loaded SLNs, irrespective of the drug used. However, encapsulation efficiency and drug loading varied for different NSAIDs as estimated by high performance liquid chromatography analysis. Additional investigations are being performed to assess the drug release profile from SLNs. SLNs are suitable carrier systems for the incorporation of lipophilic NSAIDs. Microwave technology is a novel and simple procedure for SLN formulation that has produced stable, smaller SLNs with improved encapsulation properties.

Increasing Viscosity without Sacrificing Resolution: Atomic Scale Imaging at Solid-Liquid Interfaces

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Atomic force microscopy (AFM) is widely used in liquid environments, where true atomic resolution at the solid–liquid interface can now be routinely achieved. It is generally expected that AFM operation in more viscous environments yields poorer performance due to an increased noise contribution from the thermal motion of the cantilever resulting in a reduced signal-to-noise ratio (SNR)¹. Thus, viscous fluids such as ionic liquids and organics have been generally ruled out for high-resolution AFM studies. This is in stark contrast to the relevance of viscous liquids and their liquid–solid interfaces. Here, AFM studies would be of great interest as they enable in situ investigations of various processes including chemical reactions², lubrication³ and molecular ordering⁴. Despite the scientific need for studies on such systems with high spatial resolution, AFM in highly viscous liquids remains underutilized.

Here, we investigate the thermal noise limitations of dynamic AFM operation in both amplitude and frequency modulation mode. We report that these limitations for high viscosity environments are significantly different from the well-known equations for ambient and vacuum environments. In particular, we found that the assumption of a reduced SNR in viscous environments is not a property inherent to the technique. We demonstrate that SNR values comparable to ultra-high vacuum systems can be obtained in high viscosity environments and show true atomic resolution images of highly ordered pyrolytic graphite and mica surfaces. This new understanding of the noise contributions to the imaging process serves as a basis for widening the scope of high-resolution AFM away from water based applications to a wide variety of energy related materials, ionic liquids and organic solutions.

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Compartmentalisation in Ionic Liquids

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Compartmentalisation is one of the features of prebiotic environments believed to be essential to the origin of life. To date investigations of prebiotic environments have understandably focused on the self-assembly of compartments like micelles and vesicles in aqueous systems. However, the possibility of self-assembling systems developing in non-aqueous solutions such as ionic liquids is a largely unexplored area that may yield new insights into the postulated uniqueness of water, or form the basis of truly alien forms of life. Preliminary investigations have demonstrated that some lipids self-assemble into swellable lamellar structures in a range of ionic liquids, as they do in water. These lipids also exhibit a gel-to-lamellar phase transition on warming, and vesicle budding from myelenic figures.

These self-assembled structures have the potential to form vesicles and other compartments in ionic liquids, which could lead to protocell formation. This raises the possibility of water-free, synthetic life-forms, which would also significantly broaden the range of the ‘goldilocks zone’ of planetary orbits which could potentially support life.

Synthesis of Hierarchically Porous Materials by the Co-Micelle/Emulsion Templating Method

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The synthesis and characterization of novel porous materials, especially mesoporous materials, have received a significant amount of attention during the past two decades. The co-micelle/emulsion templating (CoMET) method were recently developed by Sarvi and co-workers to create hierarchically porous beads [1]. In this synthesis technique a block copolymer is used to stabilise an oil emulsion while also forming micelles in the continuous aqueous phase. The aqueous phase also contains tetraethyl orthosilicate (TEOS) and acrylamide, which undergo condensation and polymerization reactions, respectively to capture the hierarchical structure of the emulsion and micelles. The organic components are then removed by means of calcination and the resulting material has a macroporous structure with mesopores in the walls as shown in Figure 1.

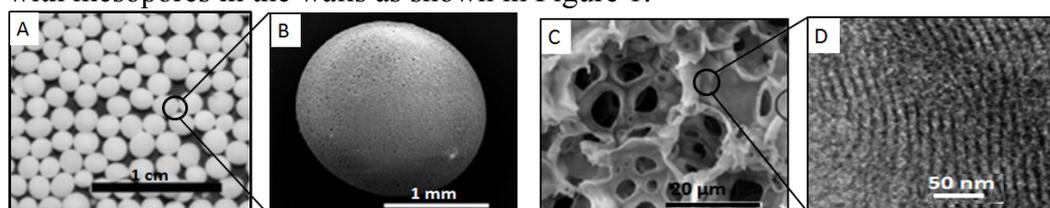


Figure 1: A) Silica beads, B) SEM image of the silica beads, C) cross section SEM of the beads displaying the macropores, D) TEM of the beads showing the cylindrical mesopore structure in the macropore walls [1].

A number of applications for hierarchically macro/mesoporous materials are emerging due to the favourable properties that arise from the combination of pores on these different length scales. These beads have potential in separation and adsorption processes as well as a support material in biocatalysis due to enhanced diffusion in the macropores while the mesopores provide a high surface area for active sites. The beads synthesized by Sarvi and co-workers had a 2D hexagonal mesopores structure and so a lower adsorption efficiency for larger biomolecules compared to 3D mesopore structures, which offer less steric hindrance due to the interconnection of the mesopores [2]. The aim of the present work is to increase the interconnectivity in the CoMET materials. Our initial investigations have involved using different block copolymers and synthesis conditions. Here we represent results of a systematic investigation of the role of the chemical species and synthesis parameters in the resultant CoMET structure. These data provide greater insights and predictability in the development of the mesopore and macropore structures.

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The Significance of Filamentous Bacteria for Floc Stability

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In the activated sludge process filamentous bacteria become dominant under certain operating conditions or feed compositions. Excessive filamentous growth normally results in the formation of stable foam due to the characteristic of these species as having hydrophobic cell walls and an ability to produce surfactants. Foam and solids on the surface of aeration tanks is a common problem encountered at wastewater treatment plants. Some of the current treatment methods involve operating at lower solids retention times, mechanical removal of the foam, and the use of chlorine sprays and chlorination of the return activated sludge line. These methods are not target specific and are mostly not very effective. It is therefore proposed to use target specific biophages [1] to reduce the filamentous bacteria to quantities lower than the foaming threshold. It is important to consider the possible side effects of this method since some studies [2-4] have suggested that the filamentous bacteria form the backbone of flocs and consequently are responsible for floc stability.

The use of phages to treat foam might be an effective solution to the foaming problem however removal of the filamentous bacteria might result in poor floc stability. When activated sludge flocs are introduced to excessive turbulence, primary particles are eroded from the surface and fragmentation of the flocs causes the maximum floc size to become smaller. This leads to the formation of pinflocs and turbid supernatants. It is therefore important to ensure that the flocs remain stable enough to withstand the turbulent conditions in the aeration basins. The significance of the filamentous bacteria for floc stability was evaluated by introducing activated sludge flocs, with different extents of filamentous growth, to a range of turbulent intensities. From this study it can be concluded that the filamentous bacteria provides additional resistance to floc breakup. Complete removal of the filamentous bacteria is therefore not the optimum solution for the foaming problem. In the ideal case, just the filaments protruding from the flocs should be removed while keeping the filamentous backbone intact.

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Extraction of Aggregate Densification Parameters via Raked Settling Analysis for the Incorporation into Thickener Modelling

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Shear processes during sedimentation has been shown to have a significant effect on predicted solids throughputs in gravity thickeners. After 100 years of research, accurate thickener modelling still remains a challenge because shear effects such as raking, are poorly understood. By understanding these effects, modelling accuracy will be enhanced, providing both environmental and economic benefits.

The proposed mechanism for shear effects is aggregate densification, where fractal flocculated aggregates become less fractal and achieves faster sedimentation rates. To describe the dewatering of flocculated mineral slurries, modified material properties such as the hindered settling and compressibility behaviour of the flocculated slurry are determined through a series of raked settling tests where the extent and rate of aggregate densification as a function of shear can be determined.

Raked settling analysis has shown that there is a lower rotation rate boundary where there is a significant jump in the rate of aggregate densification as well as an upper boundary where aggregate breakage is believed to occur causing a decrease in settling rate. This indicates that as long as a thickener is operated within these bounds, and the residence time is sufficient, exploitation of the phenomenon of aggregate densification can be achieved.

Discrepancies between the predicted settling profiles and experimental data suggest that the functional form used may not fully capture the densification behaviour of aggregates in shear. Further work must focus on more complex functions, which include effects such as the impact of concentration on the rate of densification, and aggregate breakage.

This knowledge will be incorporated into thickener modelling to quantify the influence of shear processes in enhancing thickener performance.

From Slip to Stick: A Study of the Hydrodynamic Boundary Conditions at Room Temperature Ionic Liquid-Gas Interfaces

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Room Temperature ionic liquids (RTILs) are organic salts in liquid state at room temperature. They typically consist of bulky organic cations and smaller organic or inorganic anions. RTILs have recently attracted the interest of both academy and industry due to their unique properties such as negligible vapour pressure, non-flammability, and thermal stability. However, their most appealing characteristic is the possibility to tune various physicochemical properties of these liquids to suit specific applications by introducing small changes in the alkyl side chain of the cation, or varying the cation/anion IL pair. For example, they are commonly used as task specific solvents [1], tribology studies concluded that certain RTILs are promising novel lubricants [2, 3], and their potential in foam flotation was recently revealed [4].

Applications such as the latter ones suggest that a thorough understanding of RTILs flow behaviour over surfaces, i.e., knowledge of the appropriate hydrodynamic boundary conditions (BCs) is very important. We carried out a systematic investigation on the BCs at RTIL-gas interfaces by using the rising bubble technique combined with high-speed video-microscopy and image analysis. The RTILs we have used were imidazolium based, with different alkyl side chain length of the cation, as well as ethylammonium nitrate (EAN), which have been reported to behave as Newtonian liquids [5].

