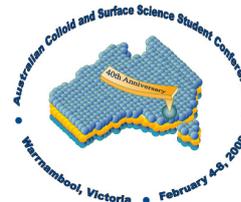


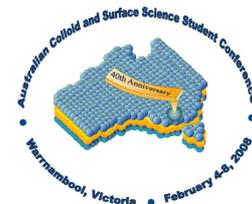
# Program and Abstracts

# Contents



<b>Foreword .....</b>	<b>3</b>
<b>Preface .....</b>	<b>4</b>
<b>Campus Map and Additional Information .....</b>	<b>5</b>
<b>Sponsors.....</b>	<b>6</b>
<b>Previous Conferences .....</b>	<b>7</b>
<b>List of Participants .....</b>	<b>8</b>
<b>Scientific Program.....</b>	<b>10</b>
<b>Conference Awards .....</b>	<b>16</b>
<b>Abstract: CSIRO Plenary Lecture, Prof. Hans-Jürgen Butt.....</b>	<b>17</b>
<b>Abstracts: Oral Presentations .....</b>	<b>18</b>
<b>Poster Index .....</b>	<b>57</b>
<b>Abstracts: Poster Presentations .....</b>	<b>60</b>
<b>Experimental Techniques .....</b>	<b>90</b>
<b>Index of Presenters.....</b>	<b>101</b>

# Foreword



*Roger Horn*

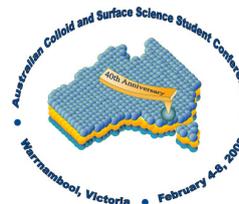
This is the Greatest Little Conference on Earth. Seriously, it is. Some of us older folk are habitual conference animals who swan off to meetings all around the world as often as time and money will allow. And speaking on their behalf, I can confidently assure you that the Australian Colloid and Surface Science Student Conference is the greatest of them all. Obviously not in size, but definitely in value.

How can we justify such a claim? There are several reasons:

1. The quality of talks and posters is outstanding. Naively one might think that experienced researchers would give better presentations than “raw” PhD students, but it is not true. The truth is that students give much better talks because they are closer to the work (especially experimental data and analysis) than established researchers who are often distracted by other duties; and because they (students) spend more time preparing their slides or posters; work harder on getting the presentation right, especially with timing; and actually rehearse carefully.
2. The ambiance in the scientific sessions – especially at question time – is special! Continually informative (both for the audience and for the speaker), entertaining, funny, educational, irreverent, and deadly serious. Not to be missed.
3. The scientific discussion does not end when the sessions end. Attendees often pick up new scientific ideas or knowledge in conversations over tea and coffee, or a meal, or a social event (which might possibly include beer and wine). Don’t forget to keep your ears open while you drink and eat.
4. Students meet other students and benefit from the “group therapy” – you discover you are not the only one who has problems with non-functioning equipment, inexplicable data, and absent supervisors. Some of your peers might have useful tips on how to deal with the trials and tribulations of doing a PhD, research Masters or Honours degree.
5. Outside of the scientific sessions the social activities are a blast. Where else would you find a week-long party, all in the line of duty and all paid for by someone else? But you have to join in, or half the value of the conference will be lost.
6. Thanks to the previous items 5, 4, 3, 2 and 1 (in no particular order) you will meet a lot of people who are all different but who all have a lot in common. Try to meet as many of them as you can, and some of them will become your lifelong friends. That’s a pretty valuable commodity to acquire.
7. The long and storied history of the ACSSSC is proof of how successful these conferences are. Australia is widely known as one of the strongest nations in the world in colloid and surface science, and this is largely due to the important educative experience and the strong networks (see #6) developed by all those who have attended over the past 40 years. And we won’t stop now. Join in with enthusiasm and you will become part of our continuing strength in this field in the decades to come.

So there you have it – welcome to the Greatest Little Conference on Earth. Seize the opportunity to have fun and make new friends at the same time as you are learning a lot of new things about colloid and surface science. Enjoy it all!

# Preface



It has been 40 years since the inaugural Australian Colloid and Surface Chemistry Conference was held in Melbourne in 1967 to enable Bob Hunter's and Tom Healy's students to meet, exchange ideas and present their research in an informal environment, not to mention exposing them to robust questioning and constructive criticism! The collegial spirit within the colloid community today is in no small part due to the success of these early meetings.

The 26<sup>th</sup> Australian Colloid and Surface Science Student Conference is proudly hosted by the Victorian College of Pharmacy, Monash University. We have 74 students attending this conference, from as far afield as Japan, Sweden and Israel. Welcome to all students and we hope that you enjoy the academic and social activities that we have planned. A special welcome also to Prof. Hans-Jürgen Butt from Germany, and Prof. Brian Vincent from the UK for travelling all this way to attend our student conference, and thank you for agreeing to provide the Plenary and after-dinner talks respectively.

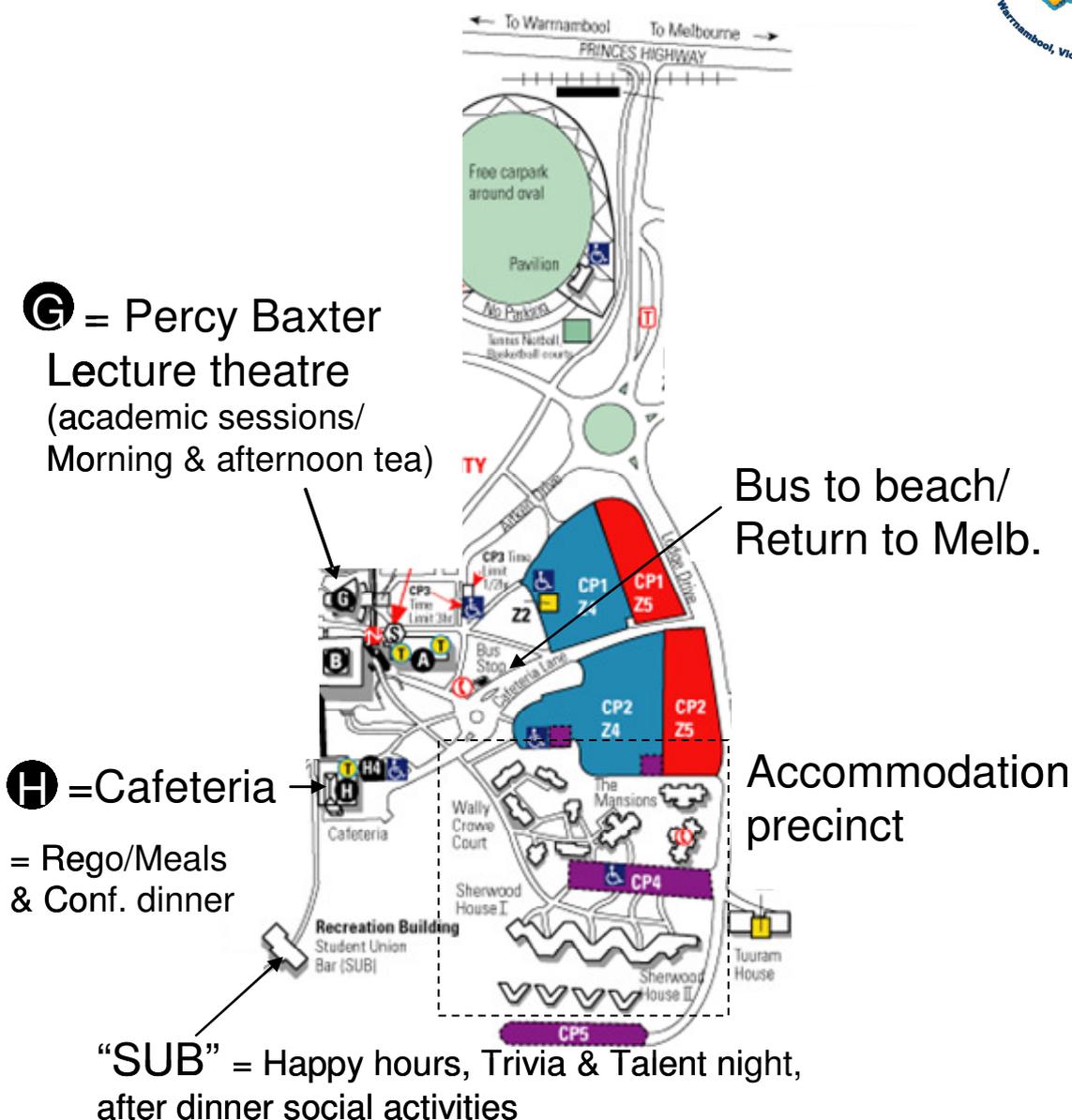
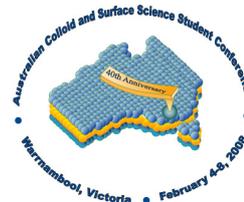
A big thank you to our sponsors! Without their generous support the affordable conference registration and aspects of the social activities would not be possible. Thank you also to the student committee for their fabulous assistance in putting together many aspects of the conference, in particular Luke Parkinson (Academic Program), Donna Menzies (Social Program), Tim Hunter (Accommodation and Venue), Charlie Dong (AV), Chris Honig (Merchandise) and Stephanie Wallace (Transport).

We hope that you find the Deakin University campus in Warrnambool a pleasant venue for the conference, please make full use of the Student Union Bar (the "SUB"), and enjoy meeting/catching up with the many colleagues from across Australia and around the world to gain full value from attending 'the Greatest Little Conference on Earth'!

Ben Boyd and Ian Larson

Conference Co-Chairs, 26<sup>th</sup> ACSSSC.

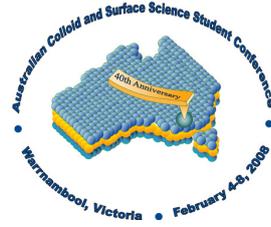
# Map and Additional Information



**Accommodation: Please note:** The rooms are fitted with extremely sensitive thermal fire alarms – smoking, incense, candles, excessive use of deodorant(!) can all trigger the alarms - be aware that the CFA must respond to triggered alarms \$1000/alarm. This charge **will** be passed on to those that trigger the alarm.

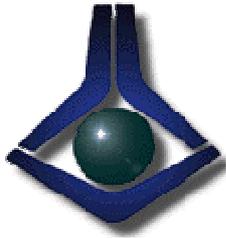
Your key will access the external doors of the unit and only your room. While this provides good security it also means that if your key is missing all external doors of the unit must be fitted with new locks and keys cut at a cost of approx. \$400. **DO NOT LOSE YOUR KEY!** Again this cost will be passed onto you if this occurs.

# Sponsors



The 26<sup>th</sup> Australian Colloid and Surface Science Student Conference Organising Committee would like to extend their sincere thanks for the generous support that the following sponsors have provided:

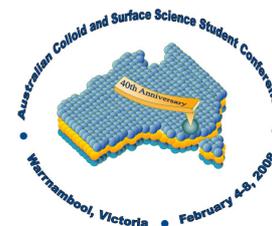
## PLATINUM SPONSORS



## GOLD SPONSORS

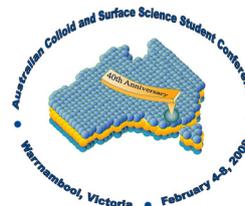


# Previous Conferences



<b>Year</b>	<b>Location</b>	<b>Total No Attendees</b>
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	Yarrawood	
1980	Kioloa	50
1982	Mt. Eliza	75
1983	Yarrawood	51
1985	Roseworthy	49
1987	Kioloa	55
1988	Albury	107
1990	Camden	
1991	Roseworthy	118
1993	Deakin Uni	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	Beechworth	135
2008	Warrnambool	126

# List of Participants



## Bragg Institute, ANSTO

Jamie Schulz

## Australian National University

Christine Henry

Shaun Howard

Vincent Craig

## CSIRO

Donna Menzies

Alan Chan

Anastasios Polyzos

Ben Muir

Peter Harbour

Mi Xu

Michelle Emin

## Latrobe University

Eben Quill

Lauren Sharp

James Hunter

John Wells

Mike Angove

## Monash University

Mandeep Jeswan Singh

Jayani Chandrapala

Benjamin Wong

Ian McKinnon

## Swinburne University of Technology

Natasa Mitik-Dineva

Russell Crawford

Elena Ivanova

## University of Bristol, UK

Brian Vincent

## University of Queensland

Kym Ford

## University of Newcastle

Jason Mann

Kurt Nicholson

Tim Hunter

John Tulloch

Andrew Stapleton

Deborah Wakeham

Erica Wanless

Rob Atkin

Grant Webber

## University of Otago, NZ

Jan Scholz

Luigi Petrone

## Victorian College of Pharmacy (Monash)

Charlie Dong

Aurelia Dong

Stephanie Wallace

Ben Boyd

Ian Larson

## University of Sydney

Bob Hunter

## Particulate Fluids Processing Centre-

## University of Melbourne

Stefanie Sham

William McMaster

Joannelle Bacus

Zubaidah Ningsih

Andrew Rapson

Anna Mularski

Emily Meyer

Ray Dagastine

Sawsan Freij

## Victoria University

Gayle Morris

**Ian Wark Research Institute (UniSA)**

Iliana Sedeva  
Luke Parkinson  
Nasrin Ghouchi Eskandar  
Terry Dermis  
Jairo Garnica  
Audrey Beaussart  
Robert Acres  
Mani Paneru  
Kai Ying Yeap  
Diana Tran  
Santanu Ray  
Mingzhao He  
Karyn Jarvis  
Sin Ying Tan  
Lorena del Castillo  
Srinivas Parimi  
Anuttam Patra  
Artem Borysenko  
Rossen Sedev  
Clive Prestidge  
Tim Barnes  
Daniel Fornasiero  
Vera Lockett  
David Beattie  
Dennis Palms  
John Ralston  
Jonas Addai-Mensah  
Marta Krasowska  
Mihail Popescu  
Renate Fetzer  
Roger Horn

**ACeSSS (UniSA)**

Jason Du

**The Hebrew University of Jerusalem**

Anna Kogan  
Shoshana Rozner

**Tohoku University**

Atsushi Kobayashi

**University of Adelaide**

Kristen Bremmell

**University of Melbourne**

Christopher Ochs  
Adam Brotchie  
Glenna Drisko  
Jenny Zuo  
Shashi Parcha  
Alisa Becker  
Hanna Whiteside  
Yuanhua He  
Scott Fraser  
Boon Teo  
John-Paul O'Shea  
Cameron Kinnane  
Nathan Nicholas  
Chris Honig  
Ofer Manor  
Josephine Lim  
Anat Kiviti-Manor  
Rudi Spehar  
Rory Anderson  
Woojoo Han  
Daan Curvers  
George Franks  
Michelle Gee  
Paul Mulvaney  
Steven Carnie  
Tom Healy  
Franz Grieser  
Haihong Li (AMSRI)

**Royal Melbourne Institute of Technology**

Vincent Martinez

**Max Planck Institute, Mainz, Germany**

Hans-Jürgen Butt

**Stockholm University**

Linnéa Andersson

**RLA**

Drew Evans

**KTH, Stockholm, Sweden**

Mark Rutland

# Scientific Program

	4/2/08	5/2/08	6/2/08	7/2/08	8/2/08
07:00 -8:30	8-9 Breakfast for o'night stays only	<b>Breakfast in caf</b>	<b>Breakfast in caf</b>	<b>Breakfast in caf</b>	<b>8-9:30 Breakfast in caf</b>
9:00	Registration In caf 9am-2pm	Mani Paneru	Talent night prep	Glenna Drisko	
9:20		Tim Hunter		Jianhua Du	
9:40		Jairo Garnica		Boon Teo	
10:00		Christine Henry		Natasa Mitik-Dineva	
10:20		<b>Morning Tea</b> (posters mounted at SUB)	<b>Morning Tea</b>	<b>Morning Tea</b>	
10:50		Luke Parkinson	Linnéa Andersson	Shoshana Rozner	
11:10		Anna Kogan	Charlie Dong	Jayani Chandrapala	
11:30		Santanu Ray	Karyn Jarvis	Chris Honig	
11:50		Adam Brotchie	Luigi Petrone	Mingzhao He	
12:10		Shyamal Das	Audrey Beaussart	Anat Kiviti-Manor	
12:30	<b>Lunch (in caf)</b>	<b>Lunch (in SUB for posters)</b>	<b>Lunch (in caf)</b>	<b>Lunch (in caf)</b>	
2:00	Welcome	Diana tran	Staff-Student Beach Cricket (Bus transport provided)	John-Paul O'Shea	
2:20	Plenary lecture Hans Jurgen-Butt	Shaun Howard		Srinivas Parimi	
2:40		Shashi Parcha		Donna Menzies	
3:00		Iliana Sedeva		Nasrin Ghouchi-Eskandar	
3:20	<b>Afternoon Tea</b>	<b>Afternoon Tea(in SUB for posters)</b>			<b>Afternoon Tea</b> (RACI CSS divisional meeting)
4:00	Joannelle Bacus	Poster session		Yuanhua He	
4:20	Robert Acres		Jan Scholz		
4:40	Vincent Martinez		Alisa Becker		
5:00	Anuttam Patra		William McMaster		
5:20	Free time/ Happy Hour	Free time	Free Time/ Happy Hour	Free Time/ Happy Hour	
6:00					
6:30	BBQ	Dinner Asian theme	Dinner Italian theme	Conference Dinner 6.00-10.30	
8.30	SUB	Quiz Night - SUB	'Talent' Night	SUB	
1 am	SUB closes	SUB closes	SUB closes	SUB closes	

## Monday 4/2/08

<b>2:00pm</b>	<b>WELCOME</b>	<b>Luke Parkinson</b>
<b>2:20-3:20pm</b>	<b>CSIRO Plenary Lecture Prof. Hans-Jürgen Butt</b>	<b>Chair: Patrick Hartley</b>
<b>4:00-5:20pm</b>	<b>Oral Presentations</b>	<b>Chair: Luke Parkinson Co-chair: Patrick Hartley</b>
4:00pm	Profiling the Drainage of a Thin Film Between a Deformable Liquid Droplet and a Solid Surface using Imaging Ellipsometry ..... <i>abstract on page</i> 18 <u>Joannelle Bacus</u> , Michelle Gee and Geoff Stevens	
4:20pm	Combining Laboratory and Synchrotron Based Techniques in the Study of Mineral Surface Heterogeneity ..... 19 <u>Robert Acres</u> , Sarah Harmer and David Beattie	
4:40pm	Dynamics of Colloidal Hard Sphere Suspensions ..... 20 <u>Vincent Martinez</u> , Gary Bryant and Willian van Egen	
5:00pm	Design of Photoresponsive Surfaces ..... 21 <u>Anuttam Patra</u> , John Ralston and Rossen Sedev	
<b>6:30pm</b>	<b>BBQ</b>	

---

## Tuesday 5/2/08

<b>9:00-10:20am</b>	<b>Oral Presentations</b>	<b>Chair: Ian Larson</b>
9:00am	Electrowetting in Solid/Liquid/Liquid Systems ..... 22 <u>Mani Nath Paneru</u> , Craig Priest, Rossen Sedev and John Ralston	
9:20am	Influence of Esterified Coating Agents on the Foamability of Nano-Silica ..... 23 <u>Tim Hunter</u> , Graeme Jameson and Erica Wanless	
9:40am	Metallic Superhydrophobic Surfaces ..... 24 <u>Jairo Garnica</u> , Rossen Sedev, Daniel Fornasiero and John Ralston	
10:00am	Apparent Hydrodynamic Boundary Slip on Rough Surfaces and its Dependence on AFM Cantilever Geometry ..... 25 <u>Christine Henry</u> , Chris Honig, William Ducker and Vincent Craig	

**10:50am-12:30pm Oral Presentations****Chair: Anuttam Patra  
Co-chair: Ian Larson**

10:50am	Film Drainage and Disjoining Force between Bubbles and Planar Glass, and Titania Surfaces .....	26
	<u>Luke Parkinson</u> , Rossen Sedev, Daniel Fornasiero and John Ralston	
11:10am	Nonionic Microemulsion as Nano-Reservoirs for Controlled Crystallisation of the Non-Soluble Drug .....	27
	<u>Anna Kogan</u> , Inna Popov, Vladimir Uvarov, Shmuel Cohen, Abraham Aserin and Nissim Garti	
11:30am	Relating Wetting Dynamics to the Work of Adhesion on a Chemically Heterogenous Surface .....	28
	<u>Santanu Ray</u> , Rossen Sedev, Craig Priest and John Ralston	
11:50am	Sonochemistry and Sonoluminescence under Dual-Frequency Conditions .....	29
	<u>Adam Brotchie</u> , Muthupandian Ashokkumar and Franz Grieser	
12:10pm	Salmeterol Xinafoate powders for Inhalation – Performance and Related Factors during Long Term Storage at Different Environmental RH .....	30
	<u>Shyamal Das</u> , Ian Larson, P. Young and P. Stewart	

**2:00-3:20pm Oral Presentations****Chair: Erica Wanless**

2:00pm	Novel Fine Particle Separation – Particles at the Air-Water Interface .....	31
	<u>Diana Tran</u> , Catherine Whitby, Daniel Fornasiero and John Ralston	
2:20pm	Study of Adsorption Kinetics Using Optical Reflectometer with Improved Sensitivity and Stability .....	32
	<u>Shaun Howard</u> and Vincent Craig	
2:40pm	Measuring the Mechanical Properties of Cardiac Cells by AFM .....	33
	<u>Shashikanth Parcha</u>	
3:00pm	Influence of a Polymer Depressant on the Wettability of Model Surfaces .....	34
	<u>Iliana Sedeva</u> , Daniel Fornasiero, John Ralston and David Beattie	

**4:00-6:00pm****CSIRO POSTER SESSION**  
*see pages 57-89 for index and poster abstracts***6:30-8:30pm****DINNER**  
*Asian Theme***8:30pm****QUIZ NIGHT**  
**SUB**

## Wednesday 6/2/08

9:00-10:20am

**Talent Night Preparation Time**

10:50am-12:30pm **Oral Presentations**

**Chair: Joannelle Bacus  
Co-chair: Erica Wanless**

- 10:50am Expandable Microspheres as a Novel Pore Former in Alumina Gel Casting: Surface Features, Behaviour and Interactions..... 35  
Linnéa Andersson and Lennart Bergström
- 11:10am Adsorption and Interaction of Loaded Liquid Crystalline Particles at Surfaces..... 36  
Yao-Da Dong, Ian Larson and Ben Boyd
- 11:30am The Interfacial Chemistry and Structure of Porous Silicon: Towards Drug Delivery Applications ..... 37  
Karyn Jarvis, Timothy Barnes and Clive Prestidge
- 11:50am Mussel Larvae Adhesion: Unravelling Mechanism and Functional Groups Using ATR-IR Spectroscopy ..... 38  
Luigi Petrone, Norman Ragg and James McQuillan
- 12:10pm AFM Investigation of Adsorbed Polymer Morphology on Hydrophobic Mineral Surfaces ..... 39  
Audrey Beaussart, Agnieszka Mierczynska-Vasilev, Kristen Bremmel and David Beattie

12:30-1:15pm

**LUNCH**

1:30pm

*Bus pick-up for transport to beach*

2:00-5:00pm

**STAFF-STUDENT BEACH CRICKET**  
*Bus departs beach for campus at 5:00pm*

7:00pm-8:30pm

**DINNER**  
*Italian theme*

8:30pm-

**CSIRO TALENT NIGHT - SUB**

## Thursday 7/2/08

### 9:00-10:20am Oral Presentations

Chair: Rob Atkin

9:00am	Metal Oxide Polyelectrolyte Composites for the Adsorption of Metals ..... 40 <u>Glenna Drisko</u> , Patricia Sklavakis, Vittorio Luca and Rachel Caruso
9:20am	Control of Clay Aggregate Structure, Settling and Dewatering ..... 41 <u>Jianhua Du</u> , Rada Pushkarova and Roger Smart
9:40am	Ultrasonic Latex Particle Synthesis ..... 42 <u>Boon Teo</u> , Muthupandian Ashokkumar and Franz Grieser
10:00am	<i>V. Fischeri</i> and <i>E. Coli</i> Adhesion Tendencies Towards Photolithographically Modified Nano-Smooth Poly( <i>tert</i> -butyl methacrylate) Polymer Surfaces ..... 43 <u>Natasa Mitik-Dineva</u> , Radu Codrin Monasca, Sarah Murphy, Elena Ivanova and Russell Crawford

### 10:50am-12:30pm Oral Presentations

Chair: Charlie Dong

Co-chair: Rob Atkin

10:50am	Competitive Solubilisation of Cholesterol and Phytosterols within Nonionic Dilutable Microemulsion System ..... 44 <u>Shoshana Rozner</u> , Abraham Aserin, Ellen Wachtel, Nissim Garti
11:10am	A New Biophysical Approach to Understanding Self-Assembly of Dairy Proteins ..... 45 <u>Jayani Chandrapala</u> , Ian McKinnon, Maryann Augustin, Punsandi Udabage
11:30am	Lubrication Forces on Colloidal Particles ..... 46 <u>Christopher Honig</u> and William Ducker
11.50am	Polymeric Dispersant Mediated Behaviour of Sericite-Chalcocite Particle Interactions ..... 47 <u>Mingzhao He</u> , David Beattie and Jonas Addai-Mensah
12:10pm	Thickener Dewatering Optimisation ..... 48 <u>Anat Kiviti-Manor</u> , Shane Usher and Peter Scales

**2:00-3:20pm Oral Presentations****Chair: Shashikanth Parcha**  
**Co-chair: Ben Boyd**

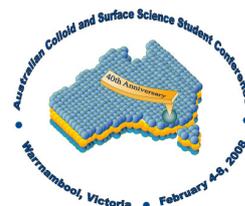
- 2:00pm Temperature Mediated Adsorption of Poly(N-isopropyl acrylamide) Derivative Polymers onto Silica and  $\alpha$ -Alumina ..... 49  
John-Paul O'Shea, Haihong Li, Luke Connal, Greg Qiao and George Franks
- 2:20pm PAMAM Dendrimer Interactions with Supported Lipid Bilayers ..... 50  
Srinivas Parimi, Timothy Barnes and Clive Prestidge
- 2:40pm Investigating the Protein Repellent Nature of Biomedical Plasma Polymer Thin Films ..... 51  
Donna Menzies, John Forsythe, Patrick Hartley, Thomas Gengenbach, Celesta Fong and Ben Muir
- 3:00pm Interfacial Characterisation and Stability of Nanoparticle-Encapsulated Emulsions as Potential Drug Delivery Systems for Model Lipophilic Agents ..... 52  
Nasrin Eskandar, Spomenka Simonovic and Clive Prestidge

**4:00-5:20pm Oral Presentations****Chair: Ben Boyd**

- 4:00pm Sonophotocatalytic Degradation of Methyl Orange in Aqueous Solutions ..... 53  
Yuanhua He, Muthupandian Ashokkumar and Franz Grieser
- 4:20pm Competitive Adsorption of Carbonate and Sulphate by *in situ* IR Analysis ..... 54  
Jan Scholz and James McQuillan
- 4:40pm Biomolecule Encapsulation within Degradable Polymeric Microcapsules ..... 55  
Alisa Becker, Alexander Zelikin, Angus Johnston, Fabio Turatti, Kim Wark and Frank Caruso
- 5:00pm Synthetic Bone Substitutes ..... 56  
William McMaster and Frank Caruso

**CLOSING REMARKS****6:00-10:30pm****CONFERENCE DINNER**  
*Sponsored by SCIENTIFIC SOLUTIONS*

# Conference Awards



## Healy-Hunter Award



The most outstanding oral presentation will be awarded the Healy-Hunter Award. This award is a prize of a \$1500 travel grant and is voted by the staff.

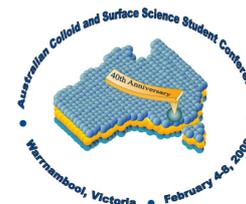
## Best Poster Award

The most outstanding poster presentation will be awarded the Best Poster Award. This award is a prize of \$300 cash and is voted by the staff.

## The Most Probing Question and the Most Memorable Moment Awards

As part of the tradition, there will be a presentation of specially designed trophies for both the Most Memorable 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!

# CSIRO Plenary Lecture



## Capillary forces: Influence of roughness and heterogeneity

**Prof. Hans-Jürgen Butt**

*Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*

*butt@mpip-mainz.mpg.de, Fax: +49-6131-379-310, Phone: +49-6131-379-111*

The interaction between hydrophilic surfaces or particles in air is often dominated by capillary forces. In this case capillary forces are caused by liquid menisci forming in the gap between the surfaces by capillary condensation. Significant progress has been made during the last decade in understanding capillary forces. In particular the influence of surface roughness is now better understood. After giving an introduction into the subject recent results are presented.

To analyse capillary forces we measured the adhesion forces between atomic force microscope (AFM) tips or particles attached to AFM cantilevers and different solid samples. Humidity was adjusted relatively fast to minimize tip wear during one experiment. It is demonstrated that the results can be interpreted with simple continuum theory of the meniscus force. The capillary force between two fine particles or between the AFM tip and a sample depends on the precise geometry of the contact region on the 1 nm length scale. We demonstrate that vice versa from a measurement of the adhesion force versus humidity one can calculate the shape of the AFM tip. Finally, a simple, approximate formalism is described to calculate capillary forces between solid surfaces analytically.

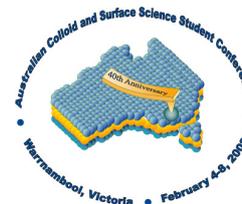
Farshchi-Tabrizi, M., M. Kappl, Y. Cheng, J. Gutmann & H.-J. Butt: On the adhesion between fine particles and nanocontacts: An atomic force microscope study. *Langmuir* **2006**, 22, 2171-2184.

Butt, H.-J., M. Farshchi-Tabrizi, M. Kappl: Using capillary forces to determine the geometry of nanocontacts. *J. Appl. Phys.* **2006**, 100, 024312.

Butt, H.-J.: Capillary forces: Influence of roughness and heterogeneity. *Langmuir* **2008**, submitted.

# Abstracts

## Oral Presentations



### **Profiling the drainage of a thin film between a deformable liquid droplet and a solid surface using imaging ellipsometry**

Joannelle Bacus, Michelle Gee, Geoff Stevens

*Particulate Fluids Processing Centre, School of Chemistry  
Department of Chemical and Biomolecular Engineering  
The University of Melbourne, VIC 3010, Australia*

*bacusj@unimelb.edu.au*

The phenomena that occur during film drainage are of importance to numerous processes in which control of emulsion stability is a critical element. In particular, the drainage of thin liquid films between droplets dispersed in a continuous phase and between solid surfaces and droplets are of interest when studying the factors governing the stability of these dynamic systems.

Thin films between a solid surface and a liquid droplet have been the focus of these studies. Imaging ellipsometry is used to observe the thin aqueous film formed when an oil droplet in an aqueous continuous phase approaches a solid silica surface. Changes in the film profile throughout the drainage process, and hence, the factors which contribute to film drainage can be studied from time-resolved measurements of the thin film.

In previous studies of solid/liquid systems, the liquid droplet is usually attached to its dispensing capillary such that the dynamics of the droplet and the film drainage are affected. Recent studies have therefore focused on developing experimental techniques to allow for a droplet which is freely dispersed in the continuous phase to be studied.

# Combining Laboratory and Synchrotron Based Techniques in the Study of Mineral Surface Heterogeneity

Robert Acres, Sarah Harmer and David Beattie

*Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA, 5095*

*Robert.Acres@postgrads.unisa.edu.au*

Mineral sulphides, as with all materials, interact with their environment by way of their surface and it is the properties of the surface which determine how these interactions proceed. The surfaces of minerals are inherently heterogeneous and these heterogeneities may take many forms such as inclusions of other minerals, differing oxidation products, physical defects and changes in stoichiometry. Mineral sulphides are separated from other mined ores by the flotation process and the heterogeneity of their surfaces impacts upon their flotation recovery and processing. Hydrophobicity is the key property influencing flotation response and it is highly dependent on surface composition. In this study, synchrotron Scanning Photoelectron Microscopy<sup>1</sup> (SPEM), laboratory X-ray Photoelectron Spectroscopy (XPS) and surface morphology measurements with Atomic Force Microscopy (AFM) have been used to spectroscopically and physically probe oxidised surfaces of chalcopyrite. Polished samples of Chalcopyrite ( $\text{CuFeS}_2$ ) were exposed to 0.1 M  $\text{KNO}_3$  solutions of pH 4 for up to 1 hour in order to encourage surface oxidation. AFM images of these surfaces showed the evolution of growth features in the range of 100 nm up to  $\sim 1 \mu\text{m}$  in size. These features presented primarily along scratches and defects, proceeding to form clusters. SPEM imaging of oxidised chalcopyrite surfaces was conducted at the National Synchrotron Radiation Research Centre (NSRRC), Taiwan. SPEM chemical maps of a  $20 \times 20 \mu\text{m}$  area show regions of lower sulphur and higher copper and oxygen concentration relative to the surrounding higher sulphur region. Point spectra have been taken from each region. Summed images of all channels during imaging provide a general indication of topography.

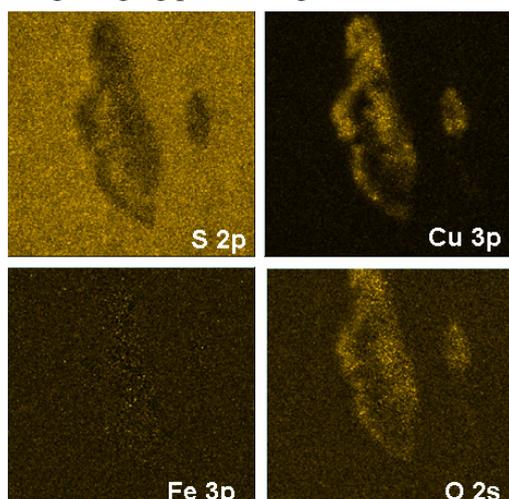


Figure 1: SPEM images of oxidised  $\text{CuFeS}_2$

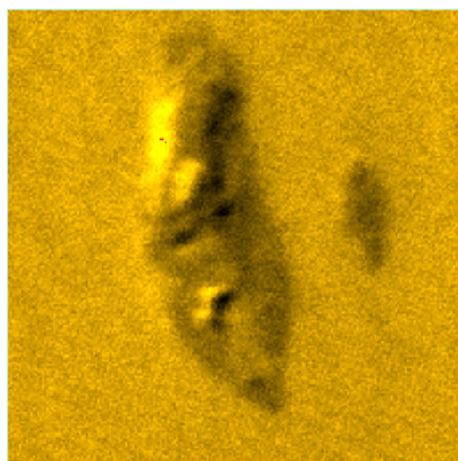


Figure 2: Summed S 2p SPEM images of oxidised  $\text{CuFeS}_2$

<sup>1</sup> R. Klauser, C. H. Chen, M. L. Huang, et al., Journal of Electron Spectroscopy and Related Phenomena **144-147**, 393 (2005).

## Dynamics of Colloidal Hard Sphere Suspensions.

Vincent Martinez, Gary Bryant, Willian van Megen

*Department of Applied Physics, Royal Melbourne Institute of Technology, Melbourne, Victoria 3000, Australia.*

*Vincent.Martinez@student.rmit.edu.au*

Suspensions of colloidal hard sphere particles exhibit both fluid-to-crystalline and fluid-to-glass transitions. Colloidal particles are larger than atoms by several orders of magnitude, so phase transitions occur on much slower time scales, making it possible to measure the dynamics of phase transitions in real time. Colloidal hard spheres begin to crystallize at volume fractions above 0.494. Above 0.545 the entire sample will crystallize. Between these two volume fractions, the equilibrium state is a two-phase fluid-crystal co-existence. Samples above  $\sim 0.57$  do not crystallize, but rather form a glass. Above this critical volume fraction, the particles can no longer move freely through the sample and the system is “arrested” in an amorphous state. Such a system is named a colloidal glass. Because the mobility of the particles is severely reduced, these systems are “frozen” in configurations, which are far from thermodynamic equilibrium and therefore exhibit very slow dynamics.

Colloid hard spheres have been extensively used for the last two decades as a simple experimental system for investigating fundamental mechanisms of freezing and the glass transition, with relevance to phase transitions in atoms, small molecules and polymeric materials. Such systems are also of a great interest for potential industrial applications – slow dynamics in colloidal systems are important in a range of systems including gels, pastes, blood and foams. In addition colloidal crystals are desirable as templates for protein crystallization, photonic devices, and other ordered system. However, the lack of a fundamental understanding of these phenomena means that the development of new materials with the desired properties is often performed on an ad hoc basis.

The aim of this research is to resolve fundamental issues in our understanding of freezing and glass transitions by systematically studying the dynamics of colloidal hard sphere suspensions in their metastable state as functions of volume fraction  $\phi$  and scattering wave vector  $q$ . We used several Dynamic Light Scattering techniques to characterize the dynamics of colloidal hard sphere suspensions, consisting of PHSA-grafted PMMA in cis-decalin with a radius of 200 nm. Improved data and analysis allow for the extraction of parameters which can be used to better understand the behaviour of metastable fluids, and may lead to a deeper understanding of crystallisation and glass transition.

In this talk I will present our recent results, and discuss their implications for understanding crystallization and the glass transition.

## Design of Photoresponsive Surfaces

Anuttam Patra, John Ralston and Rossen Sedev

*Ian Wark Research Institute, University of South Australia  
Mawson Lakes, SA 5095*

*Anuttam.Patra@postgrads.unisa.edu.au*

Pyrimidine molecules dimerise on exposing to UV radiation of wavelength 280 nm; the reverse reaction occurs when the dimer is irradiated with light of wavelength 240 nm. The process is reversible over a number of cycles. Pyrimidine molecules were attached to surfaces with long alkyl chains terminated with methyl (non-polar) or thiol (polar) groups. The molecules were used to dip-coat flat quartz surfaces. The thiol terminated molecules were grafted on flat gold surfaces as self-assembled monolayers. Surface dimerisation was carried out reversibly. The progress of the reaction was monitored with UV & FTIR spectroscopy. The changes in the surface structure reflected in the surface energy and were followed with contact angle measurements. The pyrimidine groups, chain length, chain structure and metal surfaces were varied and it was found that uracil head groups, flexible alkyl chains and gold surfaces are best for surface dimerisation. These surfaces may have applications in switching devices, photoresists, computer data storage, molecular recognition, etc.

## Electrowetting in Solid/Liquid/Liquid Systems

Mani Nath Paneru, Craig Priest, Rossen Sedev, and John Ralston

*Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus,  
Mawson Lakes, Adelaide, SA 5095, Australia*

*Mani.Paneru@postgrads.unisa.edu.au*

We have compared the electrowetting behaviour of an aqueous salt solution and an ionic liquid in an ambient phase of hexadecane. Our aim was to investigate some fundamental aspects of electrowetting - maximum contact angle change, contact angle saturation and reversibility of operation.

The surface electrode was a layer of indium tin oxide which was electrically insulated from the droplet by a layer of an amorphous fluoropolymer (Teflon AF1600). The cell was filled with hexadecane and a conducting droplet (0.1 M aqueous KCl or BMIM.BF<sub>4</sub>) was deposited on the insulated electrode. A platinum wire was used to electrically contact the droplets and apply an external voltage. Contact angles were measured using the sessile drop and capacitance techniques.

Using DC potential, Contact angle changes in excess of 100° could be achieved and the reversibility was very good for both water and ionic liquid. The saturation contact angle appeared to be independent of the type of conducting liquid. Similar electrowetting curves were obtained with AC voltage. However, contact angle saturation for BMIM.BF<sub>4</sub> was significantly reduced and the reversibility was also excellent.

The large contact angle changes observed in liquid/liquid systems together with their reversibility and predictability may be well suited for several applications. Our results are also significant for elucidating the mechanism of contact angle saturation.

## **Influence of Esterified Coating Agents on the Foamability of Nano-Silica**

Timothy Hunter<sup>a</sup>, Graeme Jameson<sup>a</sup> & Erica Wanless<sup>b</sup>

<sup>a</sup> *Centre for Multiphase Processes & <sup>b</sup> Department of Chemistry – The University of Newcastle, Callaghan, N.S.W, 2308 Australia.*

*Timothy.hunter@studentmail.newcastle.edu.au*

The use of nanoparticles as stabilisers in foams and emulsions has gained great attention in recent years, and is a subject of interest for many scientific and industrial fields; such as food colloids, cosmetics, novel ceramics, metal foams and mineral flotation. The particular use of nanosized particles to stabilise, say, an aqueous foam, is based on very different mechanisms to traditional detergents and much work has still to be done in defining what characteristics give rise to optimum foamability. While classic surfactants stabilise foams by reducing the air-water surface tension, particles act as steric stabilisers, creating physical barriers to bubble coalescence and drainage. Hence characteristics such as particle size, concentration, network structures and hydrophobicity are critical in determining their interactions in particular situations.

Work was conducted with 300nm silica nanoparticles, and focused on the effects of changing concentration and hydrophobicity on network formation and foamability. The hydrophobicity of particles was altered via esterification of different long chain alcohols (butanol, octanol & dodecanol) to the silica surface. Langmuir-Blodgett trough deposition and SEM images were used to characterise the two dimensional network formations, as a way to describe their possible structures at foam interfaces. Dynamic Bickerman column and static shake tests were used to analyse the foam behaviour, and turbidity measurements helped determine particle partitioning between the bulk and foam phases.

Particles of moderate hydrophobicity (octanol esterified) gave the best foamability, which correlates well to the theory of particle stability; taking into consideration both the interfacial detachment energy of particles and effects on the lamellar interfilm (such as capillary pressure). There were also some interesting differences between dynamic and static foam behaviour observed for butanol and dodecanol esterified particles.

## Metallic Superhydrophobic Surfaces

Jairo Garnica, Rossen Sedev, Daniel Fornasiero, and John Ralston

*Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095*

*garji001@students.unisa.edu.au*

It is well known that on hydrophobic surfaces, if suitably rough, water can display contact angles larger than 150-160°. Strictly speaking, superhydrophobic surfaces are those on which the contact angles are very large and the contact angle hysteresis is very low. Because of the roughness the liquid contacts only the highest points on the surface, *i.e.* pockets of air are trapped under the wetting liquid (the so called “Cassie state”). The average adhesion is very low and superhydrophobic materials are of significant interest in diverse applications: surface protection, low-friction systems and microfluidics. Their use, however, is often limited due to complex fabrication and fragility of the surface features.

We have developed a simple protocol for producing superhydrophobic surfaces with improved structural resistance and durability. The surface of metals and alloys were chemically etched to induce an appropriate surface roughness, and then chemically modified with a self-assembled monolayer of an alkane thiol, to reduce the intrinsic surface wettability. Our superhydrophobic surfaces display water contact angles of about 165° and, at the same time, a hysteresis lower than 2°.



Metallographic analysis showed a strong influence of the chemical composition and grain distribution on the topography developed during etching. Etching conditions were manipulated to achieve the surface roughness required for superhydrophobic behaviour. Scanning electron microscopy and laser profilometry were used to characterise the topography of the solid surface.

# Apparent Hydrodynamic Boundary Slip on Rough Surfaces and its dependence on AFM Cantilever Geometry

C.L. Henry,<sup>1</sup> C. Honig,<sup>2</sup> W.A. Ducker<sup>2</sup> and V.S.J. Craig<sup>1</sup>

<sup>1</sup>*Department of Applied Maths  
Research School of Physical Sciences and Engineering  
ANU ACT 0200*

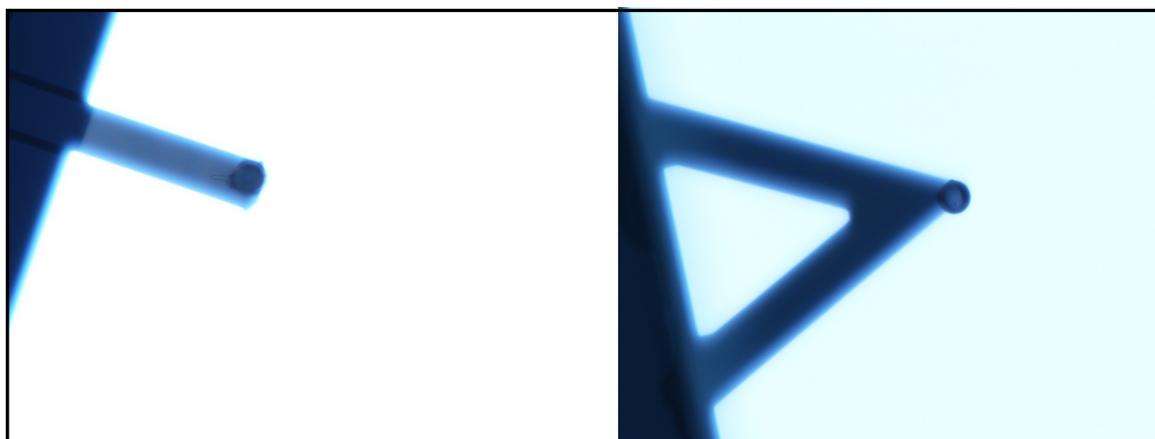
<sup>2</sup>*Department of Chemical and Biomolecular Engineering  
University of Melbourne  
Victoria 3010*

*christine.henry@anu.edu.au*

The drainage force originating from squeeze flow between a 10-micron radius sphere and a flat surface is measured using the technique of Atomic Force Microscopy (AFM). These measurements can be used to explore the boundary condition for the flow of a Newtonian fluid near a hard wall. A partial slip boundary condition has been hypothesised for Newtonian fluids such as water. This has been the subject of considerable controversy.

We investigated the effect of surface roughness on hydrodynamic boundary slip. The apparent degree of slip depends upon the cantilever geometry used in the AFM. V-shaped cantilevers show a larger degree of slip (lower repulsive force) than do rectangular or beam cantilevers in the same conditions. This finding suggests that 'slip' is not in this system a true observation of the movement of the confined fluid.

I will also discuss hypotheses concerning the causes of cantilever-dependence, and its possible implications for other systems.



**Figure 1.**  
**Rectangular and**  
**V-shaped AFM**  
**cantilever colloid**  
**probes**

## Film drainage and disjoining force between bubbles and planar glass, and titania surfaces.

Luke Parkinson, Rossen Sedev, Daniel Fornasiero and John Ralston

*Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes Boulevard,  
Mawson Lakes 5095, Australia,*

*Luke.Parkinson@postgrads.unisa.edu.au*

The approach of a gas bubble and a hydrophilic, charged surface in an aqueous electrolyte, is influenced by hydrodynamic as well as surface forces. Repulsive electrostatic and van der Waals dispersion forces attenuate the rate of drainage from the intervening liquid film, and determine the final equilibrium film thickness ( $h_{\text{equil}}$ ). Very small bubbles are ideal for making such measurements as their small buoyancy, combined with their high Laplace pressure, minimises deformation.

This study uses high-speed, dynamic, thin-film interferometry, to measure film drainage and  $h_{\text{equil}}$  as a function of buoyancy force. Very small air bubbles were formed in the range 20  $\mu\text{m}$ -120  $\mu\text{m}$ . These bubbles were allowed to rise freely, before colliding with a clean, planar, transparent glass or  $\text{TiO}_2$  surface, in aqueous  $10^{-2}$  M, and  $10^{-4}$  M KCl at various pH values. Recording the collision process by high-speed video microscopy at 1000 frames per second, through a 550 nm monochromatic filter enabled determination of the film thickness. Film drainage was fastest for larger bubbles due to their larger buoyancy force. The equilibrium film thicknesses were greatest for both  $\text{TiO}_2$  and glass surfaces at pH 8.0, and  $10^{-4}$  M KCl. Increasing ionic strength to  $10^{-2}$  M caused a reduction in equilibrium film thickness. At pH 3.5, in  $10^{-4}$  M KCl (ionic strength,  $10^{-3.4}$  M), streaming potential measurements indicate a positive zeta ( $\zeta$ ) potential at the  $\text{TiO}_2$  surface, whilst the bubble  $\zeta$ -potential remains negative. The film thickness data were described using bubble surface potential as a variable, and using the measured values of surface potential for  $\text{TiO}_2$  and glass.

## Nonionic microemulsion as nano-reservoirs for controlled crystallization of the non-soluble drug

Anna Kogan<sup>1</sup>, Inna Popov<sup>2</sup>, Vladimir Uvarov<sup>2</sup>, Shmuel Cohen<sup>3</sup>, Abraham Aserin<sup>1</sup>, Nissim Garti<sup>1</sup>

<sup>1</sup> *Casali Institute of Applied Chemistry, The Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

<sup>2</sup> *The Unit for Nanoscopic Characterization, The Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

<sup>3</sup> *Department of Inorganic and Analytical Chemistry, The Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

*annak@chem.cc.huji.ac.il*

In this study we utilized nonionic microemulsions as nano reservoirs for specific interfacial crystallization of carbamazepine (CBZ), an antiepileptic drug. The drug is characterized by a slow and irregular gastro intestinal absorption due to its low solubility in water (0.11 gr/lit at 25°C). Crystallization from microemulsions can be an effective method for the formation of desired crystal structure and habit modifications. The fully dilutable microemulsions based on pharma-grade components provide a thermodynamically stable, monodispersed nanometric reservoir for appropriate control of the crystallization process and, accordingly, the crystal structure and habit of the precipitating agent.

We correlated the structure of microemulsion (water-in-oil, bicontinuous, and oil-in-water) with the crystalline structure and morphology of the crystallized CBZ. The precipitated CBZ was studied by DSC, TGA, powder XRD, single crystal XRD, SEM, and optical microscopy. The results suggest that the microstructure of the microemulsions influences the crystallization process and allows crystallizing polymorphs that exhibit different thermal behavior and dissimilar crystal structure and habits.

Water-in-oil nanodroplets orient the crystallizing CBZ molecules to form a prism-like anhydrous polymorphic form with monoclinic unit cell and  $P2_1/n$  space group. Bicontinuous structures lead to plate-like dihydrate crystals with orthorhombic unit cell and  $Cmca$  space group. The oil-in-water nanodroplets cause the formation of needle-like dihydrate crystals with monoclinic unit cell and  $P2_1/c$  space group.