We measured the terminal velocity of a single, isolated bubble, away from walls and RTIL-gas interface as a function of bubble size. As the experiments were conducted at low Reynolds numbers ($Re \ll 1$) the experimental values of terminal velocity were scaled by the Stokes' velocity (a sphere with no-slip hydrodynamic BC). The obtained ratio was used to infer the mobility at the RTIL-gas interface.

The results show a peculiar transition from (partially) mobile to rigid RTIL-gas interface with decreasing bubble size. The transition occurred at a bubble diameter of ca. 500 μm irrespectively of RTIL viscosity. In order to determine whether this is a specific feature of RTIL we carried out experiments with other viscous, Newtonian liquids (glycerol and silicone oil (Silicone Oil 200 Fluid 350cs, LABCHEM, Ajax Finechem Pty Ltd)). A similar transition (at ca. 500 μm) was observed for both liquids. Our tentative conclusion is that the transition between (partial) mobility and rigidity of RTIL-air interface could be a characteristic of high-viscosity Newtonian liquids.

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PH-dependent structures and surface activities of chaplin proteins: a simulation study

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Studies show that the chaplins, a family of secreted proteins, are critical for raising aerial hyphae in *Streptomyces coelicolor* and have a high potential to act as foaming and emulsifying agents or stabilizer in food products. Such functional properties are highly related to the adsorption of these proteins at the air-water and oil-water interface. Although it is known short chaplin proteins are able to self-assemble in solution into amyloid like fibrils, to date the formation of chaplin fibrils at the air/water interface and the adsorption and behaviour of these proteins at this interface is unknown.

Computer simulations are complementary to experimental studies and can be used to study the interfacial behavior of systems, including surface active agents and to elucidate aggregation mechanisms at a molecular level. In this study, molecular dynamics simulations are used to study the pH-dependent conformation of the chaplins in an aqueous medium and in the presence of a polar/non-polar interface. Non-equilibrium simulations are also used to estimate the free energy for protein adsorption at the air-water interface. This work serves as a foundation for the rational computational design of effective surfactant proteins for enhancing food products.

Inducing Colloidal Instability to Increase Hexosome Adsorption to Mucosal Surfaces

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This study assessed the colloidal stability and the mucoadhesiveness of a pH triggered vesicular to hexosomal liquid crystalline (LC) system and highlights its potential to enhance and sustain drug delivery.

Certain amphiphilic lipids can spontaneously self-assemble to form LC phases in excess water. This study focused specifically on the dispersed particles of the inverse hexagonal (H_2) LC phase, termed ‘hexosomes’, which has been shown to exhibit mucoadhesive properties^{1,2}. Mucoadhesive materials have the potential to increase the residence time of incorporated drugs at biological surfaces, thus enhancing drug bioavailability and sustaining drug absorption. Unlike liposomal systems, which can form colloiddally stable dispersions, hexosomal systems readily flocculate without sufficient stabiliser. A novel approach proposed in this study was to formulate colloiddally stable vesicles that can be triggered to destabilise and form the H_2 phase. The addition of oleic acid (OA) into LC matrices have been shown to impart pH sensitivity³, therefore, was incorporated to assist the transition. The phase behaviour of OA in phytantriol (PHYT) was identified and characterised using synchrotron small angle X-ray scattering (SAXS) and the optimal composition for vesicles to hexosomes transition was found to be at 30% w/w OA in PHYT. The nanostructure of the various dispersions was further verified using cryogenic transmission electron microscopy (cryo-TEM) where vesicles and hexosomes were observed at pH 8 and pH 5, respectively. Stable vesicles were formed at pH 8 without stabiliser, and as a proof of concept, fluorescent and radiolabelled markers was incorporated into this optimised OA/PHYT system. The system was applied onto excised porcine buccal membrane to assess the mucoadhesiveness of the system and the fluorescence were detected using confocal laser scanning microscopy (CLSM), while the radioactivity was quantified using scintillation counting. The results indicated that the difference in pH between the optimised system and buccal surface caused the colloiddally stable vesicles to aggregate and form hexosomes on the buccal membrane, which are significantly more mucoadhesive ($p < 0.0001$) than control vesicles that are not pH responsive.

In conclusion, this study highlights the potential for an induced mucoadhesive LC formulation to adhere on various mucosal membranes, which may have the ability to localise and provide sustained drug release via the oral cavity, nasal, respiratory, rectal and vaginal routes.

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Surface Force Measurements between Atomic Layer Deposition Prepared Mineral Surfaces

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Direct measurement of surface forces between materials requires that the surfaces are prepared in a suitable geometry with minimal surface roughness. For this reason, very few direct surface force investigations of mineral oxide surfaces have been reported as they generally cannot be prepared in a suitable form. Recently, Atomic Layer Deposition (ALD), a process whereby a film of material is grown in a layer by layer fashion onto a substrate has been successfully employed in surface force measurement. In this project hafnium oxide and zirconium oxide will be prepared by ALD technique and the surface forces between them (which has not been previously investigated) will be directly measured. We have produced extremely smooth ALD hafnium oxide films with properties representative of bulk phases and once these surfaces are characterized by numerous techniques the Atomic Force Microscope (AFM) will be used to measure the surface force. Subsequently, we will investigate how surfactants adsorbed to these surfaces alter the interaction forces. This may reveal conditions under which these two materials can be readily separated using inexpensive means.

The influence of sodium isopropyl xanthate (SIPX) concentration on the flotation of coarse and composite Zn/Pb ore particles

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In this study, the flotation response of a typical zinc-lead (Zn/Pb) ore has been investigated, in particular with respect to the coarse and composite sphalerite (ZnS) particles. A detailed characterisation was carried out by optical microscopy, chemical analysis, quantitative X-ray diffractometry (QXRD), scanning electron microscopy (SEM) and QEMSCAN techniques. The ore assayed 19% Zn and 5.7% Pb, being predominantly composed of sphalerite liberated, locked with non-sulphide gangue or associated with galena (PbS) and minor amounts of pyrite (FeS₂). Dolomite was the major gangue mineral. Flotation experiments were carried out for a selected feed particle size range of -600+75 µm, at P₈₀ of 390 µm. The recovery of Zn composite particles was analysed on un-sized and size by size basis. It was established that due to the very coarse particle size distribution the use of more collector was required to impart a sufficient degree of hydrophobicity to favour particle-bubble attachment and stability in flotation. The best results were achieved in the presence of 75 g/t of sodium isopropyl xanthate (SIPX), contributing a total Zn recovery of 78%, with significant improvement at the coarse end of the particle size distribution. The results also showed different flotation rate performance among the SIPX concentrations tested. QEMSCAN and SEM analysis on the flotation products showed coarse and composite particles of sphalerite in the concentrate, which indicates that sphalerite locked in hydrophilic gangue, can still be floated provided it is sufficiently hydrophobised by collector addition.

Wetting liquid films: A technique for Probing Microscopic Liquid Wetting using White Light Interferometry

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The affinity between a liquid and a solid in a gas phase is characterised by the contact angle and its hysteresis. Traditional contact angle measurement techniques such as sessile drop and Wilhelmy balance methods give a macroscopic view of the solid-liquid-vapour contact line. The knowledge of the microscopic details is rather incomplete due to severe experimental limitations in resolution. In order to examine the microscopic region of the liquid meniscus we adopted the white light interferometry (optical technique) employed in the Surface Force Apparatus. Using this technique it is possible to extract from the interference patterns the film thickness with nanometre resolution and details of the meniscus shape over tens of micrometres. It is possible to resolve small contact angles (below 5°). In this paper, we describe the technique and its application as well as demonstrate its validity by showing an example of a 0.1 mM KCl droplet spreading on a freshly cleaved sheet of mica. The film profile during the initial spreading and later, during the evaporation of the droplet was recorded. The microscopic details obtainable with this technique can provide a check for theoretical descriptions of precursor films in wetting. They offer a unique insight into the early stages of coating, liquid creeping and surface reactivity. In practice these details are relevant to corrosive films creeping on pipes in process plants, evaporation from heat exchangers, and the application and drying of paints and adhesives.

Dewetting of Hyperbranched Polystyrene Thin Films

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The stability of thin polymer films depends on the surface wettability of the substrate: polymer films on non-wettable substrates are unstable and dewet from the solid surface upon annealing above the glass transition temperature (T_g).¹⁻³ In the present work, we compared for the first time the dewetting behaviour of non-linear hyperbranched polystyrene (*hbPS*) to that of linear polystyrene. Our results showed that the molecular architecture of hyperbranched polymers affects significantly the morphology of the dewetting pattern of *hbPS* films. Dewetted holes in *hbPS* films showed high rim instability, resulting in the formation of short unstable viscous fingers which decayed into isolated droplets before complete dewetting of the film (Figure 1). The rim instability observed in *hbPS* films is due to the minimal chain entanglement of hyperbranched polymers with respect to linear polymers of similar M_w .