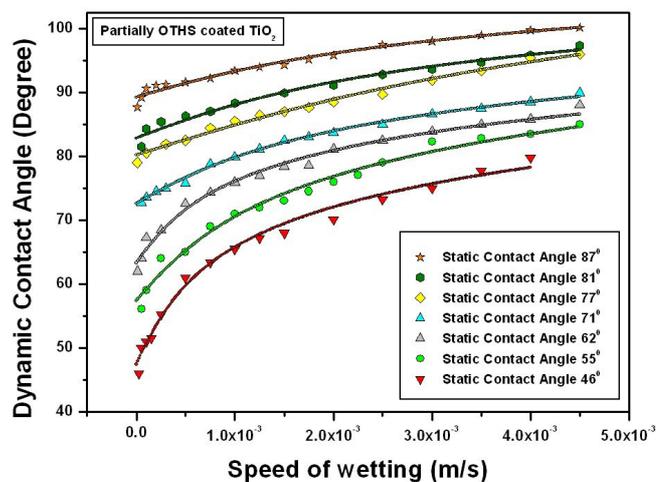
# Relating Wetting Dynamics to the Work of Adhesion on a Chemically Heterogeneous Solid Surface

Santanu Ray, Rossen Sedev, Craig Priest, and John Ralston

*Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus,  
Mawson Lakes, Adelaide, SA 5095, Australia*

*Ray.Santanu@postgrads.unisa.edu.au*

Dynamic contact angles were measured on chemically heterogeneous surfaces. Titania surfaces were prepared by sputtering titanium on thin glass slides. The hydrophilic titania surface was gradually hydrophobized with octadecyltrihydrosilane. The resulting surfaces were heterogeneous with a known wettability (water contact angle from  $46^\circ$  to  $87^\circ$ ) and patch size and distribution (obtained with atomic force microscopy and x-ray photoelectron spectroscopy). Dynamic contact angles of glycerol-water mixtures were determined at wetting speeds ranging from 10 to  $5000 \mu\text{m/s}$  using the Wilhelmy plate technique.



Dynamic contact angle of a 90% glycerol-water mixture on partially hydrophobic titania.

The molecular kinetic theory of wetting was used to interpret the dynamic contact angles and evaluate the contact line friction coefficient. The theory successfully predicts the observed wetting behaviour. We demonstrate experimentally that a relationship between the contact line friction coefficient (a kinetic parameter) and the reversible work of adhesion (a thermodynamic parameter of the solid/liquid interface) exist - in agreement with theoretical speculations.

## Sonochemistry and Sonoluminescence under Dual-frequency Conditions

Adam Brotchie, Muthupandian Ashokkumar and Franz Grieser

*Particulate Fluids Processing Centre, School of Chemistry,  
University of Melbourne, VIC 3010, Australia*

*a.brotchie@pgrad.unimelb.edu.au*

A recent approach taken to improve the efficiency of sonochemical processes and ultrasound reactors is to combine multiple transducers, operating at either the same or at different fundamental frequencies. In this presentation, several different dual-frequency systems will be discussed, looking at their potential advantages and limitations in ultrasonic processes. The efficiency has been assessed through an analysis of the sonoluminescence (SL) emission and also of the comparative reaction rates of selected sonochemical reactions. The influence of various different parameters on the relative efficiency of the dual-frequency mode has been studied. Specifically, it is seen that acoustic power, pulse modulation, the presence of certain solutes, solution temperature, transducer type (plate, focused) and dimensions are all important determinants of the efficiency of cavitation in the dual-frequency sound field. Some of these factors will be discussed and used to gain insight into the mechanisms responsible for the enhancement or attenuation of sonochemistry observed.

## **Salmeterol Xinafoate Powders for Inhalation - Performance and Related Factors during Long term Storage at Different Environmental RH**

S. Das<sup>1</sup>, I. Larson<sup>1</sup>, P. Young<sup>2</sup> and P. Stewart<sup>1</sup>

1. *Department of Pharmaceutics, Victorian College of Pharmacy, Monash University, 381, Royal Parade, Parkville, Victoria 3052, AUSTRALIA*

2. *Advanced Drug Delivery Group, Faculty of Pharmacy, University of Sydney, NSW 2006, AUSTRALIA*

*Shyamal.das@vcp.monash.edu.au*

This study investigated the performance of salmeterol xinafoate (SX) during storage in different environmental conditions for 18 months, and related factors like surface energy and particle size.

Five formulations, SX alone and four SX-coarse lactose (CL) mixtures containing 0%, 5%, 10% and 20% fine lactose (FL), were kept at 33%, 55%, 75% and 95% RH. In vitro aerosol performance (expressed as Fine Particle Fraction - FPF) was determined. Dispersive ( $\gamma^D$ ) and specific ( $\gamma^{SP}$ ) surface energies at infinite dilution of unstored and stored (three months at 75%RH) samples were determined by Inverse Gas Chromatography (IGC). Particle size distributions (PSD) were measured with a Malvern Mastersizer 2000.

The FPF of the SX mixture containing 20% FL significantly decreased from 11.3% to 7.7% at 75% RH and to 4.9% at 95% RH within the first 8 weeks. Other formulations showed no significant change in performance up to 75% RH. The  $\gamma^{SP}$  decreased for all samples. The  $\gamma^D$  of CL and FL stored alone decreased, while that of SX increased, and the SX mixture containing 20% FL remained unchanged. No change was observed between the PSD of unstored and stored SX, CL and M0F. However, the PSD of the stored FL and M20F showed a right shift indicating a decrease in the concentration of small particles (<3  $\mu\text{m}$ ) and an increase in larger size particle fractions.

The study concluded that the critical factors in the decreased performance of SX powders for inhalation were storage relative humidity of 75% or greater and the presence of high concentrations of FL. There was no correlation between the changes in surface energies and the changes in FPF. At high RH, possible solid bridging of FL with other FL and the CL carrier in M20F reduced the amount of free FL and possibly resulted in the decreased performance.

## Novel Fine Particle Separation – Particles at the Air-Water Interface

Diana Tran, Catherine Whitby, Daniel Fornasiero and John Ralston

*Ian Wark Research Institute, University of South Australia,  
Mawson Lakes, SA, 5095*

*diana.tran@postgrads.unisa.edu.au*

Particle separation is of importance in the food, pharmaceutical and mining industries. The separation of colloidal particles relies on differences in the surface chemistry of the particles. For example in flotation, mixtures of hydrophobic and hydrophilic particles are separated by attaching the hydrophobic particles to bubbles rising through the particle dispersion. However, fine hydrophobic colloidal particles with their low mass and inertia have a low flotation recovery because of their low collision efficiencies with bubbles.

The aim of this project is to control the selective attachment of fine particles at the air-water interface by avoiding the inefficient collision step through direct contact between the particles and the air-water interface. We are investigating the interactions between colloidal particles and manipulating the interaction forces to separate these particles under conditions where the transport of these particles to the air-water interface is optimised. In proof of principle experiments, we separated a mixture of hydrophobic and hydrophilic particles by selectively attaching the hydrophobic particles to a water surface. Using a modified version of the film flotation technique (Williams and Fuerstenau 1987; Fuerstenau, Diao et al. 1991), we took advantage of the spontaneous wetting of the hydrophilic particles at the air-water interface to separate graphite and silica colloidal particles.

The outcome of this study indicates we can investigate the separation of fine particles at a larger air-water interface (foam) to improve the efficiency and throughput of the separation process.

### References

- Fuerstenau, D. W., J. Diao, et al. (1991). "Characterization of the wettability of solid particles by film flotation. 1. Experimental investigation." *Colloids and Surfaces* **60**: 127-44.
- Williams, M. C. and D. W. Fuerstenau (1987). "A simple flotation method for rapidly assessing the hydrophobicity of coal particles." *International Journal of Mineral Processing* **20**(1-2): 153-157.

# Study of Adsorption Kinetics Using Optical Reflectometer with Improved Sensitivity and Stability

Shaun C. Howard, Vincent S.J. Craig

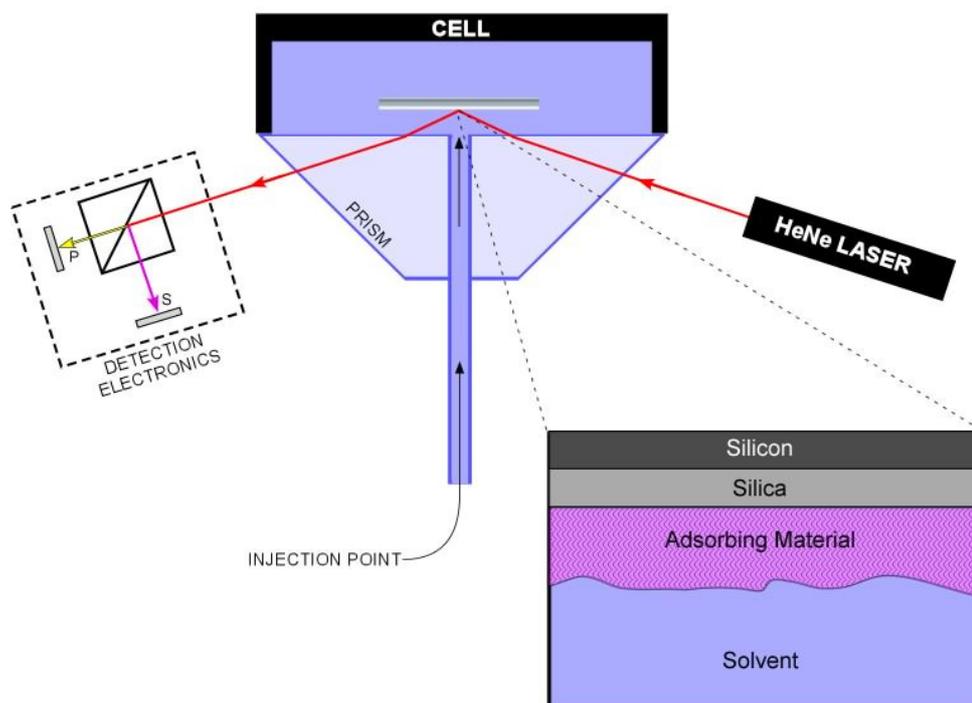
Department of Applied Mathematics, Research School of Physical Science and Engineering, the Australian National University. Canberra, ACT 0200.

shaun.howard@anu.edu.au

Optical Reflectometry (OR) is a form of ellipsometry that is used to measure adsorption of surfactants, polymers and particles at the solid-liquid interface and is ideal for following the kinetics of adsorption. We have designed and constructed a new optical reflectometer with significant improvements to sensitivity and long-term stability. These improvements allow us to examine behavior(s) that were previously undetected due to drifts and noise in the raw data.

A robust software-based optical model has been developed allowing us to expand the range of surfaces that can be studied beyond silica. This model will be explained and supporting data presented.

Results on the kinetics of surfactant adsorption will be presented and discussed.



## General References:

- Atkin, R; Craig, VSJ; Wanless, EJ; Biggs, S. 2003. *The influence of chain length and electrolyte on the adsorption kinetics of cationic surfactants at the silica-aqueous solution interface.* Journal of Colloid and Interface Science 266 (2): 236-244.
- Atkin, R; Craig, VSJ; Biggs, S. 2000. *Adsorption kinetics and structural arrangements of cationic surfactants on silica surfaces.* Langmuir 16 (24): 9374-9380.

## Measuring the mechanical properties of cardiac cells by AFM

Shashikanth B Parcha

*School of Chemistry, The University of Melbourne, Vic 3010, Australia*

*b.parcha@pgrad.unimelb.edu.au*

Each cell type in the animal body performs a characteristic function. For example the tissue cells, muscle cells, bone cells etc. During a disease condition each type of cell exhibits abnormal structural and functional properties. The former is directly related to the elasticity of an individual cell. The overall mechanical properties of a cell are dependant on the dynamic role of individual cytoskeleton elements. One can effectively probe the local structural and mechanical stability properties of the cell through direct interaction between the cell surface and the cantilever tip using Atomic Force Microscopy (AFM). Images of live cells (*in vitro*) are obtained in contact mode, then approach and retract cycles (force curves) are taken across the cell surface in uniformly spaced grid pattern. Localized elastic properties can be determined with the use of an appropriate indentation model from the force curves. Results for two systems, cardiac cells and nerve cells are studied.

Sarcomere regions of mouse left ventricular cardiomyocytes are imaged in contact mode and simultaneous force grids were generated as a function of time. Results are discussed.

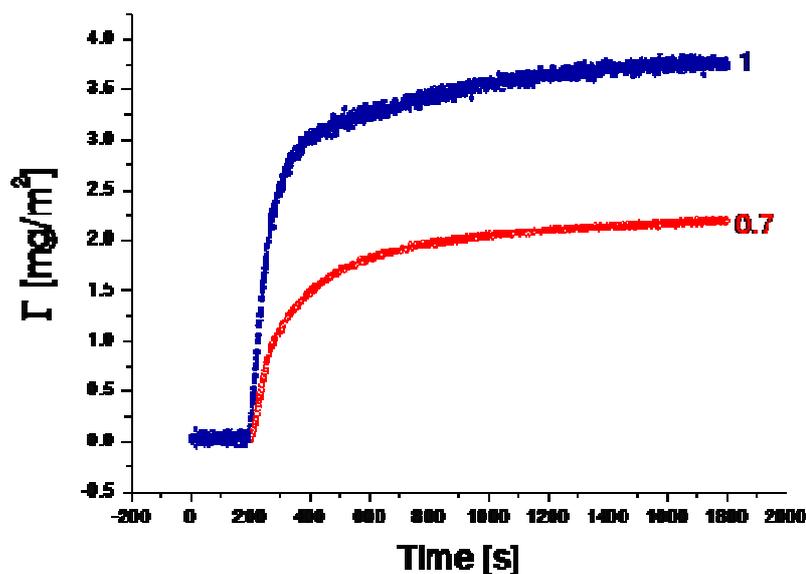
## Influence of a Polymer Depressant on the Wettability of Model Surfaces

Iliana Sedeva, Daniel Fornasiero, John Ralston, David A. Beattie

*Ian Wark Research Institute, University of South Australia,  
Mawson Lakes, Mawson Lakes Blvd., SA 5095*

[sedig001@students.unisa.edu.au](mailto:sedig001@students.unisa.edu.au)

The adsorption of a modified polyacrylamide polymer (Polymer-H, a commonly used depressant in mineral flotation) on substrates of varying hydrophobicity was studied, and its performance as a depressant investigated, using the quartz crystal microbalance (QCM-D), atomic force microscopy (AFM) and captive bubble contact angle measurements. The substrates were generated through the formation of self assembled monolayers on gold from single and double component solutions of CH<sub>3</sub>- and HO- terminated alkanethiols in ethanol (substrate  $\theta_c$  varied from 20° to 119°). The polymer was found to adsorb strongly only on the surfaces with high initial hydrophobicity, and the adsorption kinetics were also faster on the more hydrophobic surfaces, pointing toward the importance of hydrophobic interactions in the bonding of the polymer with the substrates. The greater adsorbed amounts determined with QCM correlate with the *in situ* AFM imaging of the polymer adsorbed on the various substrates, with coverages and layer thicknesses increasing with the hydrophobicity of the underlying surface. Contact angle measurements indicate that the receding contact angle of the hydrophobic surfaces decreased dramatically after adsorption of Polymer-H. However, the polymer only had a modest effect on the receding contact angle of the initially more hydrophilic surfaces.



**Figure 1** – Kinetic curves of adsorption of Polymer-H on SAMs with 0.7 and 1 methyl mole fraction (from QCM-D experiments)

## Expandable microspheres as a novel pore former in alumina gel casting: Surface features, behavior and interactions

Linnéa Andersson, Lennart Bergström

*Materials Chemistry Research Group,  
Department of Physical, Inorganic and Structural Chemistry, Arrhenius Laboratory,  
Stockholm University, SE-106 91 Stockholm, Sweden*

*linneaa@inorg.su.se*

Expandable microspheres were successfully incorporated in a gel-casting suspension to form macroporous alumina<sup>1</sup>. The commercially available expandable microspheres consist of a copolymer shell covered by a surface colloid, which can be either negatively or positively charged. When the temperature is increased to 80 °C the microspheres expand up to 40 times in volume. As a result of the expansion the colloid will spread over the surface exposing the underlying copolymer to the suspension. A sketch of an expandable microsphere and the scattered surface colloid after expansion as well as the resulting macroporous alumina is shown in figure 1.

With this novel process we have achieved macroporous ceramic bodies with porosities up to 86 vol%. The pores were created by the imprint of the expandable microspheres, which were burned out later in the process. The choice of microspheres governed the pore sizes which ranged mainly between 5 and 130 µm in presintered alumina.

To understand and tune the formation of the porosity, the behaviour of the microspheres in the gel-casting suspension needs to be clarified. There are numerous constituents which interact with the microspheres. Parallel processes, such as the polymerisation of the monomer and crosslinker, are of importance as well.

This presentation focuses on the microspheres; their surface features as well as behaviour during expansion. It will be shown how temperature and plasticizing agents affect the microspheres. Finally, possible mechanisms explaining the creation of the homogenous porosity in the gel-casting suspension will be shown and discussed.

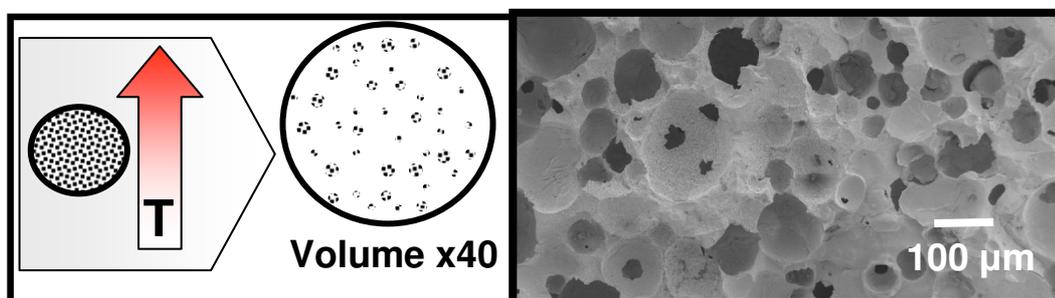


Figure 1: To the left a schematic picture of the expansion of the expandable microspheres upon heating and the scattering of the surface colloid. To the right the resulting macroporous presintered alumina.

1 – Andersson, L. and Bergström, L. (2007) Blowing Holes in Ceramics: Producing Macroporous Materials with Expandable Spheres. *10th International Conference and Exhibition of the European Ceramics Society*. Berlin

## Adsorption and Interaction of Loaded Liquid Crystalline Particles at Surfaces

Yao-Da Dong, Ian Larson, and Ben J Boyd

*Department of Pharmaceutics, Victorian College of Pharmacy, Monash University, VIC, 3052*

*yao-da.dong@vcp.monash.edu.au*

Self-assembled systems such as inversed cubic and hexagonal phase liquid crystals may in some cases be dispersed to form submicron particles (eg. cubosomes and hexosomes), which retain the internal bulk phase structure. Our previous investigation (published) indicated that, unlike GMO-based cubosomes, phytantriol-based cubosomes and hexosomes do not change their lattice structure with addition of Pluronic F127 block co-polymer as stabilizer. Further investigation using particle-solid surface adsorption via FTIR and surface adhesion force measurement using AFM found although F127 is used to stabilize GMO and phytantriol-based liquid crystalline dispersions, the specific mechanism of interaction between F127 and the liquid crystalline dispersed particles differs, affecting the mode of adsorption particle characteristics on solid surfaces. As we are interested in using these systems as novel delivery system for agrochemicals, these findings lead to the hypothesis that such differences in adsorption at surfaces will influence their behavior in the delivery of actives to model plant surfaces and their subsequent interaction with surfaces for penetration enhancement.

A model hydrophobic model surface (tristearin) was immersed in cubosome and hexosome dispersions loaded with radio-labeled diazepam and DDE. The surface adsorption was quantified by measuring the amount of radioactivity remaining on the surface post immersion after repeated rinsing. 2. Loaded cubosomes and hexosomes were applied to the model surface and allowed to dry completely overnight. The surface was immersed in water with constant agitation with visual observation of surface integrity and residual radioactivity on the surface quantified to determine retention of radiolabelled probe on the surface.

All active loaded systems showed significantly greater adsorption at hydrophobic surfaces than at hydrophilic surfaces. Phytantriol based cubosomes showed the greatest adsorption, whilst phytantriol-based hexosomes showed the lowest adsorption, in agreement with with previous FTIR adsorption experiments with unloaded systems. 2. Phytantriol-based cubosomes systems showed minimal susceptibility to rinsing off and the model surface remained intact after rinsing. In contrast, GMO-based systems were readily removed from the surface by rinsing and induced fracturing and damage to the model surface.

Differences in the mode of interaction between F127 and the lipid particles resulted in significant differences in particle-model surface adsorption and interactions and subsequent delivery of actives to model surfaces. These results pave the way to improve the selection of optimal cubosome/hexosome formulations for agrochemical delivery.

# The interfacial chemistry and structure of porous silicon: Towards drug delivery applications

Karyn L. Jarvis, Timothy J. Barnes and Clive A. Prestidge

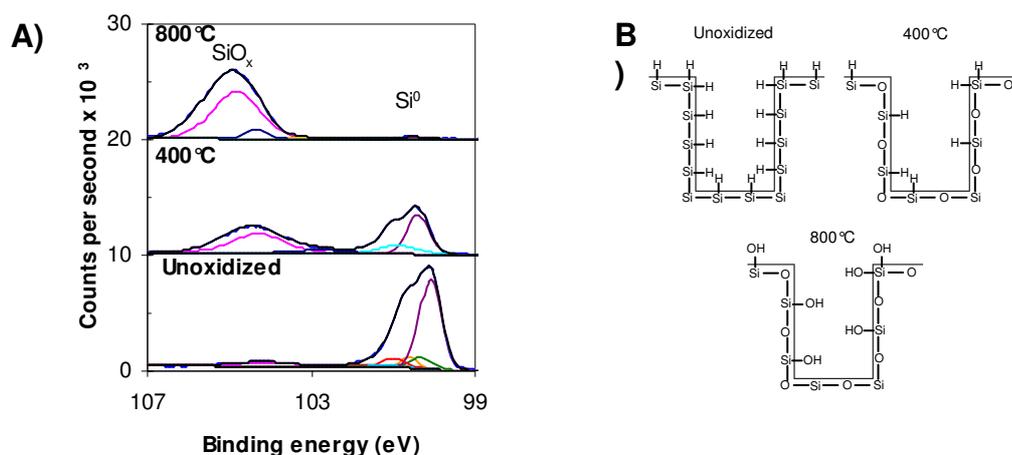
*Ian Wark Research Institute*

*The University of South Australia, Mawson Lakes, SA 5095, Australia*

*Karyn.Jarvis@postgrads.unisa.edu.au*

Porous silicon (pSi) has a number of unique properties that appoint it as a useful biomaterial. A high drug loading capacity, controllable surface chemistry and structure, in vivo compatibility and controlled release properties have resulted in its significant interest as a drug delivery vehicle [1]. To optimize the development of pSi as a delivery vehicle the aim of the project is to investigate the porous structure and surface chemical speciation. The influence of thermal oxidation in the dry and wet states has been investigated including its effect on probe molecule adsorption.

Surface chemistry of pSi has been controlled via thermal oxidation and influences molecular loading and release rates. Fourier Transform infrared spectroscopy has shown increasing oxidation temperatures modifies the native surface speciation of pSi from SiSi-H<sub>x</sub> (x=1-3) to an intermediate backbonded O<sub>y</sub>-Si-H<sub>x</sub> (y=1-3) to a completely oxidized O<sub>3</sub>-Si-OH. The transition of the silicon states from elemental silicon to fully oxidized SiO<sub>2</sub> have been ascertained via X-ray photoelectron spectroscopy (XPS). Zeta potentials of pSi particles decrease with oxidation while oxidation also reduces hydrophobicity. N<sub>2</sub> adsorption has revealed a decrease in surface area and pore volume with an increase in oxidation temperature due to expansion of the structure produced by SiO<sub>2</sub> formation within the pore. To investigate the interactions of native and oxidized pSi surfaces with varying functionalities, the adsorption of several probe molecules and proteins have also been examined.



A) Si 2p XPS spectra of pSi as a function of oxidation temperature and B) Modification of pSi surface chemistry via thermal oxidation

[1] C.A. Prestidge; T.J. Barnes; C.-H. Lau; C. Barnett; A. Loni; L. Canham, Expert Opin. Drug Deliv. 4 (2007) 101.

## Mussel larvae adhesion: unraveling mechanism and functional groups using ATR-IR spectroscopy

Luigi Petrone<sup>1</sup>, Norman Ragg<sup>2</sup>, and A. James McQuillan<sup>1</sup>

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand<sup>1</sup>  
Cawthron Institute, Nelson, New Zealand<sup>2</sup>

*lpetrone@chemistry.otago.ac.nz*

Mussels inhabit inhospitable niches in the intertidal zones. They adhere tightly to underwater surfaces using an adhesive holdfast, the byssus, which is a bundle of threads that terminate in an adhesive plaque. The role of the adhesive plaque is to anchor byssal threads to wet and irregular surfaces with enough strength to withstand turbulent waves. Mussel larvae freely swim in open water for a certain growth period before they can attach themselves to a solid foundation and metamorphose into the adult form.

This work aims to gain a better understanding of adhesion of benthic organisms that may lead to new antifouling strategies or to enhance mussel attachment and growth (aquaculture industry). We present results from adhesion of larvae of the New Zealand Greenshell™ mussel (*Perna canaliculus*) during the early stages of settlement by attenuated total reflection infrared (ATR-IR) spectroscopy. This technique has the ability to monitor the chemical functional groups at a solid/liquid interface *in situ* and in real time. Previous studies in our laboratory with adult mussels showed that it is possible to spectroscopically monitor their adhesion by following the appearance of proteins bands related to the byssus formation. In the present work a new flow cell has been used which allows working at the ocean temperature of 16 °C. The spectra showed characteristic bands from proteins and other signals arising from phosphate, sulphate and carbohydrate, distinctive of a mucus-like adhesive found in other marine invertebrates.

Spectroscopic studies were carried out on model compounds (phosphorylated/sulphated amino acids and polysaccharides) and the effect of cations ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ) which can selectively bind specific groups was evaluated. Comparison between spectra in these model compound studies and cation-induced perturbations in the spectra of larval adhesives give more information regarding the mucus composition. To date this is the first study on mussel larval adhesion and different results have been found from those of adult mussels. In conclusion, it is possible to speak in terms of ‘*ontogenetic adhesion*’, namely the secretion of different adhesives during the development of the marine organism.

1. JH Waite, Nature’s underwater adhesive specialist, *International Journal of Adhesion & Adhesives*, 7, 9-14, 1987.

2. Z Gao, MF Barker, EW Tan, AJ McQuillan, Adhesive secretion of live mussels observed in situ by ATR-IR spectroscopy, *Applied Spectroscopy*, 61, 55-59, 2007.

## AFM Investigation of Adsorbed Polymer Morphology on Hydrophobic Mineral Surfaces

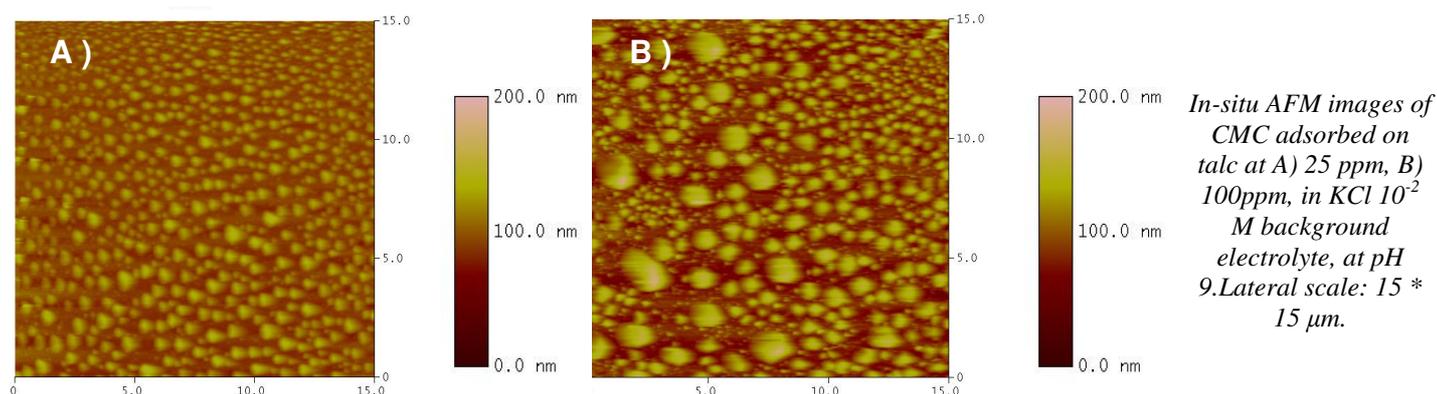
Audrey Beaussart, Agnieszka Mierczynska-Vasilev, Kristen Bremmell & David A. Beattie

*Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus, SA 5095, Australia*

*Audrey.Beaussart@postgrads.unisa.edu.au*

The adsorption of a range of polysaccharides on hydrophobic mineral surfaces has been studied using *in situ* AFM (atomic force microscope) imaging. Due to their ability to alter the wettability of minerals, polysaccharides (CMC, dextrin, guar, etc.) have been used extensively in froth flotation as depressants to help achieve a selective separation among different minerals. This study focuses on 3 naturally hydrophobic minerals: graphite, molybdenite and talc. The fundamental interest of their comparison resides in the similarities of their structure and surface properties. They are also represented in many metal sulphide flotation circuits around the world.

AFM imaging has been used to determine the morphology (i.e. rms roughness, layer thickness and fractional coverage) of adsorbed polymer layers on the surface of the freshly cleaved basal plane of the three minerals. Images have been obtained for polymers adsorbing on the surfaces as a function of increasing polymer concentration (see below), varying pH, and in the absence and presence of multivalent metal ions (i.e.  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ ). Solution pH and multivalent metal ions are known to affect the adsorption and function of polymer depressants. The differences in morphology for the various polysaccharides when adsorbed on the three minerals are discussed in relation to the ability of the polymers to alter the underlying mineral wettability.



## Metal oxide-polyelectrolyte composites for the adsorption of metals

Glenna L. Drisko,<sup>1</sup> Patricia M. Sklavakis,<sup>1</sup> Vittorio Luca<sup>2</sup> and Rachel A. Caruso<sup>1</sup>

<sup>1</sup>*Particulate Fluids Processing Centre, School of Chemistry  
The University of Melbourne, Vic 3010, Australia*

<sup>2</sup>*Institute of Materials and Engineering Science  
Australian Nuclear Science & Technology Organisation, Lucas Heights, NSW 2234*

*Glenna.Drisko@gmail.com*

The presence of toxic and radiotoxic metals in the environment from either natural or commercial sources is of great concern. A few examples include heavy metals from mining activities, arsenic in Bangladesh from naturally arsenic-rich rocks and metal contaminants released during the burning of coal. The most common means of human exposure to these potentially dangerous metals is through water. Therefore there is a need for materials capable of selectively adsorbing targeted metals in high quantities from aqueous systems. In this research, sol-gel and templating techniques are combined to produce an adsorbent.

Three characteristics of great importance for adsorbents are stability, surface area and porosity. A high surface area is important to maximize the uptake of adsorbates. Porosity is important because micropores (<2 nm) and mesopores (2-50 nm) provide high surface area. On the other hand, such small pores restrict the movement of fluids through the pore system, making the rate of adsorption quite slow. Therefore, it is important to have a hierarchy in pore sizes; mesopores to increase surface area and macropores (>50 nm) to increase the rate of diffusion through the material.

Organic molecules or polymers can be incorporated into the metal oxide to increase the metal ion selectivity and adsorption capacity. Polyelectrolytes have been investigated as adsorbents because they are capable of interacting with both the metal oxide surface and the target metals.

Polyelectrolytes can be grafted on to the surface through covalent linkages or through electrostatic interactions. Both of these approaches have been investigated in the course of this research. A covalent attachment can be formed by first functionalizing the metal oxide surface with an organosilane and subsequently forming bonds between the polyelectrolyte and the organosilane. Electrostatic attractions occur when the metal oxide surface and the polyelectrolyte have opposite charge. The method using electrostatic interactions has the benefit of simplicity, however, variation in pH can lead to changes in the surface charge of the metal oxide and the charge of the polyelectrolyte. Therefore, there may be only a narrow pH range in which the interaction can take place. This pH range may not correspond to that of polluted solutions. In addition, the complexation of metals often occurs by proton exchange. Hence, the pH will decrease as metals are adsorbed and this can cause desorption of the polyelectrolyte from the surface.

An adsorbent material was constructed from zirconium titanates functionalized with polyelectrolytes. The metal oxide was templated from 2 wt% agarose gel and characterized with gas sorption, TEM and SEM. The incorporation of the polyelectrolytes at various pHs was assessed with IR, TGA and gas sorption. Metal uptake experiments were carried out and adsorption was monitored with ICP.

# Control of clay Aggregate Structure, Settling and Dewatering

Jianhua (Jason) Du, Rada Pushkarova and Roger Smart

*Applied Centre for Structural and Synchrotron Studies, ACeSSS  
The University of South Australia, 5095 SA*

*Jianhua.Du@postgrads.unisa.edu.au*

Waste Tailings (gangue) are the rejected materials from mineral processing operation. Tailings represent the uneconomic material but can represent significant capital and operating costs that continue long after the mine closes, there are more than 10 billion tones tailings with high percentage of water every year, the tailings stream is significantly larger than the mineral concentrated stream.

Waste tailings are usually dewatered in a thickener by adding a high polymer weight flocculant to fasten the separation of solid and water. After the addition of the flocculant, the solids experience collision with flocculant and forming a loose structural flocs, the flocs will grow during the free settling zone, when the flocs settle to the hindered settling zone, a loose network structure will form to resist from further compress. To achieve a high bed density, this network structure needs to be destroyed so to release the trapped water.

Cryo-SEM allows investigating the flocs structure in the liquid without re-arrangement. A plastic cylinder (diameter of 85mm) with a rake at the top was used to simulate the industrial thickener. This study shows the distinguish structure changes during the kaolinite flocculation and the breaking of the loose network structure during raking.

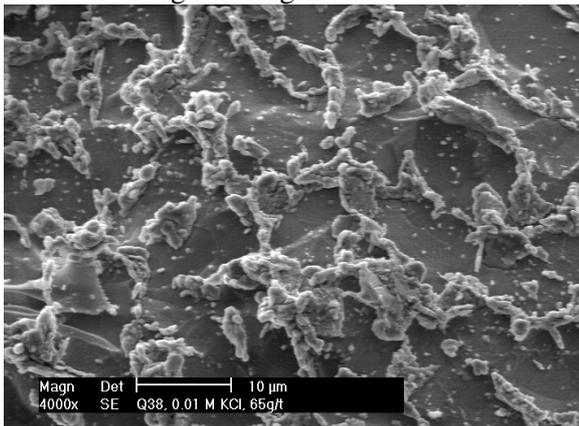


Fig.1. Kaolinite forming loose network structure during flocculation

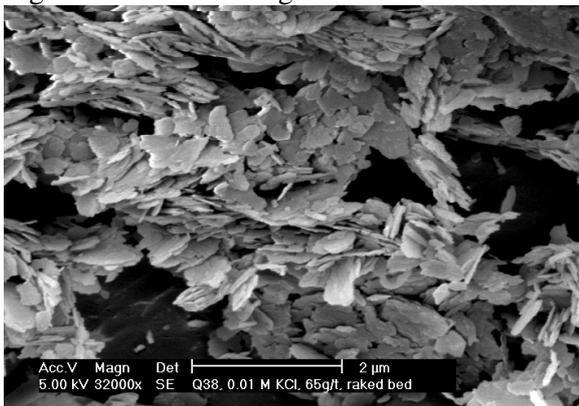


Fig.2. Kaolinite platelets restructured after 1 hour raking

## Ultrasonic Latex Particle Synthesis

Boon Teo, Muthupandian Ashokkumar and Franz Grieser

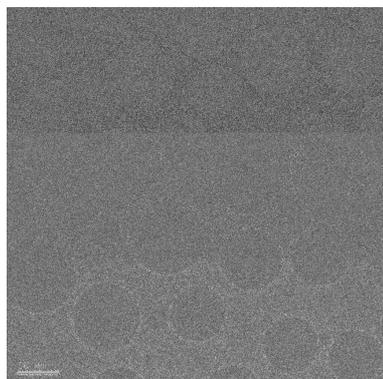
*Particulate Fluids Processing Centre, School of Chemistry,  
University of Melbourne, Parkville, Victoria 3010 Australia*

*b.teo@pgrad.unimelb.edu.au*

The synthesis of nanosized polymer latexes via ultrasound initiated miniemulsion polymerization was successfully performed, boosting many advantages such as the absence of a chemical initiator and hydrophobe, fast polymerization rate, formation of small nanosized latex particles and polymers of high molecular weights. The experimental data for the sonochemical miniemulsion polymerization of different methacrylate monomers showed significant differences in the rates of polymerization. The apparent rate trend is discussed in terms of the physiochemical properties of the monomers.

As sonochemically produced polymers have higher molecular weights than those produced conventionally, different organic liquids have been added in the monomer/water emulsion mixtures in an attempt to control the molecular weights of the polymers. The results showed markedly reduced molecular weights. The effect of organic liquids on the reduction of molecular weights of the polymers will be discussed.

By increasing the surfactant concentration, the monomer/ water mixture can be continuously changed from turbid emulsions to transparent microemulsions. An overview on the effect of surfactant concentration on the rate of polymerization, size of the latex particles, number of latex particles and molecular weights of the polymers will be discussed.



TEM image of sonochemically prepared PBMA latex particles.

## V. Fischeri and E. Coli Adhesion Tendencies Towards Photolithographically Modified Nano-Smooth Poly(*tert*-butyl methacrylate) Polymer Surfaces

Natasa Mitik-Dineva, Radu Codrin Mocanasu, Sarah Murphy,  
Elena P. Ivanova, Russell Crawford

*Faculty of Life and Social Sciences, Swinburne University of Technology, PO Box 218 Hawthorn 3122, VIC, Australia*

*NMitikDineva@groupwise.swin.edu.au*

The idea of controlling the extent to which bacterial cells adhere to solid substrates has received significant attention over the past decades. It is believed that altering the substrates' surface characteristics, wettability, charge and roughness in particular, can significantly influence bacterial adhesion. Recent advances in this area have led to the development of a number of novel nanofabrication techniques that have allowed an insight into bacterial adhesion processes.

We herein present an investigation of the impact of surface nano-topography on bacterial attachment. The photoresistant polymer, Poly(*tert*-butyl methacrylate) (P(*t*BMA)), was used to probe the effects of surface roughness on the adhesion preferences of two bacterial strains, *V. fischeri* and *E. coli*. P(*t*BMA) substrates were subjected to photolithography resulting in the alteration of the surface characteristics such as surface hydrophobicity, surface chemistry and surface topography. Contact angle measurements showing a reduction in surface hydrophobicity, together with XPS elemental analysis of the surface, confirmed that the photolithography had initiated the chemical transformation of the polymer surface. AFM analysis revealed that modified P(*t*BMA) presented a 'nano-smooth' surface with surface roughness ranging from 10-15 nm when compared to the native P(*t*BMA), which had exhibited a surface roughness ranging from 40-50 nm.

SEM and AFM images of the modified P(*t*BMA) surface in the presence of bacterial adsorption showed that after surface modification, a greater number of cells successfully attached and maintained their association with the surface. It was also found that bacterial colonization took place across the surface, with cells appearing healthy, with noticeable flagella. In addition, substantial quantities of cellular extrapolymeric substances (EPS) were produced by the bacteria that had attached to the modified, "nano-smooth" P(*t*BMA) polymer surfaces. The two bacterial strains displayed a different pattern of attachment while colonizing on the same surface, however both strains exhibited a greater degree of adhesion towards the 'nano-smooth' P(*t*BMA) surface compared to the un-modified P(*t*BMA). This may have been facilitated by an elevated production of EPS as a result of interaction with the 'nano-smooth' P(*t*BMA) surface.

## Competitive solubilization of cholesterol and phytosterols within nonionic dilutable microemulsion system

Shoshana Rozner<sup>1</sup>, Abraham Aserin<sup>1</sup>, Ellen J. Wachtel<sup>2</sup>, Nissim Garti<sup>1</sup>

<sup>1</sup>*Casali Institute of Applied Chemistry, The Institute of Chemistry,  
The Hebrew University of Jerusalem, 91904 Jerusalem, Israel*

<sup>2</sup>*Faculty of Chemistry, Weizmann Institute of Science, 76100 Rehovot, Israel*

*shoshana.rozner@mail.huji.ac.il*

The presence of cholesterol in mammals is vitally important for the cell membrane function. However, an excessively high serum cholesterol concentration is a risk factor for cardiovascular diseases (CVD). Some cholesterol-lowering drugs are causing severe side-effects in humans. Phytosterols are plant sterols structurally similar to cholesterol presumably found to be cholesterol-reducing agents by their competitive solubilization with cholesterol in the guts bile salts mixed micelles. Although the positive effect of phytosterols has been known for decades, their poor solubility in water and the unpleasant gritty texture has prevented their widespread use.

We aim to understand the competitive solubilization of cholesterol and phytosterols in the dietary mixed micelles. The present study presents nano-sized, fully dilutable microemulsions, based on food-grade components, providing effective delivery system for phytosterols serving also as a model for mimicking the dietary mixed micelles. Such delivery systems can provide enhanced bioactivity of the phytosterols.

In order to elucidate the impact of the two types of sterols (cholesterol and phytosterols) we determined the maximum solubilization capacity of each of them alone and both together and examined the solubilization effect on structural transformations and the microstructure of these nano-vehicles by measuring the viscosity and SAXS measurements. It was found that the solubilization capacity and the locus of solubilization are strongly correlated to the structural differences between cholesterol and phytosterols. Cholesterol, being more amphiphilic, is solubilized more efficiently at the water-in-oil microemulsion interface, while in the oil-in-water microemulsions phytosterols are dissolved somewhat more efficiently in the droplet core.

The understanding of the locus of their solubilization helps to better understand how these sterols compete on the microemulsion solubilization sites.

## A New Biophysical Approach to Understanding Self-Assembly of Dairy Proteins

Jayani Chandrapala<sup>1,2</sup>, Ian McKinnon<sup>1</sup>, Maryann Augustin<sup>1,2</sup>, Punsandani Udabage<sup>2</sup>

<sup>1</sup>*School of Chemistry, Monash University, VIC (3168), Australia.*

<sup>2</sup>*Food Science Australia, Sneydes Road, Werribee, Victoria 3030, Australia.*

*Jayani.Chandrapala@sci.monash.edu.au*

The thermal processing of milk changes the composition and surface properties of the colloidal particles present and alters the physical properties of the milk. Whilst some changes such as those used to improve the texture of products such as yoghurt and are hence, for this purpose desirable, others such as gel formation during the manufacture of *Ultra-High Temperature* milk, are highly undesirable. The aim of this work is to characterize the effect of milk composition (in particular concentration and pH) on the chemical and physical changes that occur when skim milk is heated in order to understand and control the effect of thermal processing on the functional properties of the milk.

Particularly important are :

- (i) changes to the integrity of the casein micelles and the extent to which the changes are reversible,
- (ii) changes to the speciation and distribution between the colloidal and continuous phases of the components of the milk as they re-equilibrate in response to the changed environment.
- (iii) the denaturation of the whey proteins
- (iv) interaction between the denatured whey proteins and the casein micelles leading to gelation
- (v) interaction between denatured whey proteins both with each other and with casein molecules to form *soluble aggregates* which remain in the supernatant after centrifugation at 33000 (20°C) for 60 min.

It will be shown that:

- (i) on heating skim milk to 90°C for 10 min it is the pH at 90°C that determines the types of aggregates that are formed and their composition with the effect of milk concentration having a minor role
- (ii) the change of pH on heating is strongly dependent on both the concentration and initial pH.
- (iii) varying the concentration of milks (9-21% by weight total solids) without adjustment of the milk pH, (pH values at 90 °C between 6.19 and 5.92), resulted in the formation of *soluble aggregates* with significantly different compositions
- (iv) adjusting to a constant pH prior to heating (pH 6.65) but varying milk concentration, gave pH values at 90°C between 6.19 and 6.08, also resulted in *soluble aggregates* of variable composition.
- (v) varying the concentration of milks but adjusting the initial pH so as to give a pH at 90°C of 6.33 produced *soluble aggregates* of similar composition.

## Lubrication forces on colloidal particles

Christopher D. F. Honig and William A. Ducker

*Department of Chemical and Biomolecular Engineering, and Particulate Fluids Processing Centre, University of Melbourne, Melbourne 3010, Australia*

*c.honig@pgrad.unimelb.edu.au*

We have measured the hydrodynamic force between a particle ( $R \sim 10 \mu\text{m}$ ) and a smooth, flat plate using Atomic Force Microscopy for Newtonian, concentrated sucrose–water solutions for both hydrophilic solids (hydroxyl-terminated silica) and hydrophobic solids (methyl-terminated silica or graphite). For all cases, the measured force is consistent with Reynolds Lubrication theory with the no-slip boundary condition and a constant viscosity. Our error in determining the slip length varies according to the particular experiment, but is about 2 nm. We have restricted our analysis to conditions where Reynolds lubrication is valid, i.e. films that are much greater than the molecular diameter of the fluid. Our experimental method contains two significant improvements over earlier work: the use of much stiffer cantilever springs, and the use of evanescent wave scattering as an independent check of the zero of separation. Our results are consistent with molecular dynamics simulations for thinner films and greater shear rates.

## **Polymeric dispersant mediated behaviour of sericite-chalcocite particle interactions**

Mingzhao He, David Beattie and Jonas Addai-Mensah

*Ian Wark Research Institute, The University of South  
Australia, Mawson Lakes, SA 5095, Australia*

*Mingzhao.He@postgrads.unisa.edu.au*

Attractive particle interactions which underpin the sliming of gangue mineral particles onto valuable mineral phases are encountered in a number of flotation circuits. Sliming leads to poor flotation recovery of the valuable minerals and high recovery of the gangue particles in the concentrate. To mitigate sliming, low molecular weight poly-electrolytes are commonly used as dispersants during pulp conditioning prior to flotation separation of the valuable and gangue mineral phases. However, there is a paucity of understanding of the mode of action of de-sliming dispersants which would underpin potential improvements in their design and efficacy. New knowledge of dispersant adsorption and interfacial properties which control gangue and valuable mineral particle interactions is necessary. In the present work, the influence of interfacial chemistry and two anionic copolymer dispersants (acrylic acid/acrylamide copolymer, Cyquest 3223 and sulfonate/maleic acid co-polymer, Cyanamer P80) on the sliming interactions between chalcocite and sericite were probed. It was shown that sliming occurred under solution conditions where both chalcocite and sericite particles were negatively charged, as evidenced by their apparent particle zeta potentials. The adsorption of the anionic dispersants at  $> 2500$  g polymer / t solid had a significant impact on the particle zeta potentials and hence the interactions between the two mineral phases. In the presence of the dispersants, the apparent viscosity at a given shear rate and shear yield stress of sericite dispersions were dramatically decreased. Sericite - chalcocite particulate adsorption studies showed that sliming was completely suppressed via an electro-steric repulsion mechanism resulting from anionic dispersant adsorption at the plateau adsorption density.

## Thickener Dewatering Optimisation

Anat Kiviti-Manor, Shane P Usher, Peter J Scales

*Particulate Fluids Processing Centre,  
Department of Chemical and Biomolecular Engineering  
The University of Melbourne,  
Victoria 3010 Australia.*

*a.kiviti-manor@pgrad.unimelb.edu.au*

An important requirement in the chemical, wastewater and mineral industries is the ability to separate a suspension into its respective solid and liquid constituents. This separation often occurs in gravity thickeners, where a dilute particulate suspension settles under gravity, creating a compact bed and simultaneously producing clarified liquid. Gravity thickening depends on the difference in densities between the solid and liquid phases.

Study of a range of industrial thickeners shows that current mathematical models underestimate thickener throughput at a given solids concentration by up to a factor of 100 [2]. The reasons for the discrepancy between theory and reality are associated with shear processes. Recent work [1] has shown that the reasons for this discrepancy are related to the role of shear processes (which are caused by raking, fluidisation, dewatering rods and sloped walls.) enhancing the suspension permeability whilst in the thickener. Those shear forces appear to be responsible for aggregate densification, whereby aggregates compact and become smaller. As the aggregates decrease in size, through densification, the tortuosities around the aggregates will decrease, leading to a significant net decrease in the resistance to fluid flow, consequently improving permeability and dewatering behavior. The aim of this study is to quantify the relationship between shear forces and the dewatering process for a range of aggregates formation conditions and flocculant types. A raking rig and a Couette - fluidisation rig were designed and built especially for this study, allowing us to quantify the effect of post formation shear on dewatering for a range of shear conditions.

1. Gladmad, B.R., *The Effect of Shear on Dewatering of Flocculated Suspensions*, in *Chemical and Biomolecular Engineering*. 2004, University of Melbourne: Melbourne.
2. Usher, S.P., *Suspension Dewatering characterisation and optimisation / by Shne Patrick Usher*, in *Chemical and Biomolecular Engineering*. 2002, University of Melbourne: Melbourne.



Photograph of a conventional thickener

## **Temperature Mediated Adsorption of Poly(N-Isopropyl acrylamide) Derivative Polymers onto Silica and $\alpha$ -Alumina**

John-Paul O'Shea, Haihong Li, Luke Connal, Greg Qiao, George V. Franks

*Particulate Fluids Processing Centre, Chemical and Biomolecular Engineering  
The University of Melbourne, Vic 3010, Australia*

*j.o'shea1@pgrad@unimelb.edu.au*

Polymers based upon poly(N-isopropyl acrylamide) reversibly precipitate out of aqueous solution due to an increase in temperature above a critical point. The application of these polymers as stimulant responsive flocculants, to the dewatering of mineral slurries has recently proposed.

In this study the adsorption of various molecular weight poly(N-isopropyl acrylamide) (PNIPAM) polymers onto silica and  $\alpha$ -alumina has been investigated as an aid to developing these novel stimulant responsive flocculants. The adsorption characteristics of PNIPAM at pH 5 for various equilibration conditions both above and below the lower critical solution temperature (LCST) of the polymer ( $\sim 32^\circ\text{C}$ ) were observed. It was found that adsorption increased dramatically upon increasing the temperature above the LCST across the molecular weight range investigated for both minerals. It was also shown that above the LCST, inter-polymer interactions play an influential role with regard to adsorption onto the mineral surfaces. Furthermore, above the LCST, multi-layer adsorption was observed. The molecular weight of the polymer was found to be a significant factor.