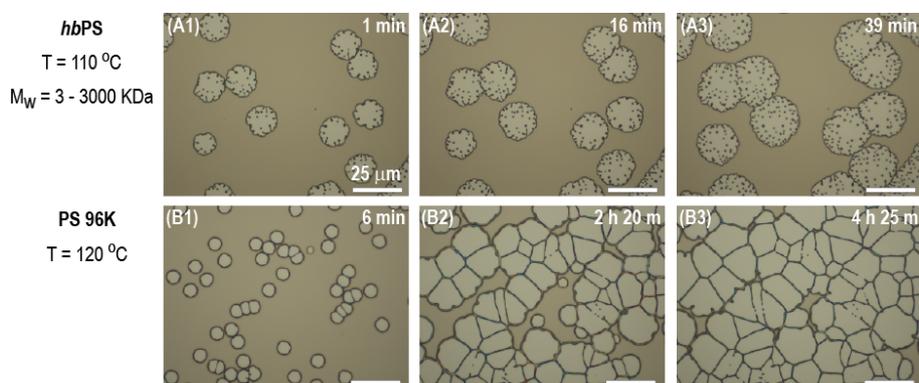


Figure 1. Optical micrographs showing the typical real-time evolution dewetting of (A1-A3) hyperbranched polystyrene (*hbPS*) with $M_w = 3 - 3000$ kDa, and (B1-B3) linear polystyrene with $M_w = 96$ kDa (PS 96K). Annealing temperature and annealing time are indicated.

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Large Scale Structural Formation in Ionic Liquids by n-Alcohol Addition

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We have studied the structural changes induced in a series of protic ionic liquids as a function of n-alcohol addition using Small and Wide Angle X-ray Scattering (SAXS/WAXS). For n-alcohols in ethylammonium nitrate (EAN), there is a pronounced correlation between the length of the alcohol chain and the induced structure. For example, ethanol in EAN induces a small increase in the low q scattering (Figure 1a), which indicates a minor rearrangement of the solution structure. In comparison, large scale structures are observed with the addition of n-hexanol (Figure 1b), which are reminiscent of either micelle formation or possibly a bicontinuous microemulsion.

We have also studied the effect of changing the cations and anions of ILs with the addition of n-alcohols ($C_nH_{2n+1}OH$, $n = 2, 4, 6, 8, 10, 12$). This study has implications for controlling the internal structure of ILs.

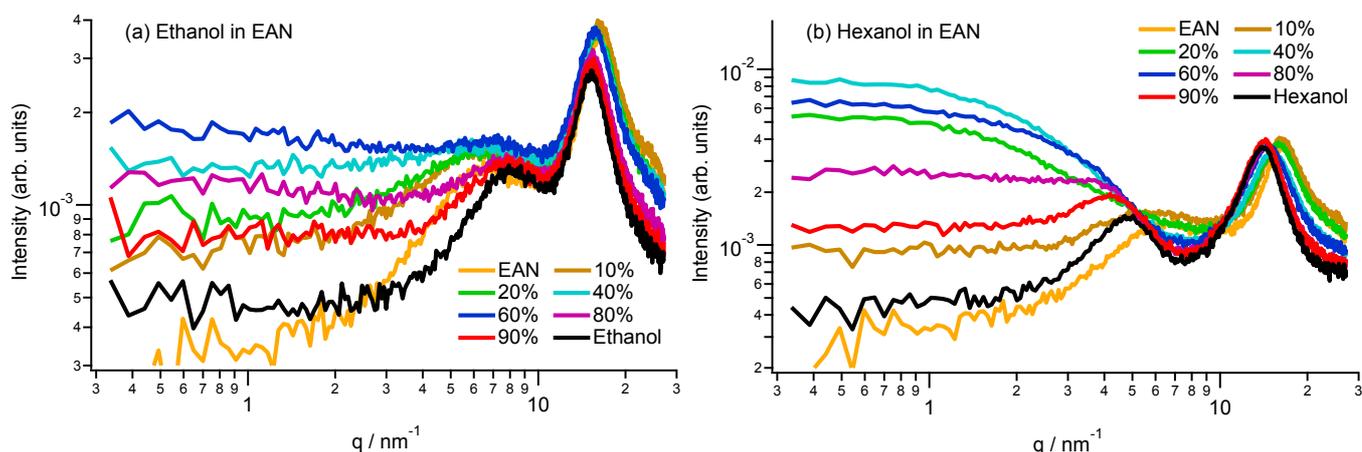


Figure 1. SAXS/WAXS data of (a) ethanol, and (b) n-hexanol added to ethylammonium nitrate (EAN).

Time-dependent Yield

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Yield stress has been a major interest in shear rheology study of particulate suspensions. It is the stress at which the transition from solid to fluid occurs. A constant stress experiment, or creep testing, is performed by applying a set of shear stress to the suspensions. When the applied stress exceeds network strength formed by the particulate suspensions, the network will fail and flow. Many models have been proposed to describe this behaviour, such as viscoplastic and viscoelastoplastic models. These models are based on Von Mises stress yielding criterion and basically imply that suspensions have a unique yield stress. However, these models cannot describe the features of viscoelasticity of suspensions seen in creep testing, such as time-dependent yield over a range of stress and propagation of yield fronts.

As an alternative, a new yield criterion, that is strain energy yielding concept, is proposed. This concept suggests that the suspension starts to yield when the energy of the system reaches the critical value. It introduces the time-dependent yield as well as lower and upper limits of yield stresses. In this talk, we will discuss the concept of the strain energy yield criterion.

Self – assembly of novel amphiphilic block co-oligomers

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In this study, a series of short amphiphilic block co-oligomers were synthesized by a living free radical polymerization technique (RAFT). The co-oligomers consist of a short hydrophilic block (5 - 10 units of acrylic acid) coupled to a variety of hydrophobic blocks (5 – 10 units of butyl acrylate, tert-butyl acrylate or ethyl acrylate). We have studied the phase behaviour and self-assembly of these novel amphiphiles into micelles and lyotropic liquid crystal in aqueous solution using optical microscopy, small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS). In some specific conditions, inverted hexagonal nanostructure of lyotropic liquid crystal was observed via optical microscopy (Fig. 1). Self-assembly is altered by changing the structure and hydrophobicity of the alkyl acrylate block and also by the degree of ionization of the acrylic acid block (pH). These amphiphilic co-oligomers show many unusual features in aqueous solution, which have diverse potential for many industrial applications as surfactants, for drug delivery and as dispersants.

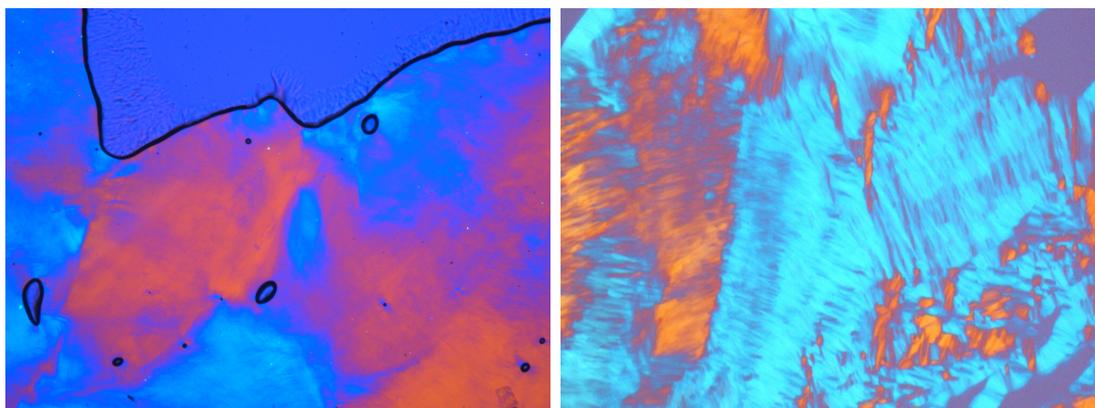


Figure 1: Polarizing optical microscopy image of inverted hexagonal nanostructure

Measurement of Nickel Laterite Agglomerate Structure Using Conventional and X-Ray Micro Tomography Methods

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Low grade nickel (Ni) laterite ore deposits are becoming the dominant feedstock for Ni production due to gradual depletion of high grade ores. Processing this ore type is favoured by low cost hydrometallurgical options, and in particular, heap leaching. In order to maintain stable and permeable heaps with efficient and uniform lixiviant flow through the heap over the long leaching period (e.g., 200-300 days), agglomeration of run-of-mine or crushed ores into robust and porous agglomerates is essential.

Previous work has established a batch drum agglomeration process that can reliably produce robust and stable agglomerates of different ore types. These agglomerates are yet to be fully characterised to provide essential fundamental information to rationalise their subsequent dynamic chemical and structural changes during column or real heap leaching. In this paper, agglomerate compressive strength, porosity and density are investigated as a function of -2 mm feed ore type, agglomerate size (10-30 mm) and moisture content (wet, air dried and oven dried) using saprolitic and goethitic nickel laterite ores. Agglomerate compressive strength is measured by determining its fracture stress under compressive load and a novel method is developed to measure porosity and density. The porosity data are compared with those obtained from agglomerate 3D microstructure characterization using an x-ray micro tomography (XMT) machine in order to validate it as a potential alternative tool to measure porosity. Agglomerate strength, porosity and density are found to depend upon feed ore type and agglomerate size and its moisture content (drying state). XMT porosity measurements are found to correlate well with those using the new porosity technique, and the implications of data reliability and reconcilability are discussed in relation to the qualitative and quantitative information the complementary techniques can provide.

Functionalization of TiO₂-Nanoparticles with Semiconducting Polymers Containing a Photocleavable Anchor-Group and Separation via Irradiation Afterwards

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One promising approach for solar cells with improved properties is the combination of inorganic nanoparticles (NPs) and organic semiconductors to exploit the advantages of both materials¹. Unfortunately cells based on this approach usually show low efficiencies. A critical aspect for the optimization is the control over interfaces and morphology¹.

Here we investigate a new approach to manipulate the morphology of hybrid films. We functionalize TiO₂-NPs with a semiconducting polymer containing a photocleavable anchor-group at the chain end. Thus the material provides improved film forming properties and optical and electrical properties of the organic and inorganic parts are combined^{2, 3}. The functionalization is confirmed before cleavage is induced by irradiation with UV-light. After cleavage the NPs can partially aggregate and the film morphology can be changed.

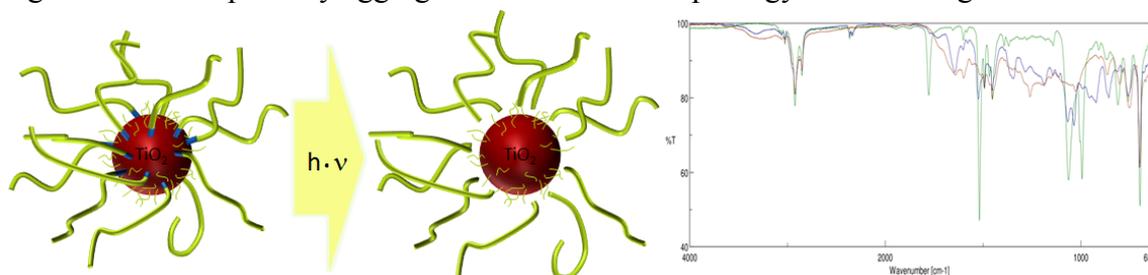


Figure 1. Photocleavage and end group reactions of the polymer can be followed by FTIR spectroscopy.

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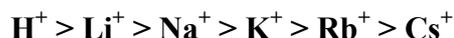
Specific Ion Effects in Non Aqueous Solvents

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The properties of concentrated salt solutions strongly depend on which salt has been used to prepare them: an injection of aqueous NaCl is harmless, whereas aqueous KCl quickly induces cardiac arrest, and is used as the deadly component in lethal injections. This happens because, at concentrations higher than 0.1 mol/L, short-range ion-specific interactions dominate in place of the long-ranged nonspecific electrostatic forces. These interactions are of fundamental importance for living organisms, as they allow for the selectivity that biology requires in order to operate. Many physical characteristics of aqueous electrolytes, like surface tension and protein stability in water, are ion-specific, generally following the Hofmeister series:



Currently no theory is available to explain and predict this behaviour. To this purpose, it is important to understand the ion-solvent interaction, but little is known about the role of the solvent.

The aim of this project is therefore to investigate specific ion effects in nonaqueous solvents. Several properties that are known to follow the Hofmeister series in water are going to be tested in polar organic liquids. Preliminary experimental results on colloid sedimentation in methanol show an ion-specific behaviour in this system. We expect that these experimental results will provide important guidance in the development of an accurate theoretical prediction of ion-specific effects in general. Understanding the mechanisms that underlie specific ion effects would mean to finally master technological fields that are still largely empirical, such as industrial formulations and drug design.

Properties and Applications of Fluorocarbon Liquid Crystals

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In this project, the properties of a novel aqueous fluorocarbon surfactant and oil mixture were analysed and the potential for liquid crystal applications explored. Lab-based optical microscopy measurements were complemented with Small Angle Neutron Scattering (SANS) and Small Angle X-ray Scattering (SAXS) to fully characterise the phases formed by this system.

Due to the unique properties of the fluorocarbon chains – bulky, rigid chains with low dispersive energy – when compared to hydrocarbon analogues, it was found that low curvature phases tended to be favoured, with lamellar liquid crystals dominating. The lamellar phases seen showed remarkably high viscosities and exceptional thermal stability, suggesting potential applications as critical lubricants.

Further exploration of the fluorocarbon liquid crystals involved the incorporation of 2D nanomaterials and use as a template for the synthesis of ordered, nanostructured silica.

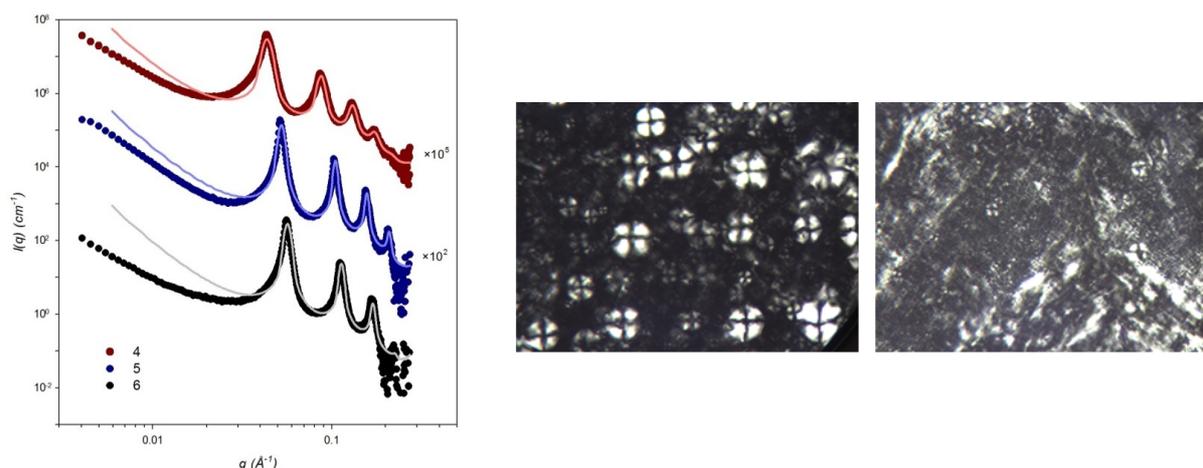


Figure 1. *Left*: small-angle X-ray scattering of fluorocarbon lamellar liquid crystal phases. *Right*: polarising light microscopy images showing the birefringence of the self-assembled phases.

Fundamental agglomeration and leaching studies of nickel laterites for improved heap leaching performance

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Complex, low-grade laterites comprise ~70% of land-based global nickel (Ni) mineralization. Heap leaching offers an economically competitive route for hydrometallurgical extraction of Ni and pay metal, cobalt (Co) from these ores for which smelting, pressure and atmospheric stirred tank leaching are not cost-effective. To date however, considerable challenges persist in designing and producing agglomerates that meet metallurgical, geological and geotechnical challenges which confront heap leaching of low grade ores. Robust but porous agglomerates of ~5-40 mm size are desirable for perennial (~180-300 days) leaching of heaps, typically of 4-10 m high, at concentrated sulphuric irrigation rates in the range 10-20 dm³/h.m². This paper presents drum agglomeration, product characterization and column leaching studies undertaken to foster the understanding of agglomerate structures and properties and leaching behaviour of nickel laterite (clay-rich saprolitic (SAP) and oxide-rich goethitic/limonitic (G)) ores for desirable quality attributes. The results show that the feed ore mineralogy/chemistry, particle size and its distribution, as well as binder type/content, all dramatically impact on agglomerate structure and strength characteristics. Whilst SAP required greater binder dosage for effective agglomeration than G ores, the resulting agglomerates of the latter were more robust than the former based upon their compressive strength and acidic solution soak test measurements. However, over 100 days of continuous column leaching, the structural stability of the SAP agglomerate bed was slightly greater than that of G agglomerates, reflecting a lesser slump of the former. This indicated that single agglomerate characteristics alone cannot be used as basis for prediction of their performance and stability during column/heap leaching process. Moreover, the leach solution analysis revealed greater Ni/Co extraction rates from the SAP than the G agglomerates. The total mass of acid consumed per ton dry ore processed was also greater for the SAP ore but the total kg acid per kg Ni extracted was markedly lower than G agglomerates. The overall results revealed that the ratio of oxide to clay minerals within laterite ores can lead to either synergistic or antagonistic effects on the resulting agglomerate robustness, bed percolation behaviour under prolonged acid irrigation periods and the overall acid consumption rate.

Investigations of the Dependence of Suspension Rheology Properties on Particle Size

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Rheology is the study of the flow and deformation of materials. Understanding the rheological properties of particulate suspensions is very important for determining their performance in various industrial applications. Particulate suspensions may be subjected to shearing forces such as in pipe flow or compressional forces such as during solid-liquid separation. In addition, there are many industrial applications where shear and compressive forces are combined, which leads to improved solid-liquid separation. Examples include belt press filtration, decanting centrifugation and raked thickening.

Particle size is a critical parameter that determines the rheology of a suspension. This work investigates the effect of particle size on the shear and compressive rheology of five different sized calcium carbonate suspensions. The suspensions are coagulated at the isoelectric point. The shear yield and viscosity are measured using a Haake torsional rheometer using a vane-in-an-infinite-cup geometry. The dewatering properties of compressibility and permeability are measured using filtration and sedimentation testing. The results show that the rheological properties are strongly dependent on the particle size of the suspension. The compressive yield stress and shear yield stress decrease with increasing particle size. Increasing particle size also reduces the viscosity at a given volume fraction.

Interactions between Gas Shales and Model Proppant Particles in Aqueous and Non-Aqueous Solutions through Atomic Force Microscopy (AFM)

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Proppants are solid particulate materials, typically treated sand or man-made ceramics, which are designed to resist natural closing and re-sealing stresses and maintain hydrocarbon permeability within unconventional oil and gas reservoirs during or following a hydraulic fracturing operation. However, little is known of the fundamental mechanical, or surface physicochemical, interactions between shales and various proppants, and specifically how proppant properties affect migration and embedment within fractures. The interactions define

the accessibility of the fracture network to proppants, and hence the proportion of unpropped fractures which are likely to close. The methodology in this research consists of collecting and analyzing carefully controlled force-distance curves of the shale and model proppant (silica or alumina particles) system under both dry and wet conditions to determine relevant properties such as the adhesive force and electric double layer phenomena. Force maps will also be generated across the shale surface heterogeneities. The wet condition consists of shale samples immersed in a saline solution of water with guar, a popular commercial viscosifier. Shale samples have also been preserved and stabilized under both oily and inert conditions for a variety of different case studies. The adhesive force is particularly valuable to create an adhesion map across a user-generated grid that takes into account surface heterogeneity. This adhesion map can be interpreted as a measure of proppant embedment and determines the stick-or-slip behavior of the proppant as it encounters the shale roughness and varying surface chemistry, with clay-rich rock being more prone to proppant embedment. The broader implication of this study is using AFM to improve our understanding of hydraulic productivity in gas shale reservoirs by assessing the microstructure and proppant migration within fractured unconventional hydrocarbon reservoirs.