Batch settling tests of the mineral slurries across a range of dosage concentrations and polymer molecular weights were also conducted using the same temperature treatments, in order to elucidate the efficiency of the PNIPAM polymers as flocculants. Three key indicators, settling rate, supernatant clarity and sediment bed density were used in these tests to gauge the dewatering efficiency. Below the LCST, the efficiency of the polymers as flocculants decreased with increasing concentration and molecular weight. However, above the LCST, the efficiency improved dramatically with an increase in these variables. Significantly, a greater improvement was shown for batch settling tests in which the temperature was initially above the LCST but then allowed to cool to below the LCST.

Information about the PNIPAM adsorption will be useful in developing novel stimulant responsive flocculants.

## PAMAM Dendrimer Interactions with Supported Lipid Bilayers

Srinivas Parimi, Timothy J. Barnes, Clive A. Prestidge.

*Ian Wark Research Institute, University of South Australia, Mawson Lakes campus.  
South Australia - 5095.*

*Srinivas.Parimi@postgrads.unisa.edu.au*

Dendrimers are hyperbranched polymers with well defined size and surface functional groups. They have potential pharmaceutical applications as drugs, delivery vehicles and transfection agents; hence significant research has been directed in understanding their interaction with biological cell membranes. Supported Lipid Bilayers (SLB), due to their mimicry of the biological cell membranes, were commonly studied as model membranes. In this study we report SLB morphological changes upon the addition of dendrimers using atomic force microscopy (AFM) and interaction kinetics of dendrimers with SLB determined using optical waveguide lightmode spectroscopy (OWLS).

The interaction of polyamidoamine (PAMAM) dendrimers with supported 1, 2- dimyristoyl-sn-glycero-3-phosphate (DMPC) bilayers was both concentration and generation dependent. Electrostatic forces predominantly influence the dendrimer interaction mechanism with the lipid bilayer. A combination of dendrimer adsorption and lipid bilayer disruption/hole formation was observed. At dendrimer concentrations of 1 and 100 nM, disruption of the SLB was the predominant mechanism, while at 10 nM, dendrimer adsorption to the bilayer and bilayer defect formation was observed. At 1nM, defects expansion was observed (Fig.1) indicating that the membrane pore boundary was the region of highest dendrimer activity<sup>1</sup>. Hole formation at 100 nM occurs due to complete coverage of dendrimers on the bilayer surface<sup>2</sup>. In dendrimer-lipid bilayer kinetic studies, an overall decrease in mass was observed for DMPC bilayers exposed to 1 and 100 nM dendrimer concentrations, indicating the disruption and loss of SLB from the surface. In contrast a significant increase in mass was observed at 10 nM dendrimer concentrations, suggesting the adsorption of dendrimer at the lipid bilayer-water interface (Fig. 2). These results highlight the importance of dendrimer structure and concentration on the development of dendrimers for use as pharmaceuticals.

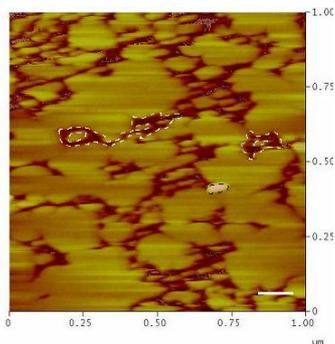


Fig.1: AFM Image of DMPC lipid bilayer 30 min after 1nM G6 PAMAM.  
(Z- scale bar: 10 nm)

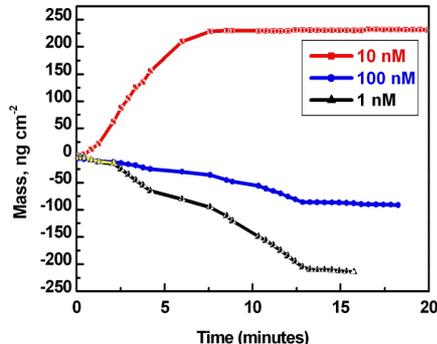


Fig.2: G6 PAMAM interaction kinetics (OWLS) with DMPC lipid bilayers

1.Mecke, A.; Srinivas, U.; T.M, S.; Lee, T. M.; Ramamoorthy, D. K.; Baker Jr, A.; Orr, J. R.; Banaszak Holl, B. G. *Chem.Phys.Lipids* 2004, **132**, 3-14.

2.Hong, S.; Bielinska, A. H.; Mecke, A.; Keszler, B.; Beals, J. L.; Shi., X.; Balogh, L.; G.Orr, B.; James R, B., Jr; Mark M, B., Holl., *Bioconjugate Chem.* 2004, **15**, 774-782.

## Investigating the protein repellent nature of biomedical plasma polymer thin films

Donna Menzies<sup>1</sup>, John Forsythe<sup>2</sup>, Patrick Hartley<sup>1</sup>, Thomas Gengenbach<sup>1</sup>, Celesta Fong<sup>1</sup>, Ben Muir<sup>1</sup>

<sup>1</sup>CSIRO – Molecular and Health Technologies, Bayview Ave, Clayton South, 3168

<sup>2</sup>Monash University – Dept. of Materials Engineering, Wellington Rd, Clayton, 3800

*Donna.menzies@csiro.au*

In the field of nanotechnology, the ongoing development of protein resistant films is of great interest for both fundamental and applied technologies, such as the development of microarray technologies, biomaterials, biosensors, and biomedical imaging. The success of these technologies relies heavily on their protein resistant properties. Poly(ethylene oxide) (PEO) is well known for its protein resistant properties and while many experimental studies have been aimed at identifying the mechanisms of protein resistance in polymeric thin films, it remains an area of ongoing contention.

Diglyme (DG) based films were deposited onto silicon wafers, using radio frequency glow discharge plasma polymerization. To observe the effect of film chemistry on protein resistance, films were deposited at systematically varied plasma load power, which affects the degree of fragmentation of the original monomer structure and hence the resulting film chemistry. Film thickness was measured using AFM and static contact angles were also measured. Results showed that film thickness increased with higher deposition powers, and the relative degree of hydrophobicity also increased. Analysis of high resolution C 1s XPS spectra and FTIR analysis confirmed that films deposited under higher load powers retained less of the original monomer (ether) structure.

The films were also characterized using NEXAFS; a relatively new technique in the characterization of plasma polymers. This enabled us to infer molecule specific information related to the chemical composition and structuring of the films, which has provided an insight into the how these films resist non-specific protein adsorption. Preliminary NEXAFS analysis on these films shows evidence of chemical structuring within the protein resistant films. A finding that has not been reported to the best of our knowledge in plasma deposited thin films.

The ability of these DG pp films to resist protein adsorption decreases in films deposited under higher plasma load power, correlating with their ether content. Furthermore, the adsorption of bovine serum albumin (BSA, negatively charged at pH 7.4,) was significantly less than Lysozyme (Lys, positively charged at pH 7.4). We attribute this to electrostatic interactions between the positively charged Lys, and the negatively charged oxygenated species (e.g. O-C=O) at the surface of the DG pp films.

Furthermore, a cell attachment study using HeLa cells showed that films deposited at a load power of 5W inhibit cell attachment significantly compared to films produced at powers above 20 W, with cell morphology, attachment and spreading being visibly affected.

In summary, the degree of protein adsorption on these DG films correlates with the degree of residual ether groups in the films, as measured by FTIR and XPS analysis. Preliminary NEXAFS analysis has shown evidence of chemical structuring within the protein resistant films. Future work will involve further NEXAFS analysis to investigate the role of chain structuring in low-fouling films, as well as QCM-D to more accurately quantify protein adsorption on these DG films.

# Interfacial Characterization and Stability of Nanoparticle-Encapsulated Emulsions as Potential Drug Delivery Systems for Model Lipophilic Agents

Nasrin G. Eskandar, Spomenka Simovic, Clive A. Prestidge

Ian Wark Research Institute, ARC Special Research Centre for Particle and Material Interfaces, University of South Australia, Mawson Lakes, South Australia

nasrin.ghouchi@postgrads.unisa.edu.au

Many commercial products based on emulsions include both surfactants and particles, hence the characterisation and mechanisms of stabilisation for emulsions with mixed interfacial layers are of great importance<sup>1</sup>. These droplet/surfactant/particle systems are also of interest in designing low-surfactant emulsion systems with enhanced stability<sup>2</sup>. The influence of hydrophilic silica nanoparticles on the emulsification of a triglyceride oil (Miglyol<sup>®</sup>812) in the presence of charged surfactants (lecithin or oleylamine) and the long-term stability of the resultant oil-in-water emulsions are reported. The complex chemical structure of Miglyol<sup>®</sup>812 as well as potential interfacial activity due to the polar species play an important role in the formation and stability of emulsions and have been specifically investigated. The calculated attachment energy from the equilibrium interfacial tension and contact angle measurements can be correlated to surfactant/silica synergy in stabilising emulsion towards coalescence only when silica is included from the oil phase<sup>3</sup>. A special focus is upon the interfacial interaction of silica nanoparticles at polar oil-water interface with the surfactants. Nanoparticle-stabilised emulsions also showed a great potential as dermal delivery systems with enhanced chemical stability of incorporated model lipophilic agents (e.g. Vitamin A – see Fig.2). The in-vitro release and skin penetration profile has been altered in the presence of silica nanoparticle layers (samples OSO and OSA) in favour of improved topical delivery characteristics.

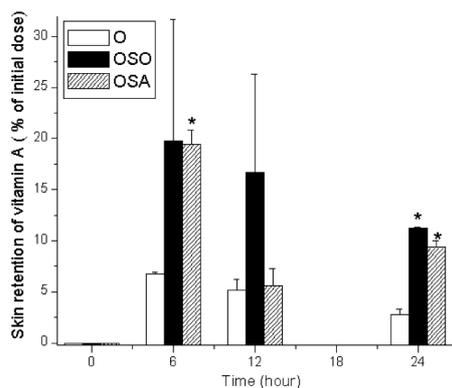
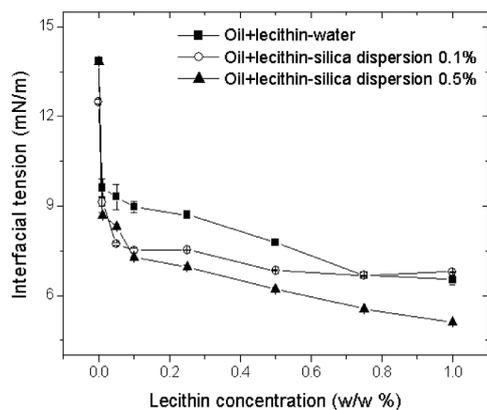


Figure 2- Oil-water interfacial tension as a function of lecithin concentration

Figure 3- Skin retention of Vit A from bare and silica-coated emulsions

## References

1. Binks, B.P., J.A. Rodrigues, and W.J. Frith, *Synergistic Interaction in Emulsions Stabilized by a Mixture of Silica Nanoparticles and Cationic Surfactant*. Langmuir, 2007. **23**(7): p. 3626-3636.
2. Midmore, B.R., *Synergy between silica and polyoxyethylene surfactants in the formation of O/W emulsions*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 1998. **145**(1-3): p. 133-143.
3. Ghouchi Eskandar N., Simovic, S., Prestidge, C.A., *Synergistic effect of silica nanoparticles and charged surfactants in the formation and stability of submicron oil-in-water emulsions*, Physical Chemistry Chemical Physics, 2007, B710256A.

## Sonophotocatalytic Degradation of Methyl Orange in Aqueous Solutions

Yuanhua He, Muthupandian Ashokkumar, Franz Grieser

*Particulate Fluids Processing Centre, School of Chemistry, University of Melbourne, Parkville, VIC, Australia*

*yuanhuah@pgrad.unimelb.edu.au*

Recently, the introduction of ultrasound to assist the photocatalytic degradation process has attracted considerable attention, as the photocatalytic oxidation could be enhanced in the presence of the ultrasonic irradiation. It is well known that the primary radicals produced during cavitation have the potential to decompose organic molecules or the primary intermediates generated during photocatalysis for the degradation of pollutants. This new methodology, sonophotocatalysis (a combination of sonolysis and photocatalysis) is expected to be a better oxidation technique for enhancing the efficiency of environmental remediation process compared to the individual methods.

In our study, the orthogonal array method was adapted to establish the correlation between operation parameters and the performances of sonolysis, photocatalysis and sonophotocatalysis. Our results suggest that the efficiency of sonophotocatalytic degradation is significantly controlled by the frequency, power of the applied acoustic field and the ambient pH of the aqueous solution. The efficiency of degradation is correlated with the rate of production of the highly reactive radicals, which in turn is influenced by the applied ultrasound irradiation; 213kHz and 355kHz are the optimal frequencies for maximum degradation efficiency compared to 647 and 1056kHz. The investigation of pH value effect shows that the pH plays a key role in governing the adsorbed amount of methyl orange on TiO<sub>2</sub>.

The chromatographic analysis of methyl orange solutions during sonication showed that there is no significant synergistic feature on the degradation of parent organic compound. However, the synergistic effect of combined oxidation system has been observed in the reduction of the products generated from methyl orange degradation process. Our results also show that the sonophotocatalytic technique is likely to lead to a complete mineralization of organic pollutants in aqueous solutions.

## Competitive adsorption of carbonate and sulphate by *in situ* IR analysis

Jan Scholz and A. James McQuillan

*Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand*

*jscholz@chemistry.otago.ac.nz*

Adsorption processes are often found to be key steps in chemical conversions occurring at reactive interfaces such as those of clays, oxides, carbons or biopolymers in contact with either a gas or liquid. Both textural properties and a heterogeneous surface of the adsorbing material accounts for the selective affinity of a certain species (ion, molecule) adhering to a particular adsorbent. However, adsorption processes from aqueous solutions are extremely common in environmental as well in biological contexts and have furthermore versatile industrial implementations. In this study *in situ* IR spectroscopy was applied to reveal surface structural information of metal oxide films exposed to solutions of pervasive oxyanions like nitrate, sulphate or phosphate since some metal oxides have interesting acidic properties once oxyanions are adsorbed. Furthermore XRD and zeta potential measurements were performed to draw attention to (i) polymorphism, (ii) particle size and (iii) net charge of the metal oxide adsorbents, as all have effects on the nature of the adsorbate.

It's generally agreed that metal oxide surfaces exhibit two different kinds of charged adsorption sites. The relative amount of each is dependent on the degree of hydration which is a rather slowly occurring process. Therefore, in a wet environment amphoteric hydroxyl groups, so-called Brønsted sites (M-OH) are believed to prevail over acidic Lewis sites (M<sup>m+</sup>). The former however tend to alter in respect to a solution to which they are exposed, so that either protonated (M-OH<sub>2</sub><sup>+</sup>) or deprotonated (M-O<sup>-</sup>) groups are favoured at the metal oxide surface in acid or alkaline conditions, respectively. In addition carbonate species affect the surface chemistry of metal oxides significantly. Originating from atmospheric CO<sub>2</sub>, chelating carbonates (bidentate) as well more loosely bound (monodentate) carbonates and bicarbonates are commonly identified, even though they were found to readily desorb under alkaline conditions<sup>1</sup>. Interestingly, carbonates were found to promote the adsorption of sulphate to iron oxide and aluminium oxide at concentrations smaller 1 mM, whereas at higher concentrations indifferent interactions become more dominant.

Here we report *in situ* ATR-IR spectroscopic findings, which suggest the replacement of adsorbed carbonate species through strongly bound sulphate at the surface of zirconium dioxide nano-particles. The observed adsorbed sulphate spectrum was very similar over a wide range of sulphate concentrations. However, it was not possible to obtain a satisfactory adsorption isotherm, which may be due to hydration processes competing with the sulphate adsorption.

<sup>1</sup> Dobson, K. D. and McQuillan, A. J. *An Infrared Spectroscopic Study Of Carbonate Adsorption to Zirconium Dioxide Sol-Gel Films from Aqueous Solution*. Langmuir (1997), 13(13), 3392-3396

## Biomolecule Encapsulation within Degradable Polymeric Microcapsules

Alisa L. Becker<sup>1</sup>, Alexander N. Zelikin<sup>1</sup>, Angus Johnston<sup>1</sup>, Fabio Turatti<sup>2</sup>, Kim L. Wark<sup>2</sup>, and Frank Caruso<sup>1</sup>

<sup>1</sup> Centre for Nanoscience and Nanotechnology, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia

<sup>2</sup> CSIRO, Preventative Health Flagship & Division of Molecular and Health Technologies, 343 Royal Parade, Parkville 3052, Australia

a.becker@pgrad.unimelb.edu.au

Encapsulated biomolecules have applications ranging from bioreactors to therapeutic delivery vehicles. Encapsulation can provide compartmentalization or protection. In particular, DNA and proteins can require protection from degradation. A semi-permeable membrane, such as a thin polymer film, can restrict nuclease and protease access. Hollow polymeric capsules can be formed using the layer-by-layer (LbL) technique for thin film formation followed by removal of the colloidal template. LbL assembly involves the deposition of alternating polymer layers onto a template surface, forming a thin film. In this work, capsules were formed from poly(methacrylic acid) (PMA) and poly(vinylpyrrolidone) (PVPPON). Since these polymers use hydrogen bonding, the film is unstable above the pKa of PMA at physiological pH. To improve film stability at physiological pH, the PMA was modified with thiol functional groups (PMA<sub>SH</sub>) that can form cross-linking disulfide bonds between layers [1]. The cross-linking disulfides can be broken in a reducing environment, causing the capsules to degrade and release their contents. Several types of DNA have been encapsulated within microcapsules, including plasmid, linear double-stranded DNA and short oligonucleotides [2,3]. The encapsulation method was the same for all DNA samples used, and involves the following steps: adsorption of DNA onto amine-functionalized silica (SiO<sub>2</sub><sup>+</sup>) particles; thin film formation using LbL assembly; and removal of the sacrificial SiO<sub>2</sub><sup>+</sup> particles, see Fig 1.

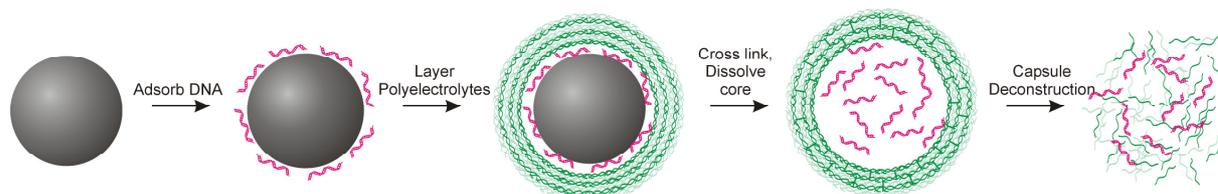


Figure 1. Encapsulation of DNA within polymeric microcapsules. 1. Adsorption of DNA onto positively charged silica. 2. LbL thin film formation. 3. Core removal by hydrofluoric acid. 4. Capsule deconstruction and DNA release

DNA adsorption onto the silica template particles occurred rapidly and with high efficiency. Below the surface saturation point of the silica particles, almost the entire DNA content is adsorbed onto the particles. The deposition of PMA<sub>SH</sub> was dependent on the surface coverage of DNA on the SiO<sub>2</sub><sup>+</sup> particles. Stable microcapsules were formed from particles with 50% DNA coverage. The amount of encapsulated DNA was determined to be ~300 plasmid molecules or more than ten thousand 20-mer oligonucleotides. To determine that the DNA is still functional after encapsulation the DNA was released and used in a common biochemical reaction, the polymerase chain reaction (PCR). PCR is a very sensitive reaction that requires successful DNA hybridisation and protein recognition for product generation. Long and short, single and double-stranded DNA was successfully used as reagents in PCRs.

- [1] A. A. N. Zelikin, J. F. Quinn, and F. Caruso, *Biomacromolecules* **7** (1), 27 (2006)
- [2] A. N. Zelikin, A. L. Becker, A. P. R. Johnston et al., *ACS Nano* **1** (1), 63 (2007)
- [3] A. N. Zelikin, Qi Li, and Frank Caruso, *Angew. Chem., Int. Ed.* **45** (46), 7743 (2006)

## Synthetic Bone Substitutes

William McMaster and Rachel Caruso

*Particulate Fluids Processing Centre, School of Chemistry,  
The University of Melbourne, VIC 3010, Australia*

*w.mcmaster@pgrad.unimelb.edu.au*

Bone fractures may result from injury or disease, and if serious, are usually treated by a bone graft. However, the two available bone grafting techniques – autograft (using bone from another part of the body) and allograft (using donated bone tissue) – are not without complications. Hence, novel materials based on metals, polymers, hydroxyapatite and ceramics, which can substitute for bone are actively researched.

A bone-like graft material must be biocompatible, and ideally, has a porous interconnected structure (pore size in excess of 100  $\mu\text{m}$ ), causes no significant fibrous tissue response, can be modified, and is at least as strong as the bone which it has replaced.<sup>1,2</sup>

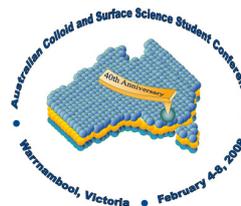
In this study, a templating technique is combined with sol-gel chemistry to prepare structured, porous hydroxyapatite materials; the long-term aim is to mimic both bone mineral and structure. Hydroxyapatite, a form of calcium phosphate, is biocompatible and is a chemically idealised version of bone apatite. Precursors of calcium and phosphorus were variously infiltrated into porous, preformed scaffolds (either a nanoscale organic polymer gel or a micrometre scale, high porosity polyurethane sponge), which following reaction form an impure hydroxyapatite. Calcination of this composite removed the organic template, leaving a porous hydroxyapatite material. Analysis of the samples was by thermogravimetric analysis, nitrogen gas sorption for surface area and nanoscale porosity, x-ray diffraction for sample composition and crystallinity, and scanning electron microscopy to examine the morphology.

Synthesis of the inorganic-organic composites was facile, but mechanically strong inorganic materials (after removal of the organic) remain elusive. Fabrication of a hierarchically porous material was also explored.

1. Moore, W. R.; Graves, S. E.; Bain, G. I. ANZ Journal of Surgery 71: 354-61 (2001).
2. Gross, K. A.; Rodríguez-Lorenzo, L. M. Biomaterials 25: 4955-62 (2004).

# Posters

## Index



Concentrated Nanoparticle Synthesis in Aqueous Systems.....	60
<u>Rory Anderson</u> , Peter Scales, Paul Mulvaney and Robert Eldridge	
Measuring Forces Between Bubbles and Surfaces .....	61
<u>Lorena del Castillo</u> , Roger Horn, Satomi Ohnishi	
Electrokinetic Flow in Mesophase Material .....	62
<u>Alan Chan</u> , Yonggang Zhu, Patrick Hartley and G.M. Forde	
Assessing Flocculant Distribution with Confocal Laser Scanning Microscopy.....	63
<u>Daan Curvers</u> , Hans Saveyn and Paul Van der Meeren	
Dissolution Mechanisms and Kinetic Behaviour of Muscovite at Low pH .....	64
<u>Terry Dermis</u> , William Skinner and Jonas Addai-Mensah	
Positron Annihilation Lifetime Spectroscopy (PALS) and Small Angle X-Ray Scattering (SAXS) of Self Assembled Amphiphiles .....	65
<u>Aurelia Dong</u> , Carlos Pascual-Izarra, Yao-Da Dong, Steven Pas, Anita Hill, Ben Boyd and Callum Drummond	
Molecular Diodes.....	66
<u>Kym Ford</u> , Ian Gentle and Barry Wood	
Protein Adsorption into Self-Assembled Nanostructures .....	67
<u>Scott Fraser</u> , Patrick Hartley, Frances Separovic, John Gehman, Iko Burgar, Roger Mulder, Jo Cosgriff and Tash Polyzos	
Tailored Properties of Ultrathin Polymer Films by Click Chemistry .....	68
<u>Cameron Kinnane</u> , Georgina Such, Christopher Ochs, Angus Johnston and Frank Caruso	
Adsorption of Water on Silica Surface in Cyclohexane Studied by Colloidal Probe Atomic Force Microscopy and Sum Frequency Generation Spectroscopy .....	69
<u>Atsushi Kobayashi</u> , Masashi Mizukami and Kazue Kurihara	
Controlling Clay Behaviour in Suspension.....	70
<u>Josephine Lim</u> , Ross de Kretser and Peter Scales	
Effect of Ionic Liquid Species on Stabilisation of Lysozyme .....	71
<u>Jason Mann</u> , Adam McCluskey and Rob Atkin	

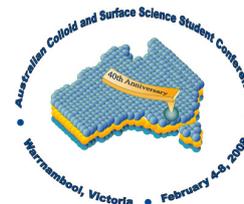
From Shapes to Forces .....	72
<u>Ofer Manor</u> , Derek Chan, Jason Connor and Roger Horn	
Investigating Melittin Partitioning Behaviour into Cholesterol Rich Regions of Supported Lipid Bilayers using Time-Resolved Total Internal Reflection Fluorescence Microscopy .....	73
<u>Anna Mularski</u> , Michelle Gee and Trevor Smith	
Humidity Assisted Triboelectric Separation .....	74
<u>Kurt Nicholson</u> , Erica Wanless and Graeme Jameson	
The Interaction of a Fluorescently Labelled Melittin Derivative with Phospholipid Membrane ....	75
<u>Zubaidah Ningsih</u> , Michelle Gee and Andrew Clayton	
Biodegradable One-Component Capsules via Click Chemistry .....	76
<u>Christopher Ochs</u> , Georgina Such, Cameron Kinnane and Frank Caruso	
The Sorption of Phytic Acid onto Goethite .....	77
<u>Eben Quill</u>	
Supported Lipid Bilayers: Formation and Characterisation .....	78
<u>Andrew Rapson</u> , Michelle Gee, Trevor Smith, Andrew Clayton and Edouard Nice	
Shear Enhancement in the Gravity Thickening Process.....	79
<u>Rudolf Spehar</u> , Shane Usher, Murray Rudman and Peter Scales	
Imaging Aerosol Particles using Atomic Force Microscopy .....	80
<u>Stefanie Pui-Shan Sham</u> and Raymond Dagastine	
Understanding the Self-Assembly of Dairy Proteins in Real Time in Skim Milk Systems with Varied Casein to Whey Protein Ratios .....	81
<u>Mandeep Jeswan Singh</u> , Ian McKinnon, Maryann Augustin and Punsundani Udabage	
Two Dimensional Organisation of Solid Polymeric Nanoparticles .....	82
<u>Andrew Stapleton</u> , Erica Wanless and W. Belcher	
Brownian Diffusion of Ultrafine Particles to an Air-Water Interface .....	83
<u>Sin Ying Tan</u> , Catherine Whitby, Daniel Fornasiero and John Ralston	
Structure and Function of Dynamin in Room Temperature Ionic Liquids .....	84
<u>John Tulloch</u> , Adam McCluskey and Rob Atkin	
Block-Copolymers as Effective Surface Agents in Ionic Liquids.....	85
<u>Deborah Wakeham</u> , Erica Wanless, Greg Warr and Rob Atkin	
Investigation of Colistin Liposomal Formulations .....	86
<u>Stephanie Wallace</u> , Ben Boyd, Jian Li and Roger Nation	

Glycation of Deamidated Wheat Proteins with Different MW Maltodextrins and the Effect on their Emulsion Properties ..... 87  
Benjamin Wong, Donald McNaughton, Li Day and Maryann Augustin

Shear Responsive Flocculation and Improved Dewaterability of Talc Suspensions..... 88  
Kai Ying Yeap, Jonas Addai-Mensah and David Beattie

Effect of High-Frequency Ultrasound Treatment of the Physico-Chemical Properties of Starch Granule Suspensions ..... 89  
Jenny Zuo, Muthupandian Ashokkumar and Sandra Kentish

# Poster Abstracts



## Concentrated Nanoparticle Synthesis in Aqueous Systems

Rory Anderson, Prof. Peter Scales, Prof. Paul Mulvaney, Dr. Robert Eldridge

*Particulate Fluids Processing Centre, Department of Chemical and Biomolecular Engineering, University of Melbourne*

*r.anderson5@pgrad.unimelb.edu.au*

Nanoparticles are the building blocks of the future. There are a host of current and potential applications that utilise nanoparticles. These include: advanced materials synthesis, smart paints and coatings, and printable electronics.