Measuring the Critical Micelle Concentration (CMC) of Molecular Solvents as Amphiphile Self-assembly Media

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Prior to 2006, there were only a handful of non-aqueous solvents that had been reported to support amphiphile self-assembly.¹ Since then, many ionic liquids¹, and more recently a broad range of molecular solvents², have been shown to have this capability². Specifically, low molecular weight polar solvents including amides, alcohols and diols. The self-assembly can be described by the “solvophobic effect” which is analogous to the hydrophobic effect in water. There is a strong correlation between the solvents cohesive energy density, as measured by the Gordon Parameter, and the solvophobic effect.²

Continuing on our work on short-chained alcohols, amines and diols, we have explored these solvents in terms of their ability to support micelle formation. Cationic surfactants, hexadecyltrimethylammonium bromide (CTAB) and hexadecyl-pyridinium bromide (C_{16} PyrBr) were used in solvents with a range of different Gordon parameters. Hanging drop surface tensions measurements were used to determine the CMC (see Figure 1). Correlations will be made between the CMC values, solvent chemical structures, and their Gordon parameters.

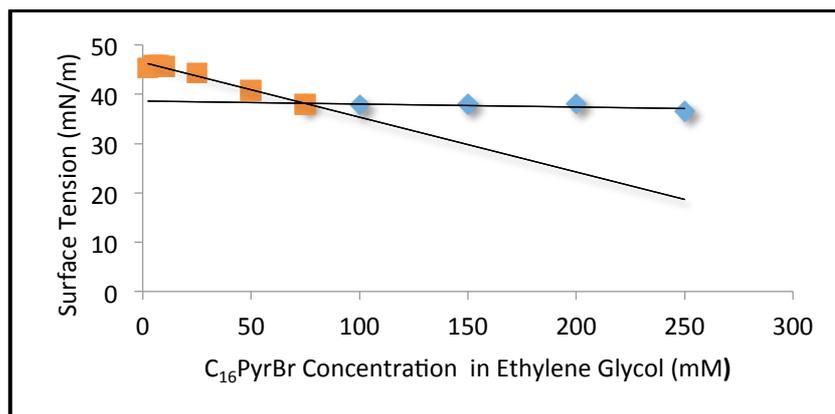


Figure 1. Surface tension measurement in Ethylene Glycol with various C_{16} PyrBr concentrations

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Experimental Techniques

Atomic Force Microscope (AFM)

The Atomic Force Microscope is one of a family of Scanned Probe Microscopes derived from the Scanning Tunnelling Microscope. They all share three attributes: a mechanism for translating a surface in three dimensions typically with the precision on the atomic scale, a probe which is sensitive to a particular surface phenomenon which decays as a function of distance normal to a surface, and a feedback mechanism which can couple the previous two elements. In AFM the translating element is piezoelectric element, and the probe is comprised of either (i) a sharp tip or (ii) particle (so-called “colloid probe”) affixed to the free end of a cantilever.

Laser light from a solid state diode is reflected off the back of the cantilever and collected by a position sensitive detector (PSD) consisting of two or four closely spaced photodiodes whose output signal is collected by a differential amplifier. Angular displacement of the cantilever results in one photodiode collecting more light than the other photodiode, producing an output signal (the difference between the photodiode signals normalized by their sum) which is proportional to the deflection of the cantilever. It can detect cantilever deflections $<1 \text{ \AA}$ (thermal noise limited) - see Fig. 1. A long beam path (several cm) amplifies changes in beam angle. Because of AFM’s versatility; it has been applied to a large number of research topics. The AFM has also gone through many modifications for specific application requirements.

Measuring forces

Because the atomic force microscope relies on the forces between the tip (or “colloid probe”) and sample, knowing these forces is important for proper imaging. The force is not measured directly, but calculated by measuring the deflection of the lever, and knowing the stiffness of the cantilever. Hook’s law gives $F = -kz$, where F is the force, k is the stiffness of the lever, and z is the distance the lever is bent. Typical force curve is presented in Fig. 2.

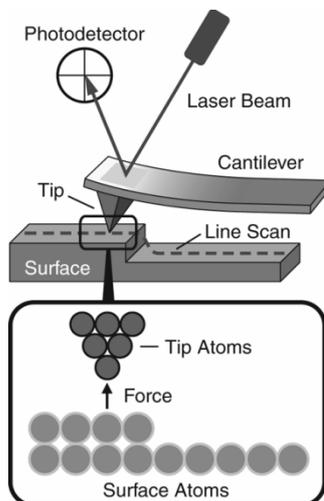


Fig. 1. Schematic of AFM

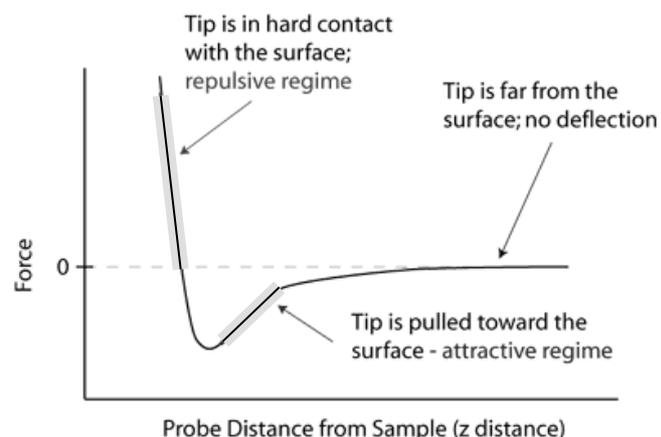


Fig. 2. Typical force curve

Binnig, Quate, and Gerber invented the Atomic Force Microscope (AFM) in 1985. Their original AFM consisted of a diamond shard attached to a strip of gold foil. The diamond tip contacted the surface directly, with the interatomic van der Waals forces providing the interaction mechanism. Detection of the cantilever’s vertical movement was done with a second tip - an STM placed above the cantilever.

Cyclic Voltammetry (CV)

Cyclic Voltammetry is an electrochemical technique that is the most widely used to obtain qualitative information about electrochemical reactions. It offers a rapid location of redox potentials of the electroactive species, and evaluation of the effect of media upon the redox process. CV can also provide information on the thermodynamics of redox processes and the kinetics of heterogeneous electron-transfer reactions as well as on coupled chemical reactions and adsorption processes.

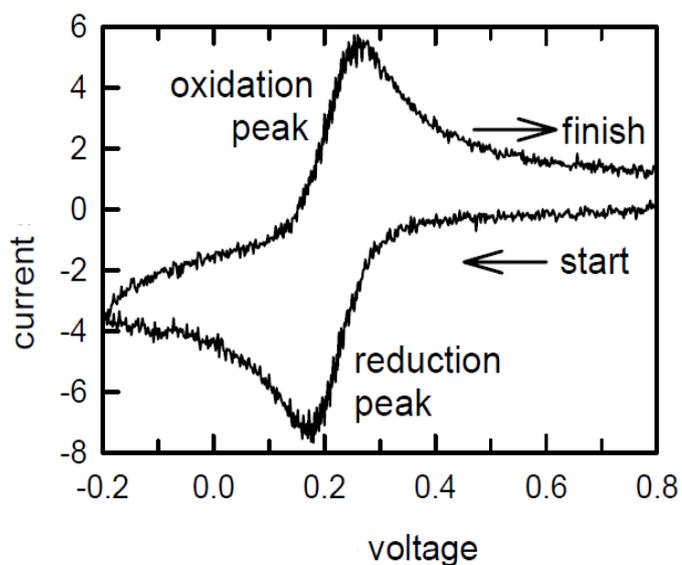


Fig. 1. A typical voltammogram of a reversible redox process

Summary provided by Vera Lockett

Dynamic Light Scattering

The Dynamic Light Scattering (DLS) technique measures particle size. Sub-micrometre sized particles in a dispersion move constantly in a random, Brownian motion. When a laser beam is shone through the dispersion, the light is scattered by the particles. The Brownian movement of the particles causes the intensity of the scattered light to fluctuate. By measuring the rate of fluctuation, the speed at which the particles are diffusing (the diffusion coefficient) is determined. Using the Stokes Einstein equation the particle diameter (d) is calculated from the particle diffusion coefficient.

DLS measures the hydrodynamic diameter of the particles. That is the size of a particle with the same diffusion coefficient as the scattering particles. The particle shape is assumed to be spherical. The hydrodynamic diameter includes molecules adsorbed to the surface and the solvation layer that moves with the particle. The diffusion coefficient of the particles, and hence the hydrodynamic radius, can be sensitive to changes in the ionic strength of the dispersion and conformational changes of adsorbed species on the particles.

DLS instruments use a correlator to construct a correlation function of the intensity of the light scattered by the particles. The correlation curve is fitted to an exponential function. The diffusion coefficient is proportional to the lifetime of the exponential decay. The particle size distribution obtained from the correlation function is an intensity size distribution, a plot of the relative intensity of light scattered by particles in various size classes. The intensity of light scattered by a particle is proportional to d^6 (Rayleigh approximation). Thus the intensity size distribution tends to be biased towards the larger particle sizes in a polydisperse distribution.