Current synthetic routes generally produce particles at low concentrations in organic solvents. This is problematic in that: Industrial production is not economically viable at such low concentrations, and the use of organic solvents and the associated wastes is not environmentally sustainable.

The aim of this project is to produce highly concentrated nanoparticle dispersions using novel polymeric stabilisers for consumer applications. The production of these particles is to be environmentally benign; hence synthesis occurs in an aqueous medium. A range of particle systems are being investigated, with particular emphasis on metal particles in addition to these a range of metal oxides and metal salts are also being examined.

The primary aim is the optimisation of novel polymeric stabilisers to allow high concentration synthesis. Current research indicates that graft copolymers provide more effective stabilisation than linear molecules in aqueous systems [1,2,3]. Therefore structural parameters that are likely to impact on the nucleation, growth and stabilisation potential of the polymer are being investigated. These include: the graft side chain length, polymer backbone length, number and type of adsorbing functional groups, and hydrophobicity of the polymer.

Once a suitable polymer has been identified for high concentration synthesis, the next phase will be to model the growth of particles and determine the impact of the stabilisers on particle nucleation and mechanic as well as characterising the rheology of concentrated dispersions for further industrial processing.

1. Chen, M., P.T. Elliott, and J.E. Glass, *Influences of monomer and oligomer structures on their adsorption on metal oxide surfaces*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2001. **183-185**: p. 457-474.
2. Sakai, T. and P. Alexandridis, *Single-Step Synthesis and Stabilization of Metal Nanoparticles in Aqueous Pluronic Block Copolymer Solutions at Ambient Temperature*. Langmuir, 2004. **20**(20): p. 8426-8430.
3. Sidorov, S.N., et al., *Stabilization of Metal Nanoparticles in Aqueous Medium by Polyethyleneoxide-Polyethyleneimine Block Copolymers*. Journal of Colloid and Interface Science, 1999. **212**(2): p. 197-211.

## Measuring forces between bubbles and surfaces

Lorena del Castillo, Roger Horn, Satomi Ohnishi

*Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes 5095 SA, Australia*

*Lorena.delcastillo@postgrads.unisa.edu.au*

Air bubbles are everywhere and they play important roles in physics, chemistry, medicine, and technology. Nevertheless, their behavior is still not well understood. An understanding of the forces acting between air bubbles and other surfaces and how they are influenced by various factors is important in many practical applications ranging from the release of bubbles in beers and wines, to the production and transport of oil, to mineral flotation, to ultrasound diagnostics. In order to understand, control and optimize these processes, a study of these forces is essential.

This study will build on and contribute to the work in determining interaction forces between a gas-liquid (G-L) interface and another surface. Although studies in this field have come to a conclusion that the G-L interface is charged [1-5], the question of the origin of these charges has not yet been answered and despite the many attempts to measure the surface potential [1,4-9], which determines long-range interactions involving bubbles, its magnitude still remains ambiguous.

Numerous studies have been done in the attempt of measuring air-air or air-solid surface forces in liquid [1-9]. Initial work has also been done by Pushkarova [4,10] in doing measurements between an air bubble and a mica surface using a modified form of the surface force apparatus (SFA) wherein direct measurements of forces between an air bubble and the mica immersed in aqueous solutions were done. While these experiments provided initial values for the surface potential, it is the aim of the present project to provide additional insight into the charging mechanisms at the G-L interface by doing further experiments in a wider range of electrolyte concentrations and pH. Of particular interest is at the higher electrolyte concentrations to observe whether there will be significant effects on the G-L surface potential due to differences in the size, hydration or chemical nature of the ions used. Intriguing hydrodynamic effects observed by Pushkarova will also be explored in more detail. Other techniques for measuring interactions involving the G-L interface will also be explored as adjuncts to the SFA experiments.

1. K. Karraker, C. Radke, *Adv. Colloid and Interface Sci.*, 96 (2002) 231-264.
2. K. Ciunel, M. Armelin, G. Findenegg, R. von Klitzing, *Langmuir* 21 (2005) 4790-4793.
3. C. Stubenrauch, O. Rojas, J. Schlarmann, P. Claesson, *Langmuir*, 20 (2004) 4977-4988.
4. R. Pushkarova, R. Horn, *Colloid and Surfaces A*, 261 (2005) 147-152.
5. C. Li, P. Somasundaran, *J. Colloid Interface Sci.*, 146 (1991) 215-218.
6. P. Saulnier, J. Lachaise, G. Morel, A. Graciaa, *J. Colloid Interface Sci.*, 182 (1996) 395-399.
7. S. Usiu, H. Sasaki, H. Matsukawa, *J. Colloid Interf. Sci.*, 81 (1981) 80-84.
8. D. Exerowa, N. Churaev, T. Kolarov, N. Esipova, N. Pachev, Z. Zorin, *Adv. Colloid Interface Sci.*, 104 (2003) 1-24.
9. A. Graciaa, G. Morel, P. Saulnier, J. Lachaise, R. Schechter, *J. Colloid Interface Sci.*, 172 (1995) 131-136.
10. R. Pushkarova, PhD Thesis, Univ. South Australia (2005).

## **Electrokinetic flow in Mesophase Material**

Alan S.Chan<sup>1,3</sup>, Yonggang Zhu<sup>1</sup>, P.G. Hartley<sup>2</sup> and G.M. Forde<sup>3</sup>

*1C.S.I.R.O Material Science and Engineering, P.O. Box 56, Highett, VIC 3190, Australia*  
*2C.S.I.R.O Molecular and Health Technologies, Bag 10, Clayton South, VIC 3169, Australia*  
*3Department of Chemical Engineering, Monash University, Clayton, VIC 3800, Australia*

*alan.chan@csiro.au*

Application of amphiphile self-assembly (mesophase) material in capillaries electrophoresis was evaluated using a micro-fluidic chip. A electrophoresis micro-fluidic chip consisting of sample (dye – future use) injectors and separation capillaries has been fabricated in a planar polycarbonate slide. The mesophase material was prepared by mixing Phytantriol with water under heating and then injected into the separation capillaries in the micro-fluidic chip. Ohm's law was observed in the electrophoresis experiment under applied voltage up to 600V and 2400V for mesophase material filled capillary and conventional capillary, respectively. Electrokinetic flowrate in the mesophase material filled capillary was observed to be 70% of flowrate in the conventional capillary.



## Assessing flocculant distribution with confocal laser scanning microscopy

Daan Curvers, Hans Saveyn, Paul Van der Meeren

*Ghent University, Particle and Interfacial Technology Group, Coupure Links 653, 9000 Ghent, Belgium*

*Daan.Curvers@ugent.be*

Cationic polyelectrolytes are widely used for the conditioning of activated sludge before dewatering, as they tend to result in better flocculation with lower doses (weight flocculant added/weight sludge dry matter) than inorganic salts do. Next to charge neutralization, other mechanisms such as bridging and patch flocculation have been suggested in explanation of this phenomenon. Bridging is the linking between two or more flocs by one polymer chain. Patch flocculation is a local charge reversal on the floc surface due to high charge density on the absorbed polymer, which in turn causes the electrostatic attraction of other flocs.

It was suggested by Saveyn et al. (2005) that charge neutralization is more complete on the outside of the sludge flocs, while in the inside of the flocs, a lot of free charges remain unchanged. This is due to the limited time of exposure of the inner parts to the polyelectrolyte, while the outside of the flocs stays exposed as long as there is any polyelectrolyte left in solution.

To investigate this theory, confocal scanning laser microscopy (CLSM) was used, in combination with fluorescently labelled polyelectrolyte.

CLSM is a microscopic technique which enables one to look at a certain plane of focus in a sample, rather than looking at the total sample. As such, one can make fictitious slices of the sample by changing the plane of focus.

For making the polyelectrolyte visible in the CLSM images, it was labelled with a fluorescent marker. The polyelectrolytes used were commercially available copolymers of acrylamide and quaternised dimethylaminoethyl acrylate, supplied by CIBA chemicals. The fluorescent label used was fluoresceinamine, a derivative of fluoresceine. It has been shown by Saveyn et al. that when diluted in water, at least 10% of the quaternised amino groups in the copolymer are hydrolysed into choline, leaving a free carboxylic acid group on the polymer chain (results not yet published). The free carboxylic acid group forms the target for an amide binding with the amine group of fluoresceinamine. Fluorescence correlation spectroscopy (FCS) was used for assessing this coupling reaction.

The analysis of the CLSM images, shows that, due to the limited depth of light penetration, a physical slicing method might be necessary to yield more decisive information about the polyelectrolyte distribution within the sludge flocs.

### References:

Saveyn H., Pauwels G., Timmermans R. and Van der Meeren P. *Effect of polyelectrolyte conditioning on the enhanced dewatering of activated sludge by application of an electric field during the expression phase* (2005) *Water Research*, 39(13), 3012-3020

## **Dissolution mechanisms and kinetic behaviour of muscovite at low pH**

Terry Dermis, William Skinner, Jonas Addai-Mensah

*Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia*

*Terry.Dermis@postgrads.unisa.edu.au*

Dissolution and precipitation kinetics of gangue clay (e.g. muscovite, chlorite) and metal oxide (e.g. hematite) mixed minerals play a pivotal role in determining the processability and recovery of valuable minerals (e.g. copper, gold). During mixed minerals leaching, at low pH (1 – 2) and elevated temperatures (e.g. 70 °C), the formation of a highly viscous gel ascribed to the polycondensation of Si and Al species released into the leachate by clay and other mitigating minerals, may occur. Adhoc methods to alleviate and suppress the gellation process may be implemented; however this in turn may adversely impact on valuable mineral recovery. Consequently, new knowledge and greater understanding of how the interfacial and pulp chemistry, mineralogical characteristics and particle interactions develop and control the degree of gellation, need to be established.

This study investigates the dissolution behaviour and particle surface and mineralogical characteristics of muscovite as a function of pH (1 vs. 6) and temperature (25 °C vs. 70 °C) in a batch leach system. Bulk crystallographic and chemical structure were determined by X-ray diffractometry (XRD), X-ray fluorescence (XRF) spectroscopy, and energy dispersive X-ray (EDX) analysis, whereas the surface chemistry of pristine and leached mineral were analysed using X-ray photoelectron spectroscopy (XPS) and fourier-transform infra-red (FT-IR) spectroscopy. Inductively coupled plasma – atomic emission and mass spectroscopy (ICP – AES / MS) was employed for solution speciation.

The resulting bulk and surface chemical structural data of pristine and leached pulps indicated the formation of certain Si – O – Al / Si – O – Si linkages, which change with time in the course of dissolution. It may be hypothesised that particle surface, bulk solution chemistry and thermodynamic changes may synergistically act to cause viscous gel formation.

## **Positron Annihilation Lifetime Spectroscopy (PALS) and Small Angle X-Ray Scattering (SAXS) of Self-Assembled Amphiphiles**

Aurelia W Dong<sup>1</sup>, Carlos Pascual-Izarra<sup>2</sup>, Yao-Da Dong<sup>1</sup>, Steven J Pas<sup>2</sup>, Anita J Hill<sup>2</sup>, Ben J Boyd<sup>1</sup> and Calum Drummond<sup>2</sup>,

*1. Department of Pharmaceutics, Victorian College of Pharmacy, Monash University  
381 Royal Pde, Parkville, VIC 3052 Australia*

*2. CSIRO Molecular and Health Technology, Manufacturing and Materials Technology, and Industrial Physics,  
Clayton, VIC 3168 Australia*

*Aurelia.dong@vcp.monash.edu.au*

Self-assembled amphiphile systems are utilized in a wide variety of applications, however of more recent interest has been its application in the pharmaceutical industry. Nano-scale physical and chemical interactions govern the packing of self-assembled amphiphilic molecules, resulting in thermodynamically stable phases of defined geometries. Possible phases include lamellar, micellar, hexagonal and cubic mesophases. The internal nano-structure of the amphiphile self-assembly materials play an important role in the properties of these systems and their application in drug delivery.

At present, small angle x-ray scattering (SAXS) has been the most common technique used to characterise the structure of self-assembled systems. Positron annihilation lifetime spectroscopy (PALS) offers a possible alternative technique as it is sensitive to both the internal cavities and the intermolecular forces and in combination with SAXS, may provide more detailed structural information such as trends with composition and temperature variations.

The phase behaviour of the phytantriol/water system was explored using PALS, and it was found that PALS was sensitive to phase transitions from bicontinuous cubic to reversed hexagonal to reversed micellar phases. These boundaries agreed well with SAXS data.

## Molecular Diodes

Kym Ford, Ian Gentle, Barry Wood, Geoff Ashwell and Ben Robinson

*School of Molecular and Microbial Sciences, The University of Queensland, St Lucia, Brisbane, Queensland, 4072  
Australia (U.K. group)*

*Nanomaterials Group, School of Chemistry, University of Wales, Bangor, Wales.*

Current molecular diodes are about two orders of magnitude smaller than that of the present inorganic macroscopic semiconductor diodes. Full characterisation of a bilayer type diode is underway for establishing relationships between structure and diode performance. The bilayer system under investigation consists of a monolayer of N, N'-bis-(3-acetyl-sufanylpropyl)-4, 4'-bipyridinium diiodide (acetylated sp-bipy) attached to a gold substrate and a second layer of a porphyrin or phthalocyanine based compound. At the present stage of this investigation the self-assembling process of the first layer has been studied in depth both *in situ* by quartz crystal microbalance and non-monitored depositions. The resulting monolayer was examined by high resolution X-ray photoelectron spectroscopy.

## Protein Incorporation in Self-Assembled Nanostructures

Scott Fraser<sup>1,2</sup>, Patrick Hartley<sup>1</sup>, Frances Separovic<sup>2</sup>, John Gehman<sup>2</sup>, Iko Burgar<sup>1</sup>, Roger Mulder<sup>1</sup>, Jo Cosgriff<sup>1</sup>, and Tash Polyzos<sup>1</sup>

1. CSIRO Molecular & Health Technologies, Private Bag 10, Clayton South, Melbourne, VIC 3169, Australia
2. School of Chemistry, Bio21 Institute, University of Melbourne, VIC 3010, Australia

Scott.Fraser@csiro.au

The self-assembly of amphiphilic molecules into complex structures has become an extensive and active area of scientific research. Water-amphiphile systems form a range of liquid crystalline phases (mesophases) depending on a number of properties (molecular geometry, pH, etc.), of which the inverse-cubic phase system is attracting interest. Inverted cubic phases are porous architectures that are usually stable over a broad temperature range. This class of aggregate exist in equilibrium with excess water, have a large surface-area to volume ratio (up to 400 m<sup>2</sup>g<sup>-1</sup>), and have the ability to solubilise amphiphilic molecules as well as both hydrophilic and hydrophobic substrates. These properties make their application to areas such as drug delivery and bioseparations especially promising. A further advantage of these systems is the advent of colloidal nanoparticles (or cubosomes) derived from the bulk cubic phase, which are amenable to *in vivo* applications.

The transport and surface interaction of biological macromolecules within the inverse-cubic mesophase system is not well understood. In order to determine the basis of biomolecular recognition and adsorption within an inverse cubic phase, we will investigate structural changes of the mesophase and included bio-macromolecules, which accompany bio-macromolecule diffusion, using nuclear magnetic resonance (NMR). The diffusion kinetics for given bio-macromolecule/mesophase systems are being determined together with the parameters associated with inverse cubic mesophase structure that govern bio-macromolecule diffusion into the nanosystem.

We have investigated the diffusion of water molecules within the inverse cubic phase of the surfactant, phytantriol (3,7,11,15-tetramethyl-1,2,3-hexadecanetriol). Preliminary NMR results indicate a shape-related steric effect on diffusion within the phase in comparison to free water. The diffusion constant of water within the system was reduced by a factor of 10. Furthermore, a single diffusion constant did not best describe the diffusion of water molecules and may be related to wall proximity within the mesoporous structure. This system will be further investigated using additional NMR methods, small-angle X-ray scattering (SAXS), and small-angle neutron scattering (SANS) to determine how diffusion within the system is related to the molecular organization of the system.

# Tailored Properties of Ultrathin Polymer Films by Click Chemistry

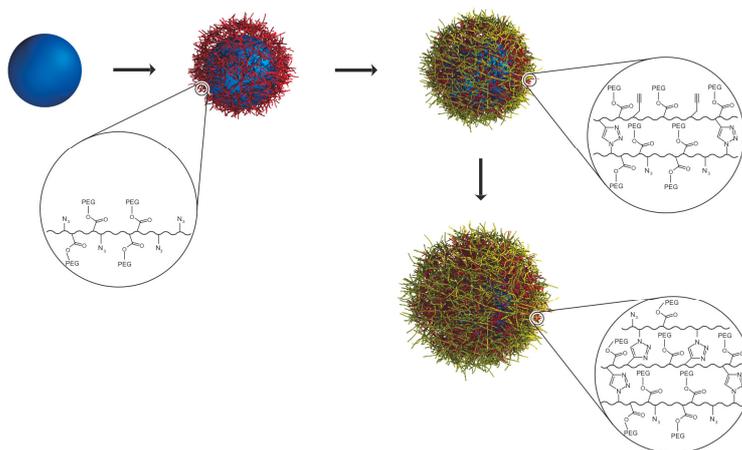
Cameron R. Kinnane, Georgina K. Such, Christopher Ochs, Angus P.R. Johnston, Frank Caruso

Centre for Nanoscience and Nanotechnology, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, Victoria, Australia, 3010

*c.kinnane@pgrad.unimelb.edu.au*

The ability to manipulate size, composition and structural order at the nanoscale is fundamental in the development of smart materials. This is specifically so for biomaterials whose surface properties have to meet strict demands, such as low fouling and functionality. Furthermore, these materials should also be produced by versatile and facile means in order to be widely employable.

An established means to achieve surface modification with nanoscale precision is the Layer-by-Layer (LbL) technique, which uses the alternate adsorption of pairing macromolecules (e.g. polycations and polyanions) to produce multilayer films [1]. A recently described method to construct materials of interest combines this LbL technique and click chemistry to assemble ultrathin films from linear polymers [2,3]. Referring to a set of powerful, highly reliable and selective reactions, click chemistry was employed to achieve cross-linking between layers of poly(acrylic acid). In particular, this approach uses a copper(I)-catalysed variant of the Huisgen 1,3-dipolar cycloaddition of azides and alkynes to form 1,2,3-triazoles [4,5].



**Figure 1:** Assembly of ultrathin poly(ethylene glycol) films using the click layer-by-layer technique

Using the click-LbL strategy described above, we report on the assembly of innovative ultrathin films with tunable properties such as composition, wall thickness and size. We also demonstrate that this method can be used to assemble single-component films from poly(ethylene glycol) (PEG) acrylate which, hitherto, had been severely limited in conventional LbL systems. Furthermore, we show that the ability to post-functionalize the films via unreacted moieties allows these films to be customized for a desired purpose. We demonstrate that by immobilizing peptide sequences onto the PEG films, we can promote specific adhesion of cells onto these surfaces. With this available control over film properties, these films offer potential as microreactors, drug delivery systems and biomarkers.

## References

- [1] G. Decher, *Science*, 1997, 277, 1232-1237
- [2] G.K Such, J.F. Quinn, A. Quinn, E. Tjijto, F. Caruso, *Am. Chem. Soc.*, 2006, 128, 9318-9319
- [3] G.K. Such, E. Tjijto, A. Postma, A.P.R. Johnston, F. Caruso, *Nano Letters*, 2007, 7, 1706-1710
- [4] H.C. Kolb, M.G. Finn, K.B. Sharpless, *Angew. Chem. Int. Ed.*, 2001, 40, 2004-2021
- [5] V.O Rodionov, V.V. Fokin, M.G. Finn, *Angew. Chem. Int. Ed.*, 2005, 44, 2210-2215

# Adsorption of Water on Silica Surface in Cyclohexane Studied by Colloidal Probe Atomic Force Microscopy and Sum Frequency Generation Spectroscopy

Atsushi Kobayashi, Masashi Mizukami and Kazue Kurihara

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,  
2-1-1, Katahira, Aoba-ku, Sendai, Miyagi 980-8577

a.koba@mail.tagen.tohoku.ac.jp

Adsorption at the solid-liquid interfaces from binary liquids is one of the important adsorption system in advanced materials science and technology in nanometer scale. Recently we found that alcohols (carboxylic acids, amide) adsorbed on the silica surface formed orderd structures extending to several tens of nanometer through hydrogen bonding(Fig.1 Surface molecule macrocluster).<sup>1,2</sup> By the study of methanol-cyclohexane binary liquids, which exhibit phase separation above ca. 9 mol% methanol.<sup>2</sup> It was revealed that the surface molecular macrocluster formation was different from wetting induced by bulk separation.

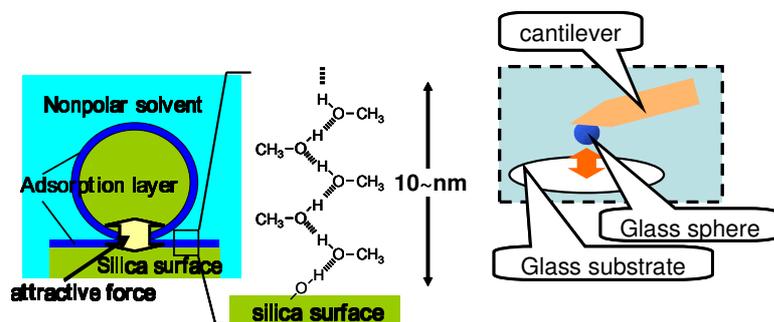
The main aim of this study is to investigate the adsorption and structuring of water on the silica surface in cyclohexane using colloid probe Atomic Force Microscopy(AFM) and Sum Frequency Generation (SFG) spectroscopy. Water is one of the most versatile polar liquid and has strong hydrogen bonding nature and has very low miscibility with cyclohexane.

Colloidal probe AFM demonstrated that at the water concentration of ca. 28~33 ppm, the attraction between the glass sphere and glass substrate was observed from a distance of 2~3 nm, which agreed with van der Waals force. At water concentration of 60~70 % of saturation (ca. 39 ppm), the long range attraction appeared at a distance of ca. 45±8.5 nm. These results indicated the formation of water adsorption layer extending to ca.20~25 nm. This distance became longer with increasing water concentration. And the maximum attraction range was 130±6.0 nm at water saturation (ca. 50 ppm.) Figure 2 show the plots of attraction range (circle) and adhesive force (square) as a function of the water concentration. This show that with increasing the water concentration, the range of attraction linealy increased to 130±6.0 nm. On the other hand, the drastic increasing of adhesive force( $F/R$ ) of 454±2.0 mN/m was also observed at water concentration of 60~70 % of saturation. And this adhesive force was decreased to 429±5.0 mN/m at water saturation (ca. 50 ppm.). This indicates the decreasing in the interfacial energy between adsorbed water and bulk.

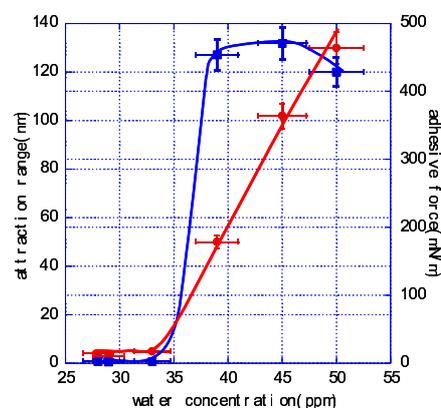
The SFG spectroscopy showed at water concentration of 60~70 % , the hydrogen bonded OH peaks appeared at ca. 3200  $\text{cm}^{-1}$ , and ca. 3400 $\text{cm}^{-1}$ . Especially the intensity of the 3200  $\text{cm}^{-1}$  peak known as “ice like water “ is stronger than that for 3400 $\text{cm}^{-1}$  corresponding for “liquid like water “, suggesting that adsorbed water on silica has a tetrahedral structure similar to ice.

We will discuss the concentration dependence in terms of the relation with pre-wetting transition which occurs near the bulk phase separation.

1. M.Mizukami and Kurihara, Chem. Lett., **28**, 1005-1006 (1999).
2. M.Mizukami, M. Moteki and K.Kurihara, J. Am. Chem. Soc., **124**, 12889-12897.
3. M. Mizukami, Y.Nakagawa and K. Kurihara, Langmuir, **21**, 9402-9405 (2005).



**Fig.1** Schematic illustration of colloidal probe AFM measurement and An example of surface macrocluster ( methanol )



**fig.2** the plots of attraction range (circle) and adhesive force (square) as a function of the water concentration.

## **Controlling clay behaviour in suspension: Developing a new paradigm for the minerals industry**

Josephine Lim, Ross de Kretser and Peter Scales

*Particulate Fluids Processing Centre, Department of Chemical and Biomolecular Engineering, The University of Melbourne, VIC 3010 Australia.*

*j.lim3@pgrad.unimelb.edu.au*

The behaviour of clays in suspension can have a controlling effect on the efficiency of mineral processing operations. Whether in ore beneficiation or tailings dewatering and disposal, the plate-like, readily dispersible nature of clays can result in problems which have significant economic and environmental ramifications. In spite of this impact, the mineral industry's understanding of the origins and solutions of clay-related processing issues remains poor and in many cases they are simply avoided altogether by deeming clay-tainted ore bodies 'unviable'.

This project will investigate the concept that a combined chemical, engineering and systems approach to the issue of clays in mining is necessary to make a paradigm shift in the way that the minerals industry currently deals with clays, namely as an end-of-pipe issue. The project will develop integrated chemical and engineering strategies for controlling the dispersion and rheology of both swelling and non-swelling clays. The result will be a novel and operationally achievable approach to dealing with clay-related processing issues, tackling new and existing clay-rich ore bodies and improving performance of operations which may not even perceive they have clay-related performance limitations.

## Effect of Ionic Liquid Species on Stabilisation of Lysozyme.

Jason Mann, Adam M<sup>c</sup>Cluskey and Rob Atkin.

*Chemistry, Centre for Organic Electronics,  
School of Environmental and Life Sciences,  
The University of Newcastle, Callaghan, 2308, Australia*

Many important proteins have marginal stability in solution and readily denature, especially at elevated temperatures, resulting in a loss of functionality and hence limiting shelf life. Lysozyme is a common model protein used to investigate the inactivation of proteins at high temperature because it is inexpensive, easy to handle, easy to denature, and has sufficient complexity such results obtained with this protein can indicate appropriate directions for studies of other more complex (and expensive) enzymes. The primary sequence of lysozyme consists of 129 amino acids and there are four intrachain disulfide bridges between sulfhydryl containing amino acid residues. It is composed of two parts, one that has a predominantly  $\alpha$ -helical structure and another that part with predominantly  $\beta$ -sheet morphology. Recent work<sup>1</sup> has shown that the addition of a simple protic ionic liquid (IL), ethylammonium nitrate, to aqueous solutions of lysozyme greatly enhances the stability of the enzyme to aggregation and hydrolysis as the protein unfolds and refolds as the temperature is cycled between 20 °C and 90 °C. The aim of this work is to investigate the effect of the ionic liquid structure on enzyme stabilisation. Several protic and aprotic ILs will be investigated as a function of IL concentration using differential scanning calorimetry and circular dichorism.

1. Byrne, N.; Wang, L.; Belieres, J. P.; Angell, A. *Chem. Commun.* 2007, 2714.

## From shapes to forces

Ofer Manor<sup>1</sup>, Derek Y. C. Chan<sup>1,2</sup>, Jason N. Connor<sup>3</sup> and Roger G. Horn<sup>4</sup>

<sup>1</sup> *Particulate Fluids Processing Center, Department of Mathematics and Statistics, The University of Melbourne, Parkville, Victoria 3010.*

<sup>2</sup> *Department of Mathematics, National University of Singapore, Singapore, 117543.*

<sup>3</sup> *PELM Centre, Central Queensland University, Gladstone, Queensland 4680.*

<sup>4</sup> *Ian Wark Research Institute, University of South Australia, Mawsons Lakes, South Australia 5095.*

Physical interactions between deformable fluid objects often determine the behavior of soft matter such as emulsions, foams and biological systems. We show that the surface force exerted between a fluid drop and another object is encoded in the deformations of the drop, regardless of how that force is mediated. A theoretical analysis of the coupling between force and deformation is supported by experimental data for the far-field shape of a mercury drop interacting with a mica surface under water, with electrical double-layer and hydrodynamic forces acting on the drop. The analysis provides a novel method of force measurement involving deformable soft matter without the need for a known applied force field such as that provided by a calibrated external spring, gravity or electromagnetic field.

## **Investigating melittin partitioning behaviour into cholesterol rich regions of supported lipid bilayers using time-resolved total internal reflection fluorescence microscopy**

Anna Mularski, Michelle Gee, Trevor Smith

*Particulate Fluids Processing Centre, School of Chemistry  
The University of Melbourne, VIC 3010, Australia*

*a.mularski@unimelb.edu.au*

Lipid rafts exist as distinct liquid-ordered regions of plasma membranes containing high concentrations of cholesterol and glycosphingolipids. It has been shown that a variety of proteins, especially those involved with signal transduction, partition into lipid rafts, suggesting that rafts are involved in the regulation of cell signalling. There are several different mechanisms by which rafts are thought to control cell signalling, but none of these are definitive.

Given the complexity of biological membranes, in this work, the partitioning behaviour of the haemolytic peptide melittin into a supported lipid bilayer, as a 'membrane mimic', will be examined. The lipid bilayer will contain fluorescently labelled cholesterol regions that will be examined using a surface selective technique, Total Internal Reflection Fluorescence Microscopy (TIRFM), which provides high axial resolution within close proximity (within ~ 10s of nanometres) of an interface. Extending these measurements using time-resolved detection allows for the collection of 2D images of the sample surface while generating time-gated fluorescence lifetime images. These images report on the microenvironment and spatial constraints of the fluorescently-labelled cholesterol within the bilayer.

## Humidity Assisted Triboelectric Separation

Kurt Nicholson<sup>a,b</sup>, Erica Wanless<sup>b</sup> & Graeme Jameson<sup>a</sup>

<sup>a</sup> Centre for Multiphase Processes & <sup>b</sup> School of Environmental and Life Sciences – The University of Newcastle,  
Callaghan, N.S.W, 2308 Australia

*Kurt.Nicholson@newcastle.edu.au*

Lack of water is an increasing problem in exploitation of mineral deposits, and economic pressures are driving towards dry processing such as electrostatic methods in which minerals are separated on the basis of differences in their electrical properties. In triboelectric separation, charge is exchanged by friction and contact collisions between particles. The properties of the particle surfaces have a strong influence on the resulting charge; as do environmental factors such as humidity and temperature. By controlling the adsorbed species on the surface of a mineral, say, a mineral sulfide, it should be possible to alter its tribological properties. In particular the adsorption of hydrophobes, such as xanthates to mineral sulfides, will result in particles that may have very different behaviour at high humidity which could be utilised to separate these minerals from gangue material.

The mineral sulfides galena and sphalerite were chosen for study and have been milled and sieved to particle size fractions of +75–40, +150–75 and +300–150 microns. Potassium ethyl xanthate (PEX) was used to alter the hydrophobicity of galena and sphalerite via adsorption. The adsorption of PEX was quantified at pH 9 by UV–visible spectroscopy. Methods to determine the contact angle of the PEX treated particles and measure the steady-state charge/mass ratio of particles by sliding tribo-electrification are currently under development.

# The Interaction of a Fluorescently Labelled Melittin Derivative with Phospholipid Membrane

Zubaidah Ningsih<sup>1</sup>, Michelle Gee<sup>1</sup>, Andrew Clayton<sup>2</sup>

*1 School of Chemistry, University of Melbourne, Parkville, VIC 3010 Australia*

*2 Ludwig Institute for Cancer Research, Post Office Royal Melbourne Hospital, Parkville, Victoria 3050, Australia*

Melittin is an  $\alpha$ -helical peptide extracted from bee (*Apis mellifera*) venom which is able to lyse cells. Due to its lytic behavior, melittin can be considered as a promising anti-cancer and anti microbial agent. However, there is still much controversy regarding the mechanism by which melittin lyses cell membranes. This research is aimed at investigating the interaction of fluorescently-labeled melittin with 1,2 Dipalmitoyl-sn-Glycero-3-Phosphatidylcholine (DPPC) vesicles, using steady-state and time resolved fluorescence spectroscopy methods and Dynamic Light Scattering (DLS). The results show that at low melittin concentration, the melittin adsorbs at the surface of the membrane. At a lipid/peptide concentration ratio at 10:1, the interaction of melittin in the membranes induces vesicle fusion, as confirmed by the increase in vesicle size. These results imply that the mechanism by which melittin lyses the phospholipid bilayers is a co-operative, involving peptide self-assembly.

## Biodegradable One-Component Capsules via Click Chemistry

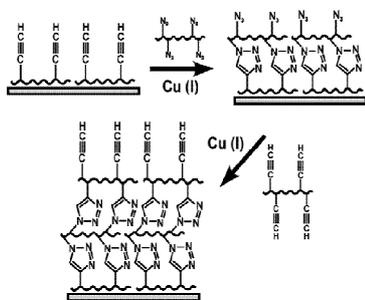
Christopher J. Ochs, Georgina K. Such, Cameron Kinnane, Frank Caruso

Centre for Nanoscience and Nanotechnology  
Department of Chemical and Biomolecular Engineering  
The University of Melbourne, Parkville, Victoria, Australia, 3010

c.ochs@pgrad.unimelb.edu.au

The assembly of alternating layers of polyelectrolytes onto sacrificial templates, known as Layer-by-layer (LbL) assembly, has been used widely in the past 20 years.<sup>1</sup> Uniform coating of a variety of templates with different materials result in core-shell particles, and after removal of the template capsules can be obtained. Furthermore, variation of the assembly conditions allows for close control of properties such as shell thickness, the material deposited, permeability and stability.<sup>2</sup>

The combination of LbL and click chemistry is highly promising and has recently been achieved by Such et al.<sup>3</sup> By means of functionalizing polyelectrolyte materials with azide and alkyne moieties (click groups) ultrathin one-component films could be assembled (Figure 1).<sup>4</sup> The resulting covalent bonds provide further stability compared to the classical polyelectrolyte pairs, whose assembly is predominantly based on electrostatic<sup>5</sup> or hydrogen bonding<sup>6</sup> interactions.



**Figure 1:** Layer-by-Layer assembly of click-functionalized polymers

Click chemistry reactions stand out due to the mild reaction conditions, high yields, the stability of the products towards hydrolysis, oxidation or reduction and, finally, the applicability to a broad range of materials.<sup>7</sup> One of the best known click reactions is the Cu<sup>I</sup>-catalyzed Huisgen variant of a 1,3-dipolar cycloaddition of azides and alkynes to form 1,2,3-triazoles.

The LbL click chemistry approach is a universal method applicable to polyelectrolyte systems functionalizable with click moieties. We report the assembly of one-component films based on natural polymers as a biodegradable alternative to the classical systems. We also demonstrate that stable capsules can be synthesized and functionalized using the click chemistry approach.

Forming a major part of the extracellular matrix, polypeptides, polysaccharides and polyesters are degraded naturally in the body. As not all click functionalities are utilised during layer assembly, remaining click groups can be used for further modification. Selective loading of biomolecules into individual layers or the introduction of antifouling surface properties are examples for possible capsule designs. Potential applications lie in the biomedical field, e.g. as carrier systems for targeted drug delivery.<sup>8</sup>

C. S. Peyratout and L. Daehne, *Angew. Chem. Int. Ed.* **2004**, *43*, 3762-3783

F. Caruso in: *Colloids and Colloid Assemblies* (Ed: F. Caruso), Wiley-VCH, Weinheim **2004**, p. 246

G. K. Such, J. F. Quinn, A. Quinn, E. Tjpto and F. Caruso, *J. Am. Chem. Soc.* **2006**, *128*, 9318-9319

G. K. Such, E. Tjpto, A. Postma, A. P. R. Johnston and F. Caruso, *Nano Lett.* **2007**, *7*, 1706-1710

M. Loesche, J. Schmitt, G. Decher, W. G. Bouwman, K. Kjaer, *Macromolecules* **1998**, *31*, 8893-8906

M. F. Rubner, W. B. Stockton, *Macromolecules* **1997**, *30*, 2717-2725

H. C. Kolb, M. G. Finn, B. K. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004-2021

A. S. Angelatos, K. Katagiri and F. Caruso, *Soft Matter* **2006**, *2* 18-23

## The Sorption of Phytic Acid onto Goethite

Eben Quill

*La Trobe University, Bendigo*

Phytic acid is a phosphorous containing organic compound that is an important source of phosphorous in many soil systems. This study investigates the interaction of phytic acid with common soils minerals such as goethite. This paper presents sorption results along with ATR-IR spectroscopy and attempts to elucidate the chemical mechanisms that control the interaction between this important organic species and the mineral surface. Phytic acid sorbs strongly across the pH range 2-12, with the highest sorption occurring at lower pH. Spectroscopy suggests that the sorption is a combination of inner- and outer-sphere complexation, with outer-sphere complexes dominating at higher pH.

## Supported Lipid Bilayers: Formation and Characterisation

Andrew Rapson, Michelle Gee, Trevor Smith, Andrew Clayton and Edouard Nice

*Particulate Fluids Processing Centre, School of Chemistry  
The University of Melbourne, VIC 3010, Australia*

*a.rapson@pgrad.unimelb.edu.au*

Biological membranes perform and regulate a number of important functions in cell life, such as transport regulation and signal transduction between the cell and its environment. The role of the lipid bilayer - the 'backbone' of the cell membrane – is crucial to these processes and thus, there is a great interest in investigating the structural and biophysical properties of membrane bilayers. However, biological membranes are complex systems that undergo many dynamic operations and thus, it is extremely difficult to elucidate specific characteristics of membrane bilayers.

Over time, there have been various systems used to mimic membrane bilayers, in order to provide control over the complexity of the system. The emergence of surface-selective techniques such as atomic force microscopy and quartz crystal microgravimetry have led to the use of planar lipid bilayers (formed at a solid-water interface) as membrane mimics, with the most popular technique for their formation being the adsorption and subsequent rupture of lipid vesicles upon the solid substrate.

There are a number of factors impacting upon the formation and characteristics of supported lipid bilayers formed through vesicle deposition, many of which are not fully understood. In this presentation, the effect of some of these factors will be discussed.

## Shear Enhancement in the Gravity Thickening Process

Rudolf Spehar<sup>1</sup>, Shane P. Usher<sup>1</sup>, Murray Rudman<sup>2</sup>, Peter J. Scales<sup>1</sup>

<sup>1</sup>*Particulate Fluids Processing Centre, Department of Chemical and Biomolecular Engineering, University of Melbourne, VIC, Australia*

<sup>2</sup>*CSIRO Manufacturing and Infrastructure Technology, Graham Road, Highett, VIC, Australia*

Gravity thickening is a dewatering process that is in high demand in the minerals and waste treatment industries as it can process high volumes of low solid concentration suspension and is relatively inexpensive. The aim of thickening is to increase the solids concentration of particulate slurries by exploiting the difference in densities between the solid and liquid phases. The unit equipment item in which thickening is conducted is referred to as a 'thickener'. A thickener is essentially a large vessel in which a particulate suspension is allowed to settle out into a particulate rich underflow and particulate free overflow using gravity as a driving force.

Although thickening is 'old' technology and the premise behind it is relatively straightforward, existing dewatering theories are yet to successfully predict industrial thickener behaviour. One of the reasons for this lack of success is that current models do not take into account in-situ shear processes. The aim of this work is to model thickener behaviour with an emphasis on shear in material dewaterability. This will allow for further optimisation of industrial thickening processes which is vital in reducing expenditure and providing sustainable process operation.

Materials can be characterised for dewatering via laboratory batch settling and pressure filtration tests. Of particular interest are the effect of shear on the compressive yield stress,  $P_y(\phi)$ , the hindered settling function,  $R(\phi)$ , which are fundamental dewatering material properties dependant on the solids volume fraction,  $\phi$ . The fundamental material properties are incorporated into a single differential equation which describes the dewatering phenomena (Buscall and White 1987).

Mathematica codes have been developed which solves the governing differential equation for 1-D thickening via explicit and semi-implicit numerical methods. These algorithms have been updated to include solids bed height control, which will enable steady state behaviour predictions. Current work involves incorporating results from laboratory & pilot scale experiments (which include shear), into the 1-D thickening algorithm in order to predict the effects of shear processes on thickener behaviour. Computational Fluid Dynamics simulations via the CFX-11 package are also being conducted in order to visualise the impact of shear from thickener raking elements and thickener walls.

### References

Buscall, R. and L. R. White (1987). "The Consolidation of Concentrated Suspensions." J. Chem. Soc. Faraday Trans. I **83**: 873-891

## Imaging Aerosol Particles Using Atomic Force Microscopy

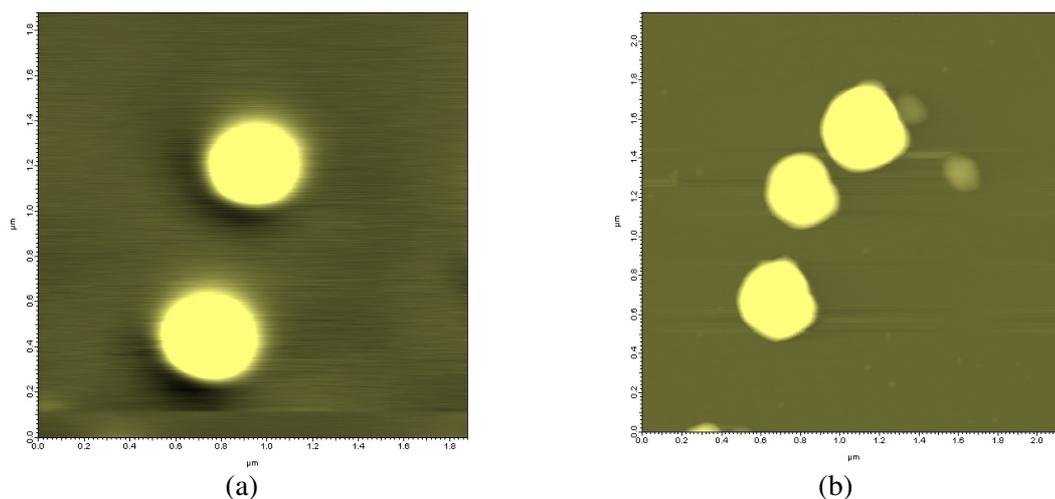
Stefanie Pui-Shan Sham and Raymond R. Dagastine

*The Particulate Fluids Processing Centre and  
the Department of Chemical and Biomolecular Engineering  
The University of Melbourne, Vic 3010, Australia*

*stefaniesham@hotmail.com*

Climate change has become a universal concern in recent years. Aerosol particles constitute one of the largest fractions of atmospheric pollution and have a significant effect on global warming. Aerosols, which are solid-liquid mixed phase systems dispersed in air, are complex combinations of organic and inorganic materials. However, despite the knowledge of their primary physical structure, the relationship between size and morphology for many atmospheric nanoparticles is not well understood.

Sodium chloride, leucine, glutaric acid, glutamic acid aerosol particles were generated and imaged using atomic force microscopy. Both the size distributions and surface morphology were observed to vary with pressure and concentration for NaCl. Specifically, the size of NaCl increased upon both pressure and concentration rise and their shape transformed from spheres into shapes exhibiting regular crystallographic faces. Conversely, organic particles exhibited vastly different shapes: leucine displayed irregular shape; glutaric acid showed platelet while glutamic acid bore a spherical shape. In brief, it was hypothesized that the variations demonstrated in both the size distribution and surface morphology of aerosols were caused by differences in their wettability, nucleation, growth and precipitation/crystallization rates.



**Figure.** Height images of NaCl particles generated from solutions (a) at 1g/L, and (b) at 5g/L.

## Understanding the Self-Assembly of Dairy Proteins in Real Time in Skim Milk Systems with Varied Casein to Whey Protein Ratios

Mandeep Jeswan Singh<sup>1,2</sup>, Ian McKinnon<sup>1</sup>, Maryann Augustin<sup>2</sup>, Punsandani Udabage<sup>1</sup>

<sup>1</sup>*School of Chemistry, Monash University Clayton, 3168 VIC Australia*

<sup>2</sup>*Food Science Australia, Sneydes Road, Werribee, 3030, VIC, Australia*

Heat treatment is an integral part of processing in the dairy industry. Its objective is to destroy microorganisms to prevent spoilage and enable longer shelf life as well as to change the functional properties of the milk through modification of the proteins. However, heat treatment causes chemical and physical changes in the milk the most important of which are the denaturation of the whey proteins and precipitation of colloidal calcium phosphate. Denaturation of the whey proteins leads to irreversible aggregation of the whey proteins with the casein micelles which can lead to thickening and gelation, and aggregation of denatured whey proteins and casein molecules leading to the formation of *soluble aggregates* – that is aggregates remaining in the supernatant after ultracentrifugation at 30,000 g (25 °C). The precipitation of the colloidal calcium phosphate leads to a drop in milk pH which in turn affects the extent and nature of the aggregation of the proteins. The aim of this work is to understand the effects of changing the ratio of the caseins to whey proteins on the behaviour of skim milk on heating – an area of increasing commercial importance as the protein content of milk is supplemented with whey protein.

Results so far demonstrate:

- a) That the drop in pH on heating is independent of the type of protein present.
- b) The application of the light scattering technique *Diffusing Wave Spectroscopy* as tool to identify whey protein denaturation and the onset of aggregation and comparison between the medium viscosity as determined by *Diffusing wave spectroscopy* and the bulk viscosity as determined by conventional viscometry.
- c) the strong pH dependence of the transfer of caseins from the micellar to the serum phase is very dependent on pH
- d) the strong pH dependence on the stability of the the casein micelles on heating.
- e) The way in which the pH of the medium mediates the extent and type of aggregation on heating.

## Two Dimensional Organisation of Solid Polymeric Nanoparticles

A. Stapleton, E.J. Wanless, W. Belcher

*Centre for Organic Electronics, School of Environmental and Life Sciences, University of Newcastle, Callaghan  
NSW 2308*

*Andrew.Stapleton@studentmail.newcastle.edu.au*

A range of polymer nanoparticles have been synthesised using a miniemulsion ultrasound process resulting in particles in the range 60-100 nm. The process involves sonication of an organic polymer solution in the presence of an aqueous surfactant solution. This results in an aqueous colloidal dispersion of polymer nanoparticles. The preparation has been characterised through control of system variables including their impact on particle size and size distribution, namely, sonication time/amplitude, surfactant concentration and polymer size. The resulting polymer dispersions have been spin coated on to a glass substrate to investigate the organisation of particle arrays. The resulting arrays have been characterised using AFM and SEM.

The findings have been extended to the fabrication of conducting polymer particles using the same technique. This study has the view to incorporate the nanoparticles into organic solar cells, enabling the control of active layer morphology and charge mobility within photovoltaic devices, greatly improving their efficiency and ease of manufacture.