Summary provided by Catherine Whitby

Electrokinetic Sonic Amplitude Effect “AcoustoSizer”

The application of an AC voltage across a colloidal dispersion causes the particles to vibrate at a velocity dependent upon their size, zeta potential and the applied frequency. At the high frequencies employed in the “AcoustoSizer”, typically around MHz, the particles emit acoustic waves in response to the alternating voltage. By pulsing the voltage signal the acoustic response or electrokinetic sonic amplitude (ESA) of the particles can be recorded as a function of frequency. The ESA signal is a linear function of the applied voltage and hence a Fourier transform of the recorded acoustic response is required.

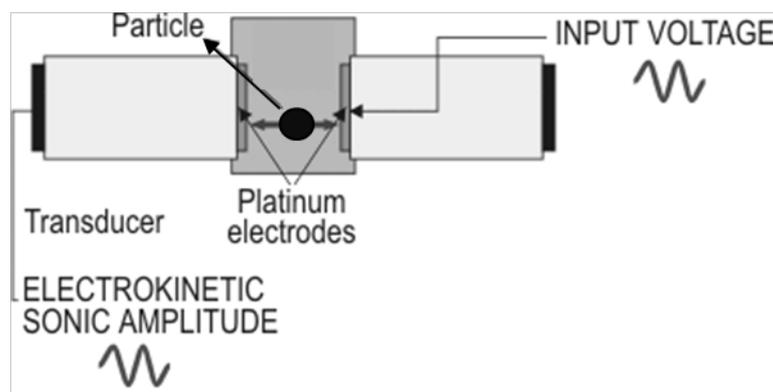


Fig. 1 Schematic diagram of the AcoustoSizer showing how zeta potential can be measured.

From the ESA spectrum the dynamic mobility is obtained from which the size and charge of the particles can be determined. The larger the difference between the densities of the fluid electrolyte and the colloid, or the larger the volume fraction the greater the ESA signal.

The dynamic mobility is a complex quantity equal in magnitude to the ratio of the particle velocity divided by the applied field. It is complex because there is a phase lag between driving frequencies and the response of the particles to that field. As the applied field tends to zero the mobility becomes a real quantity, equal to the electrophoretic mobility defined for a static (DC) applied field. Field strengths are in the order of 100Vm^{-1} , and at MHz frequencies typical particle displacements are in the order of 10^{-13}m . At low frequencies the inertia of particles is not sufficient to cause a large enough phase lag to connect dynamic mobility with particle size, and only zeta potential is accessible. However, as the frequency increases the particle motion lags more and more behind the field and both size and zeta potential become available. At higher frequencies the ESA effect is too small to give a measurable signal. It is observed for many colloid systems that the equations governing the dynamic mobility simplify such that the size is determined solely by the argument and the zeta potential from the magnitude of this complex quantity. Unlike traditional electrokinetic measurements this technique is well suited to concentrated dispersions.

Flotation

Flotation or froth flotation is a simple and inexpensive process used for the separation of particles (smaller than 500 μm) based on hydrophobicity contrast of their surfaces. Only hydrophobic particles attach to gas bubbles (smaller than 2mm) rising through the mineral pulp. At the top of the flotation cell, these gas bubbles break up allowing the floated particles to be recovered. In froth flotation, the floated particles are trapped in the froth at the top of the flotation cell before being recovered; the froth constitutes an additional separation process.

To increase the mineral separation, a variety of reagents are added to the mineral pulp. Collectors are added to increase the surface hydrophobicity of valuable material particles and therefore increase their attachment to gas bubbles (only a few minerals are naturally hydrophobic, for example talc, sulphur or molybdenite). Collectors are surfactants which consist of a head group which attaches to specific sites on the mineral surface and a hydrocarbon chain or tail which impacts hydrophobicity of the mineral surface. On the other hand, depressants such as inorganic ions or polymers are added to make the mineral surface more hydrophilic and, therefore, to depress the flotation of these minerals.

Flotation has also been used in the treatment of waste water, coal, clays, corn, proteins, dyes, rubber, glass, plastic, etc.

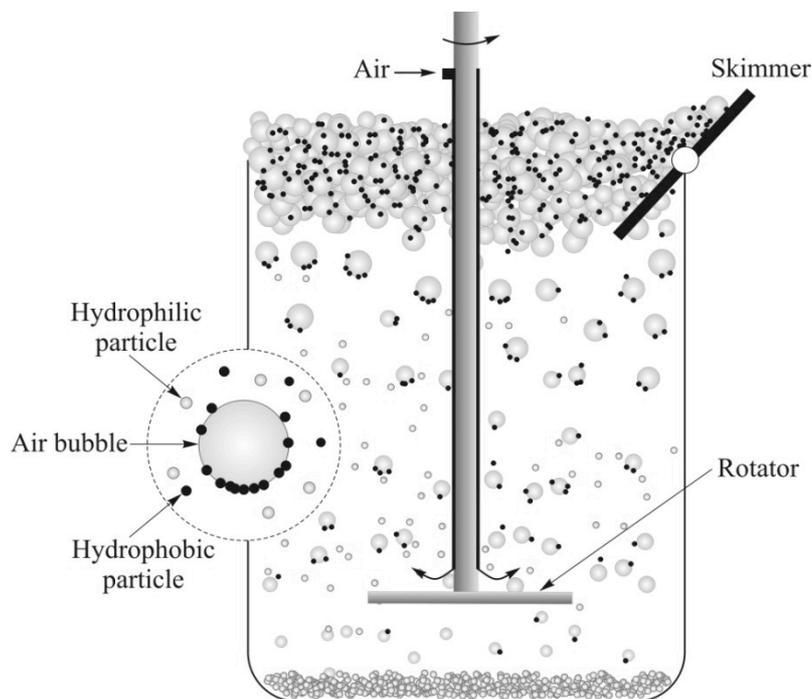


Fig. 1 A very simplified schematic of a flotation cell

Summary provided by Daniel Fornasiero

Neutron and X-ray reflectivity

Neutron reflectivity is a technique which provides structural information about surfaces and thin films. The technique involves shining a highly collimated beam of neutrons onto an extremely flat surface and measuring the intensity of reflected radiation as a function of angle or neutron wavelength. The exact shape of the reflectivity profile provides detailed information about the structure of the surface, including the thickness, density, and roughness of any thin films.

Neutron reflectivity is a specular reflection technique, where the angle of the incident beam is equal to the angle of the reflected beam. The reflection is usually described in terms of a momentum transfer vector, denoted Q_z , which describes the change in momentum of a neutron after reflecting from the material. Conventionally the z direction is defined to be the surface normal direction, and for specular reflection, the scattering vector has only a z-component. A typical neutron reflectivity plot displays the reflected intensity (relative to the incident beam) as a function of the scattering vector, $Q = \frac{4\pi \sin \theta}{\lambda}$, where λ is the neutron wavelength. The reflected intensity is a function of the scattering length density, $\rho = \sum_i n_i b_i$, where n_i is the number density of each component and b_i is its scattering length, and the variation in reflectivity with Q is a function of the adsorbed layer thickness, τ .

Neutron reflectivity is sensitive to contrast arising from different nuclei, and the feature that makes this technique so powerful is the difference in scattering lengths of hydrogen (-0.374×10^{-12} cm) and deuterium (0.676×10^{-12} cm). Hence, selective deuteration allows certain parts of molecules or ions to be highlighted, whilst the chemistry is unaltered.

X-ray reflectivity is used to probe the structure of surfaces, thin-films or buried interfaces as well as processes occurring at surfaces and interfaces such as adsorption, adhesion and interdiffusion. The technique directs a beam of x-rays on a surface and measures the intensity of x-rays reflected in the specular direction. If the interface is not perfectly sharp and smooth then the reflected intensity will deviate from that predicted by the law of Fresnel reflectivity. The deviations can then be analyzed to obtain the density profile of the interface normal to the surface.

A beam of x-rays is directed at the interface at an incident angle, θ . The reflected beam intensity, R , is measured as a function of the change in momentum transfer normal to the surface,

$Q = \frac{4\pi \sin \theta}{\lambda}$, where λ is the wavelength of the beam. The reflected intensity is a function of the scattering length density profile perpendicular to the interface. The scattering length density, ρ , of a

given species depends on its electron density, and is given by $\rho = \frac{\sum_i z_i r_e}{V_m}$, where z_i is the atomic number of an element i , V_m is the molecular volume and r_e is the Compton radius. The reflectivity profile can reveal oscillations in the reflection intensity, which arises from the interference of waves reflecting from the different layers within the system. The periodicity of these KIESSIG fringes is related to the thickness of the film.

Summary provided by Deborah Wakeham

Particle-Film ATR FTIR Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a powerful and versatile technique for the characterization of molecules and their environment [1]. The benefits of the technique for studying molecular systems have resulted in many applications to interfacial systems [2, 3]. However, the use of FTIR in wet surface chemistry is sometimes hindered by issues of sampling and spectral interference from solution species, and the bulk liquid and solid phases associated with wet interfaces. One successful method of applying infrared spectroscopy for in situ adsorption studies is attenuated total reflection FTIR [1, 4]. Passage of the probe infrared radiation through an IR transparent crystal allows light delivery to the interfacial region between the crystal and a solution without the beam undergoing attenuation by reaching the interface through the liquid phase. If an adsorbate is present in significant amounts at the interface, the internal reflection of the IR light is attenuated at the characteristic frequencies of the adsorbate molecular vibrations, resulting in the acquisition of the spectrum of the adsorbate by the FTIR spectrometer. Provided that the solution concentration of the adsorbate is below the detection limit of the instrument in ATR mode, the signal detected is solely from the adsorbed species, i.e. the technique is surface selective and surface sensitive.

Whereas ATR crystals provide ideal substrates for many in situ interfacial spectroscopic investigations, they do limit the number of substrates that can be studied (eg. IR transparent crystal materials such as germanium, silicon, zinc sulfide or selenide, etc.). One means by which users can extend this range of substrates is to use deposited films of particles atop the ATR crystal [5]. Provided that the film is stable, thin enough (i.e. sub-micron), continuous, and not too optically dense, the ATR experiment can proceed as before, but this time the interface probed is the particle-solution interface. Another advantage of the particle film approach is that the available surface area of the substrate for adsorption is increased, resulting in higher sensitivity for detection of the adsorbate, which in many cases allows in situ kinetic studies of adsorption to be performed [6].

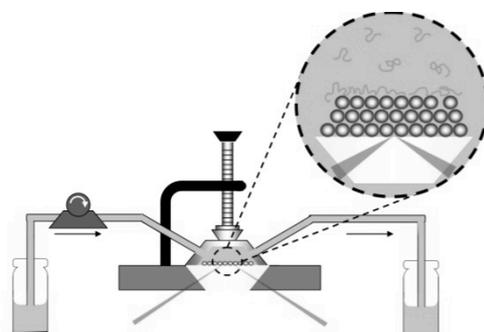


Fig. 1 – Schematic of experimental set-up for an in situ adsorption experiment using particle film ATR FTIR. The infrared beam comes from the spectrometer IR source and bounces off the crystal/particle film – liquid interface and is sent to the spectrometer detector. Diagram produced by Audrey Beaussart.

References:

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- [5] A.J. McQuillan, Adv. Mater. 13 (2001) 1034.
- [6] L.T. Cuba-Chiem, L. Huynh, J. Ralston, D.A. Beattie, Langmuir 24 (2008) 8036.

Summary provided by David Beattie

Positron Annihilation Lifetime Spectroscopy (PALS)

Positron annihilation lifetime spectroscopy (PALS) is a technique which utilises positrons to directly probe and thus characterise condensed media. It has been used extensively to characterise metals, ceramics and polymers and to some extent soft matter materials such as self-assembled amphiphile systems. Positrons are formed when radioactive isotopes such as ^{22}Na undergo radioactive decay. Figure 1 presents the nuclear decay scheme of ^{22}Na .

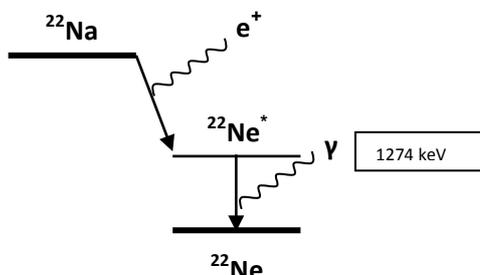


Fig. 1 - Schematic of ^{22}Na decay pathway. The birth of the positron and the emission of a gamma ray occur within 3 ps of each other and usually assumed to be a simultaneous process.

The emission of the positron and photon is regarded to occur simultaneously. Thus, the detection of the 1274 keV photon is used to tag the ‘birth’ of the positron. When the positron encounters the material of interest, it will accumulate in areas of low electron density (void space). The positron will then annihilate with an electron from the sample, and emission of two 511 keV photons signals the ‘death’ of the positron. The time difference between the 1274 and 511 keV photons provide information regarding the lifetime of the positron. The positron lifetime or in other words, the rate of positron annihilation is affected by the medium in which the positron annihilates. By measuring the lifetime of the positron in the sample, information regarding both the physical and chemical nature of the medium can be obtained. Figure 2 is a representation of a PALS experimental setup.

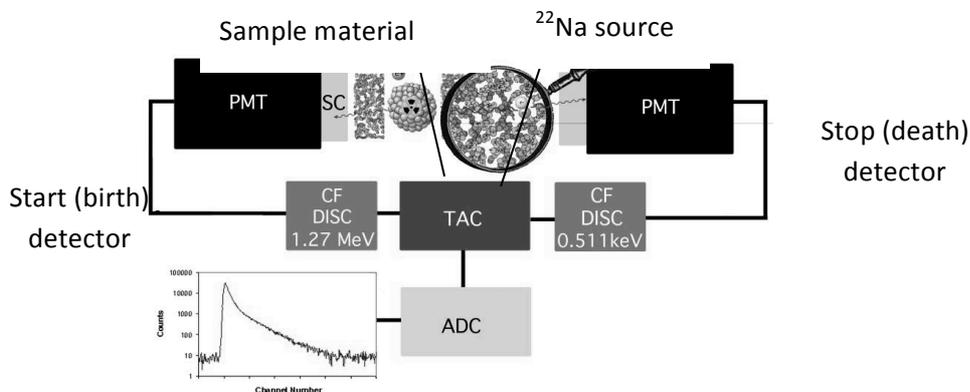


Fig. 2 - Schematic of the PALS spectrometers and electronics. The resulting PALS spectrum is a histogram of the number of counts with a particular lifetime.

Following analysis with the appropriate fitting programs two parameters can be obtained from the raw PALS spectrum – τ and I . τ represents the lifetime of the positron and is an indication of the pore size in solid state materials, while I corresponds to intensity which provides information on the number density of the pores, or in other words the porosity of the material.

Summary provided by Aurelia Dong

Small-Angle X-ray scattering (SAXS)

Static small angle scattering methods allow the characterization of structures and their organization in the mesoscopic and microscopic size range, which makes these methods important and popular for the investigation of e.g. complex fluids, colloidal suspensions, synthetic and biological macromolecules or porous materials. While light scattering is used to explore rather large length scales, the mesoscopic size range can usually only be investigated using x-rays or neutrons. The choice of the technique depends on the particular properties of the sample since some samples have a high contrast for neutrons whereas other samples have a high contrast for X-rays. The analysis of the measured angular dependence of the scattered intensity provides information on size, structure and interaction of the scattering objects.

In a typical SAXS experiment, a highly monochromatic X-ray beam is focused on the sample. Due to inhomogeneities of the electron density of the sample, X-rays are scattered and collected using a 2-dimensional multidetector. The basic principle of a SAXS experiment is also illustrated in Fig. 1.

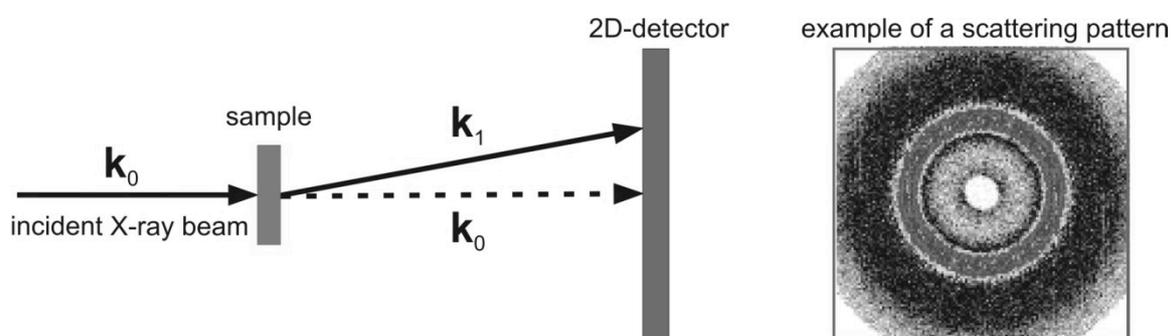


Fig.1 A typical SAXS experiment: The incident X-ray beam passes the sample and X-rays are scattered. A 2D-detector measures the scattered X-rays and a characteristic scattering pattern of the sample can be recorded. The shown pattern on the right is an example for an isotropic scatterer.

Most of the SAXS experiments can be performed without the need of large-scale facilities (as needed for experiments with neutrons) by using laboratory SAXS instruments. However, if X-rays with higher brilliance and a much higher focus are required, synchrotron sources have to be employed. A disadvantage of X-ray scattering experiments is the low scattering contrast for light atoms, since X-rays are scattered by electrons. Therefore, SAXS cannot be used for many organic samples. Another problem is damage to the sample due to the high energy of X-rays.

Summary provided by Matthias Karg

Surface Force Apparatus (SFA)

Forces are measured as a function of distance between typically two crossed mica sheets, which were back-silvered and glued onto cylindrical silica discs (Fig.1 - part 1). The forces between mica surfaces are measured from the deflection of a cantilever spring that supports the lower surfaces (Fig.1 - part 2). The separation between surfaces is determined interferometrically by using fringes of equal chromatic order (FECO) (Fig.1 - part 3). The shape and pattern of optical fringes provide information about separation between surfaces, contact geometry such as contact area and deformation, and events happening between surfaces such as condensation, adsorption, and most unwelcomed surface contamination! The distance between surfaces is controlled by a series of coarse and fine micrometers connected to stepping/DC motors or a piezo drive (Fig.1 - part 4), with a synchronous motor coupled by a cantilever spring to the other surface. Number of modified versions has been developed to extend the SFA method such as for friction measurements.

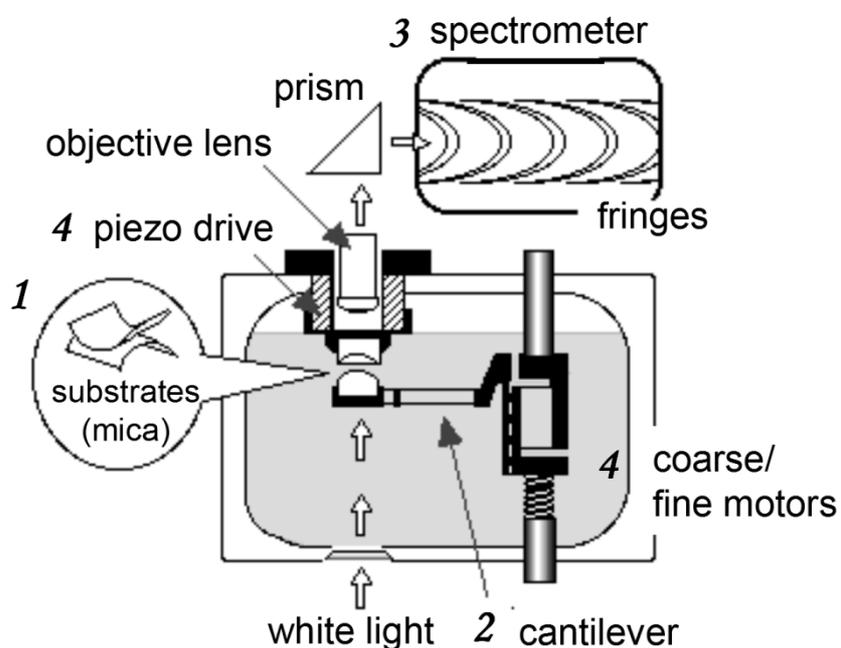


Fig.1 Surface Force Apparatus (SFA), "legendary" Mark II

Summary provided by Satomi Onishi

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

ToF-SIMS is an analytical technique for obtaining elemental and molecular information from surfaces with detection limits in the parts per billion range. In a ToF-SIMS measurement, the sample is placed in an ultrahigh vacuum (UHV) environment where a pulsed beam of primary ions bombard the surface ejecting, atoms, molecular fragments and molecules. A small portion of these “secondaries” are in a charged state (positive and negative) and are extracted into a time of flight mass spectrometer and mass spectra are built up with each pulse of the primary beam. The primary beam currents employed are so low as to only remove perhaps 1 in a 1000 species from the top few monolayers of the surface, leaving the surface essentially undamaged. Secondary ion images may be obtained by scanning, or “rastering” the primary beam and collecting mass spectra as a function of beam position. Typical spatial resolution can be better than 0.5 μm . Additionally, depth profiles may be acquired by alternating analysis and sputtering cycles using either the same primary beam or a second, sputtering ion source.

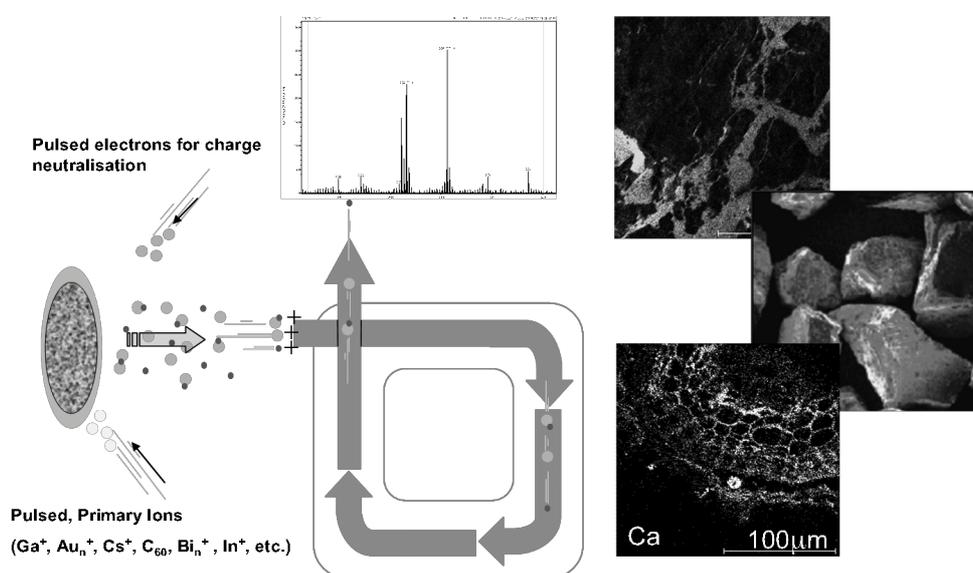


Fig. 1 Schematic of ToF-SIMS instrument with example data. Images are (clockwise from top) copper distribution in mineral section (200 μm view), 20-38 μm soil particles and Ca distribution in a tree root.

Primary beams available for modern ToF-SIMS instruments include – gallium (Ga^+), gold and gold Cluster (Au^+ , Au_n^+), bismuth and bismuth cluster (Bi^+ , Bi_n^+), cesium (Cs^+), indium (In^+), argon (Ar^+), oxygen (O^+ , O^-), SF_6 , etc. More recently, fullerene, C_{60} , primary ion sources have become available. C_{60} beams enhance the sputtering of large molecular weight molecular fragments and molecules and are therefore extremely useful analytical beams for organic materials and adsorbates.

In most ToF-SIMS instruments, samples may be cooled to liquid nitrogen temperatures to preserve species that may be volatile under UHV conditions, and insulating surface may be analysed using advanced charge neutralising electron flooding.

Suggested reading:

Vickerman, J. C.; Briggs, D. D. *ToF-SIMS: Surface analysis by mass spectrometry*, Chichester, Surface Spectra and IM Publications, **2001**

Summary provided by Bill Skinner

Total Internal Reflection Microscopy (TIRM)

Total Internal Reflection Microscopy (TIRM), developed by Prieve *et al.*^{1, 2}, is a force measurement tool that uses Brownian motion to gauge the forces between a colloidal particle levitated above a plate. Compared to force balance methods that use mechanical springs such as atomic force microscopy (AFM) and the surface force apparatus (SFA) the TIRM is much more sensitive. On a force scale, TIRM is three and five times more sensitive than AFM and SFA, respectively².

TIRM is an optically noninvasive experimental technique that measures the interaction potential energy of a levitated colloidal particle (typically 3-5 microns in diameter). The particle is illuminated by an evanescent wave created at the solid liquid interface above the critical angle, as shown in Figure 1. The intensity of the scattered light, $I(h)$, varies exponentially with the elevation with the evanescent wave decay length, β^{-1} . The decay length is on the order of 100 nanometers, which translates into a separation distance resolution on the order of 1 nanometer.

The energy is measured by tracking the particle motion. The changes in particle elevation are measured using the evanescent wave. A large number of elevations are recorded over time and used to construct a probability density function of the particle residing at any elevation above the surface. The probability density function is related to the particle potential energy using a Boltzmann distribution according to

$$p(h) = Ae^{\left(\frac{-\phi(h)}{k_b T}\right)} \quad (1)$$

where $p(h)$ is the probability density function of heights, $\phi(h)$ is the interaction potential energy, and A is a normalization constant. Optical tweezers are also employed for solution changes and to bias the heights the particle samples to better elucidate different regions of the potential energy diagram.

A range of phenomena have been examined using TIRM including the diffusion of a particle near an interface, depletion force that arise from particles or polymers, retarded van der Waals-Casimir-Lifshitz forces, steric forces and electrical double layer forces¹.

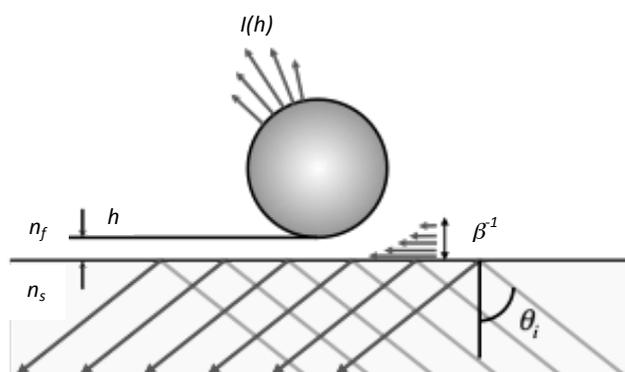


Fig. 1. A schematic of the TIRM showing a particle scatter the light from an evanescent wave generated at the solid liquid interface

References:

- [1] D. C. Prieve, F. Luo and F. Lanni, *Faraday Discussions of the Chemical Society*, 1987, **83**, 297-307.
- [2] D. C. Prieve, *Advances in Colloid and Interface Science*, 1999, **82**, 93-125.

Summary provided by Raymond Dagastine

Vibrational Sum Frequency Spectroscopy (VSFS)

Vibrational Sum Frequency Spectroscopy (VSFS) is a nonlinear optical technique used to study the details of molecular structure and dynamics at surfaces and interfaces. The extremely high surface selectivity of the VSFS process allows the thin layer of a few atoms or molecules near the interface to be probed. The surface selectivity is due to even-order nonlinear processes such as VSFS being forbidden, in the electric dipole approximation in media with inversion symmetry, e.g. gases, liquids, and isotopic solids. At an interface between two such media, the inversion symmetry is broken, and the VSFS optical signal can be generated and detected.

The VSFS technique involves two laser beams, a fixed visible beam and a tunable infrared beam, which are overlapped in space and time on the sample surface. A third beam is generated due to nonlinear effects, which carries information about the interfacial molecules. The intensity of this laser beam is proportional to the intensities of the incoming beams I_{IR} and I_{Vis} and the square of the

nonlinear susceptibility $\chi^{(2)}$, $I_{SFG} \propto \left| \chi_{eff}^{(2)} \right|^2 I_{IR} I_{Vis}$.

An important aspect of VSFS is its ability to directly measure the orientation of molecules and even fragments of molecules (e.g. methyl groups, carbonyl groups, etc.) at the surface. This is achieved by performing the measurement with different polarizations of the two incoming beams, and the generated sum frequency beam.

Summary provided by Deborah Wakeham

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