## Brownian Diffusion of Ultrafine Particles to an Air-Water Interface

Sin Ying Tan, Catherine Whitby, Daniel Fornasiero and John Ralston

*Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia*

*Sin.Tan@postgrads.unisa.edu.au*

Particle-bubble interactions are important in many industrial processes such as removal of suspended solids from wastewater, removal of ink from paper and separation of valuable minerals from gangue minerals. Particles interact with bubbles via different mechanisms, depending on their size. The interaction between large particles (diameter < 100  $\mu\text{m}$ ) and bubbles are dominated by gravity or inertial effects. The collision of finer particles with bubbles is less efficient due to their smaller mass and lower momentum. Particle-bubble interaction has been widely explored and modelled. The models that are most relevant to Brownian diffusion of particles to a bubble are those of Reay and Ratcliff (1973), Yang *et al.* (1995), Ramirez (2000), Rulyov (2001) and Nguyen *et al.* (2006). The mechanism of interaction of ultrafine particles (diameter < 1  $\mu\text{m}$ ) with bubbles is complex. It involves the diffusion of particles in solution to the bubble and their subsequent attachment to the bubble surface. The diffusion coefficient of particles ( $D$ ) in solution is given by the Stokes-Einstein equation:

$$D = \frac{k_B T}{3\pi\eta_f d_p} \quad [1]$$

It is a function of particle diameter ( $d_p$ ), solution viscosity ( $\eta_f$ ) and temperature ( $T$ ). The particle-bubble attachment process depends on the hydrophobicity and charge of particle. To enhance the interaction of ultrafine particles with bubbles, the understanding of the particle diffusion rate is crucial.

The overall aim of this study is to investigate the diffusion of ultrafine particles to an air-water interface. We have investigated the Brownian motion of silica particles in aqueous dispersions by dynamic light scattering (DLS). Silica particles of different sizes between 100 to 1000 nm were synthesized by the Stöber method (Stöber & Fink, 1968). The diffusivity of particles in solution was studied as a function of particle size and solution temperature and viscosity. These findings are important for the studies of particle diffusion to an air-water interface.

The outcome of this study is vital in understanding the role of Brownian diffusion of ultrafine particles to an air-water interface. This study suggests that with decreasing particle size, the probability of particles interaction with bubbles increases.

### References

- Nguyen *et al.*, *Chemical Engineering Science*, 61, 2494-2509, 2006  
Ramirez *et al.*, *Chemical Engineering Science*, 54, 149-157, 1999  
Reay & Ratcliff, *Canadian Journal of Chemical Engineering*, 51, 178-185, 2004  
Rulyov, *Institute of Biocolloid Chemistry of Ukrainian National Academy of Sciences*, 1-22, 2001  
Stöber & Fink, *Journal of colloid and interface science*, 26, 62-69. 1968  
Yang *et al.*, *Journal of Colloid and Interface Science*, 169, 1, 125-134, 1995

## Structure and Function of Dynamin in Room Temperature Ionic Liquids

John Tulloch, Adam M<sup>c</sup>Cluskey and Rob Atkin.

*Chemistry, Centre for Organic Electronics,  
School of Environmental and Life Sciences,  
The University of Newcastle, Callaghan, 2308, Australia*

Dynamin is a family of three enzymes essential for endocytosis of synaptic vesicles in the brain and for the internalisation of activated receptors in all cells. Dynamin has a high GTPase activity that is essential for its function in endocytosis, and mutations in dynamin have been shown to cause at least two human diseases. Recent work conducted by this group has shown that the addition of certain ionic liquids (ILs) to an aqueous protein solution can act to either increase or decrease dynamin activity, and that this change in activity is dependant on the IL concentration. Furthermore, different species of ILs can act to aid or inhibit the aggregation of dynamin into its tetrameric form. The aim of this work is to develop a comprehensive understanding of the structure and activity of dynamin in the presence of several targeted ILs as a function of the IL:water ratio.

## **Block-Copolymers as Effective Surface Active Agents in Ionic Liquids.**

Deborah Wakeham,<sup>1</sup> Erica Wanless,<sup>1</sup> Greg Warr<sup>2</sup> and Rob Atkin.<sup>1</sup>

*1. Chemistry, Centre for Organic Electronics,  
School of Environmental and Life Sciences,  
The University of Newcastle, Callaghan, 2308, Australia*

*2. School of Chemistry, Building F11,  
The University of Sydney, 2006, Australia.*

Low melting-point and room temperature ionic liquids (ILs) are substances whose physical properties have so far been vastly under-exploited. Recently increasing attention has been paid to amphiphilic self-assembly in ILs, generally using surfactants optimised over many years for use in aqueous environments. These surfactants have been found to be relatively ineffective in ILs, requiring much higher concentrations and longer hydrocarbon tail groups to produce effects corresponding to those observed in water. In this work we will investigate the solubility of a range of polymers in ILs to identify or produce co-polymers that are amphiphilic and have high surface activity in ILs. The bulk properties of block copolymers in ILs will be investigated. Following this, their use as surfactant efficiency enhancers in IL-based microemulsions and their properties adsorbed at the solid-IL interface will be studied for various ILs.

## Investigation of colistin liposomal formulations

Stephanie. J. Wallace<sup>1</sup>, Ben. J. Boyd<sup>2</sup>, Jian Li<sup>1</sup>, Roger. L Nation<sup>1</sup>

<sup>1</sup>*Facility for Anti-Infective Drug Development and Innovation, <sup>2</sup>Department of Pharmaceutics, Victorian College of Pharmacy, Monash University, Vic 3052, Australia.*

*Stephanie.Wallace@vcp.monash.edu.au*

Colistin is an old antibiotic that it is increasingly used to treat infections caused by highly resistant strains of *Pseudomonas aeruginosa* and *Acinetobacter baumannii*. Most commonly, colistin is administered in the form of an inactive prodrug, colistin methanesulphonate (CMS), either intravenously or via the lungs where it hydrolyses produce colistin. Improved formulations of CMS/colistin that provide high, sustained local concentrations may provide superior efficacy and optimal pharmacokinetics, while minimising toxicity. As a consequence, the potential for CMS/colistin to be formulated into liposomes has been investigated.

CMS and colistin liposomes were prepared by lipid hydration. Characterisation of CMS and colistin in phosphatidylcholine liposomes included zeta potential and particle sizing. An assessment of the physical stability of colistin and CMS liposome formulations was also carried out. Liposomes containing CMS have been shown to be physically and chemically unstable with the separation of oily and aqueous phases. Negatively charged CMS is known to hydrolyse to form cationic colistin, a concept supported by both zeta potential measurements (CMS liposomes became more positively charged over time) and particle size growth, indicating a charge reversal phenomenon. These results have indicated that CMS liposomes, in their simple form, are unlikely to present a useful dose form for altering the pharmacokinetics of pulmonary administered CMS.

# Glycation of Deamidated Wheat Proteins with Different Mw Maltodextrins and the Effect on their Emulsification Properties

Benjamin Wong<sup>2</sup>, Donald McNaughton<sup>2</sup>, Li Day<sup>1</sup>, and Maryann Augustin<sup>1</sup>

<sup>1</sup>Food Science Australia, 671, Sneydes Road, Werribee, Vic 3030, Australia

<sup>2</sup>School of Chemistry, Monash University, PO Box 23, Vic 3800, Australia

Tziak.Wong@sci.monash.edu.au

Protein glycation involves the conjugation of an amine group of an amino acid within a protein molecule and a reducing group of a carbohydrate. The attachment of a carbohydrate has been found to alter the functional properties of proteins. A naturally occurring glycation method based on the first step of the Maillard reaction is regarded as an acceptable method for modifying protein functionality<sup>1</sup>. Due to the interest in this reaction for altering protein's functionality, there have been numerous studies on the structure and function of glycated milk proteins<sup>2</sup>, bovine serum albumin<sup>3</sup>, soy protein<sup>4</sup> and egg protein<sup>5</sup>. To our knowledge there has been no published work on the glycation of deamidated wheat proteins.

The utilisation of wheat proteins is limited by its poor water solubility, which is a prerequisite for most physical functional properties<sup>6</sup>. Its solubility is able to be significantly improved through deamidation, which converts its many glutamine residues to glutamic acid. It has been shown that deamidated wheat proteins is able to form much stable emulsions compared to soy protein isolate, sodium caseinate and whey protein isolate, which highlights its potential to be utilised as food emulsifier<sup>7</sup>. However, the functional properties of most proteins may be altered as a result of food processing<sup>1</sup>. The aim of this study is to investigate the potential of protein glycation on the functional properties of deamidated wheat proteins. Glucose and various maltodextrins with different Mn (1 kDa, 2kDa and 4 kDa) were used in this investigation.

This study found that it is feasible to form deamidated wheat proteins-carbohydrate conjugates via the Maillard reaction at 60°C and at 75% relative humidity. In addition, it was found that the mono- and oligosaccharides that were present in maltodextrins were conjugated with approximately 5 carbohydrates attached per protein molecule. Preliminary studies using circular dichroism (CD) indicated that glycation did not change the protein structure. The ability of glycated proteins to maintain emulsion stability in different calcium chloride concentrations was altered compared to native proteins. However, the glycated proteins formed more stable emulsion compared to heated protein alone, with stability improving with increasing molecular weight of the carbohydrate used for conjugation.

[1] Kato, Food Science and Technology Research, 8, 193

[2] Shepherd et al., Food Hydrocolloids, 14, 281, 2000

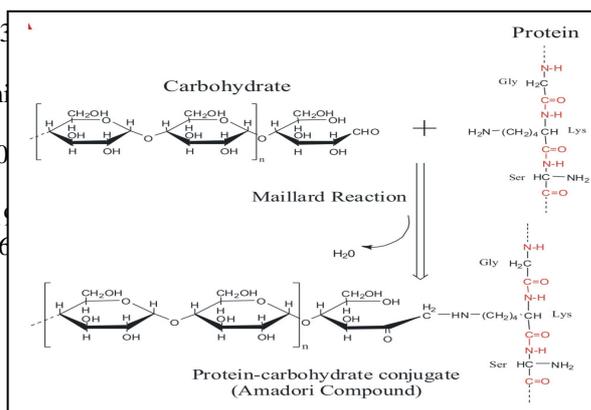
[3] Kim et al., Journal of Agriculture and Food Chemistry, 51, 2003

[4] Achouri et al., Journal of Food Science, 70, C270, 2003

[5] Campbell et al., Nahrung, 47, 369, 2003

[6] Ratel et al., In: Development in food proteins, 302, 1998

[7] Webb et al., Food Chemistry & Toxicology, 67, 2896, 2003



## Shear responsive flocculation and improved dewaterability of talc suspensions

Kai Ying Yeap, Jonas Addai-Mensah\*, and David A. Beattie

*Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia*

*kai.yeap@postgrads.unisa.edu.au*

During minerals processing, colloidal clay mineral waste tailings are produced as a result of hydrometallurgical, valuable mineral extraction activities. Conventional polyacrylamide flocculant-assisted dewatering in gravity thickeners lead to fast settling but low to moderate solid content (e.g. 25 – 35 wt%) sediments that create significant long-term tailing dam impoundment problems. Whilst thickening process optimisation involving conventional polymeric flocculants structure types, dosage and hydrodynamics may improve clay dispersion flocculation performance and enhance clarification rates, the resulting floc structures are typically not conducive to compact consolidation, even under modest shear or compression conditions [1, 2].

In this study, the influence of interfacial chemistry and shear on flocculation and consolidation behaviour of 8 wt% talc clay dispersions has been investigated using unconventional, non-ionic polyethylene oxide (PEO) flocculant at pH 7.5. The flocculation performance was strongly dependent upon the polymer concentration (100 – 500 g·t<sup>-1</sup> solid), polymer molecular weight (4×10<sup>6</sup> vs. 8×10<sup>6</sup> Da), and agitation rate (100 – 500 rpm). Significant improvement in settling rate was observed in the presence of 10<sup>-2</sup> M Mg(II) metal ion due to the reduction in particle zeta potential and at higher than at lower polymer molecular weight. Furthermore, an optimum agitation rate reflecting maximum settling behaviour was observed. However, the polymer dosage and agitation rate used in the orthokinetic flocculation step did not have any noticeable effect on the extent of sediment consolidation which was  $\approx 35 \pm 2$  wt% solid. PEO flocculated dispersions showed dramatic improvement in consolidation upon shear. Pre-sedimented flocculated pulps sheared at 100 rpm for 10 min readily dewatered further with a marked increase of 12-16 wt% in solid content. Floc structure and concomitant dewaterability are being optimized via agitation rate and PEO flocculant dosage in order to minimize volume of clay tailings and maximize process water recovery for reuse.

### References:

1. McFarlane, A., K. Bremmell, and J. Addai-Mensah, *Improved dewatering behavior of clay minerals dispersions via interfacial chemistry and particle interactions optimization*. Journal of Colloid and Interface Science, 2006. **293**(1): p. 116-127.
2. McFarlane, A.J., K.E. Bremmell, and J. Addai-Mensah, *Optimising the dewatering behaviour of clay tailings through interfacial chemistry, orthokinetic flocculation and controlled shear*. Powder Technology, 2005. **160**(1): p. 27-34.

## Effect of high-frequency ultrasound treatment on the physico-chemical properties of starch granule suspensions

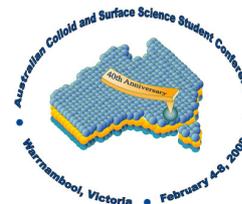
Jenny Zuo<sup>a</sup>, Muthupandian Ashokkumar<sup>a</sup>, Sandra Kentish<sup>a</sup>,  
Raymond Mawson<sup>b</sup>, Kai Knoerzer<sup>b</sup>

*a) Particulate Fluids Processing Centre, University of Melbourne, VIC 3010, Australia*

*b) Innovative Foods Centre, Food Science Australia, Private Bag 16, Werribee VIC  
3030, Australia*

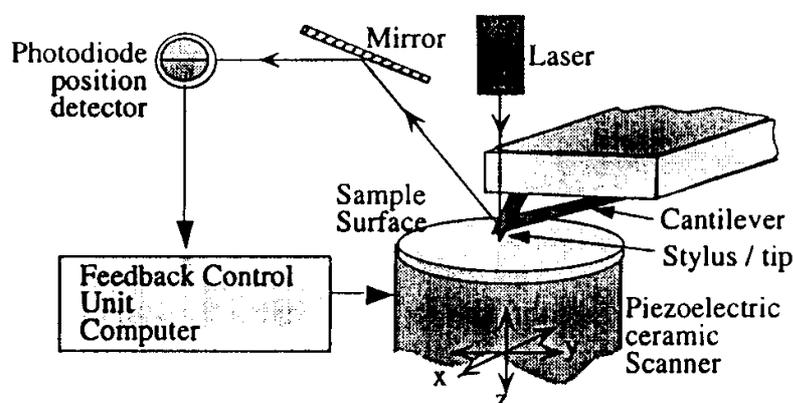
High-power ultrasound treatment, or sonication, can be used on starch pastes as an alternative method for molecular degradation, and controlling the viscosity of the starch pastes. In the present study, the effect of 211 kHz-ultrasound on the physico-chemical properties of rice starch has been investigated. A starch dispersion, of constant concentration of 5 wt%, was treated at a constant temperature of 62.9°C and different sonication times, ranging from 0 to 60 minutes. Rapid Visco<sup>TM</sup> Analyser (RVA) was used to measure the pasting curves of sonicated starch solutions. It was observed that with an increase in sonication time, peak and final viscosities of the starch solutions decreased. Light microscopy analysis had shown a significant loss of birefringence due to sonication. Both pasting curve and light microscopy results suggest that the observed effects may be due to cavitation-generated radicals and mechanochemical effects.

# Experimental Techniques



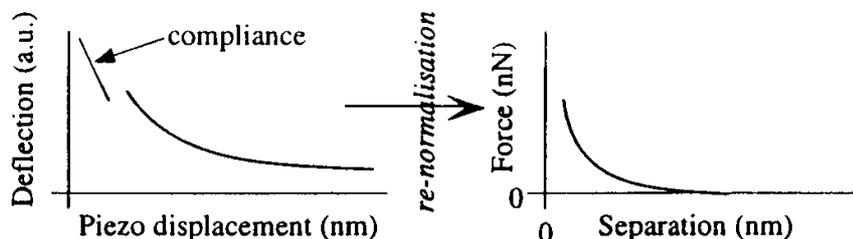
## (Atomic) Force Microscopy

The 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 a 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 the force microscope the translating mechanism is a piezoelectric ceramic, and the probe is comprised of a sharp tip affixed to the free end of a cantilever. In its simplest operation as the sample is raster scanned under the tip which traces the contours of the surface causing the cantilever to be deflected. Thus the magnitude of the cantilever deflection is recorded as a function of sample position. Using feedback the piezo can be made to react to maintain the cantilever at a present deflection, and hence force. In this mode of operation the data collected is presented graphically as a topograph. Cantilever deflection is commonly determined by the displacement of a laser beam reflected off the free end of the cantilever (light-lever) technique.



*Schematic of a light-lever force microscope*

This scheme will operate in any non-viscous, optically transparent fluid. The tip may be replaced with other materials of different chemistry and geometry. Apart from providing information about surface topography and heterogeneity the scanning function can be disabled and the instrument be controlled such that only cantilever deflection versus normal displacement of the piezo is recorded. Curves of force versus relative surface separation can be obtained by normalising this deflection curve by the slope of the linear region found when the two surfaces are in 'contact' (compliance). Thus the interaction between two surfaces can be measured on colloidal length scales, {force O(pN -  $\mu$ N), distance O( $\text{\AA}$ - $\mu$ m)}. Tip composition and geometry may be varied.

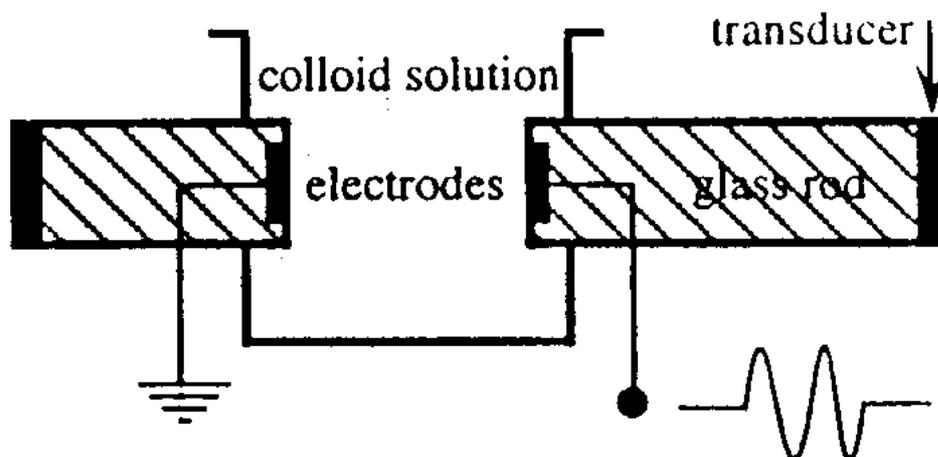


### Suggested reading:

DiNardo, J., Nanoscale Characterisation of Surfaces and Interfaces, VCH, Weinheim, (1994).

## 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 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.



*Schematic of the “AcoustoSizer” cell.*

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.

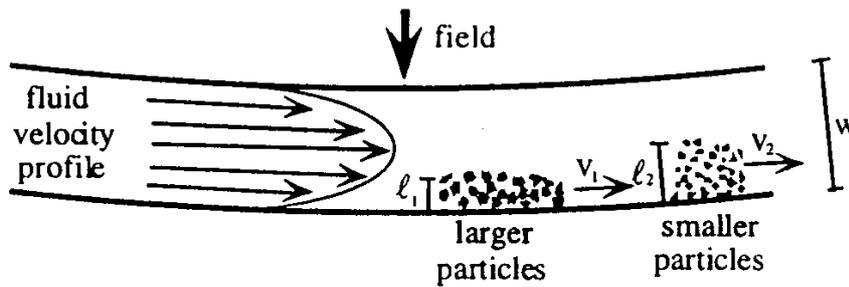
The dynamic mobility is a complex quantity equal in magnitude to the ratio of the particle velocity divided by the applied field. It is complex because there is a phase lag between driving frequency and the response of the particles to that field. As the applied field tends to zero the mobility becomes a real quantity, equal to the electrophoretic mobility defined for a static (DC) applied field. Field strengths are in the order of  $100 \text{ Vm}^{-1}$ , and at MHz frequencies typical particle displacements are in the order of  $10^{-13} \text{ m}$ . At low frequencies the inertia of the particle 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 colloids 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.

### Suggested reading:

O’Brien, R.W., Cannon, D.W. and Rowlands, W.N., Electroacoustic determination of particle size and zeta potential, *J. Colloid Interface Sci.*, 173, 406 (1995).

## Field-Flow Fractionation

Field-flow fractionation is a set of high-resolution liquid chromatography-like elution methods used for sizing and separating various samples including humic substances, clays, bacteria, viruses and polymers. There are several FFF sub-techniques (eg. sedimentation, flow, thermal and SPLITT) which are specific for certain samples. The mechanism for separation involves only physical interactions. Particles are injected onto the channel without the field turned on (i.e. centrifugal, crossflow, thermal, gravitational). The particles are evenly distributed across the channel. Then a field is applied which compresses the solute zone into a narrow layer against one wall. When the liquid flow is initiated, the solute zone is carried downstream at a rate depending on the layer thickness,  $\ell$  which can be related to the particle size.

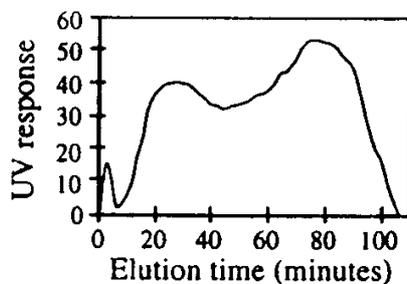


*A schematic diagram of a sedimentation FFF channel.*

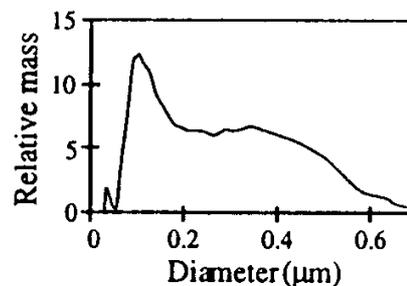
The data obtained is called a fractogram. The elution time can be converted to particle diameter using the equation;

$$d = \sqrt[3]{\frac{6kT}{\pi\omega^2 rw\Delta\rho\lambda}}$$

where,  $k$  is Boltzmann constants,  $T$  is the absolute temperature,  $w$  is the channel width,  $\Delta\rho$  is the density difference between the particle and the carrier,  $\omega$  is the field strength,  $\lambda$  is the retention parameter obtained directly from the measured retention time. Hence a particle size distribution can be calculated.



*Typical Fractogram*



*Particle Size Distribution*

### Suggested reading:

Giddings, J.C., Field-flow fractionation: analysis of macromolecular, colloidal and particulate materials, *Science*, 260, 1456 (1993).

*Summary provided by Jason van Berkel*

## Flotation

Flotation or froth flotation is a simple and inexpensive process used for the separation of particles (less than 500 microns) based on hydrophobicity differences of their surfaces. Only hydrophobic particles attach to gas bubbles (less than 2 mm) rising through the mineral pulp. At the top of the flotation cell, these gas bubbles break up allowing the floated particles to be recovered (Hallimond flotation tube). 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 mineral particles and therefore increase their attachment to gas bubbles (only a few minerals are naturally hydrophobic, for example, talc, sulfur and 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 imparts hydrophobicity to 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, fats, rubber, dyes, glass, plastics, etc.

### Suggested reading

Matis, K.A. and Zouboulis, A.I, An Overview of the Process. Flotation Science and Engineering (Matis, K.A., Ed.), Marcel Dekker, New York, pp.1-43 (1995).

Fuerstenau, M.C., Miller, J.D. and Kuhn, M.C. in Chemistry of Flotation, AIME, New York (1985).

*Summary provided by Daniel Fornasiero*

## Light Scattering

**Dynamic Light Scattering (DLS)**, also known as Photon Correlation Spectroscopy (PCS) uses the time dependence of the intensity of the scattered light to determine the translational diffusion coefficient of small particles. If a laser beam illuminates a suspension, and the scattered light is collected over a small solid angle, then the light will exhibit intensity fluctuations on the order of microseconds to milliseconds time scale. This is because the Brownian motion of the scatterers causes the phase of the light scattered from each particle to change with time, hence the total scattered intensity also fluctuates with time.

From the intensity fluctuations it is possible to determine the electric field auto-correlation function

$$|g^{(1)}(\tau)| = \exp(-\Gamma\tau)$$

Here  $\Gamma = K^2 D_T$  is the decay constant,  $D_T$  is the diffusion coefficient and  $K$  is the magnitude of the scattering vector. For spheres, the Stokes-Einstein relationship applies and the diffusion coefficient can be related to the hydrodynamic radius by

$$D_T = \frac{k_B T}{6\pi\eta r}$$

Here  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $\eta$  is the viscosity of the suspending liquid. This relationship is the basis for particle sizing by DLS.

**Classical light scattering** involves measurement of the total scattered intensity of light as a function of angle, concentration, or both. This is commonly summarised in a Zimm plot, which is described by the equation

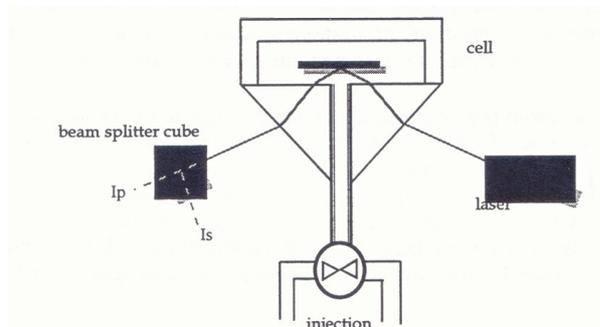
$$\frac{Hc}{R(\theta, c)} = \frac{1}{M_w} \left[ 1 + \frac{r_g^2 K^2}{3} \right] + 2A_2 c$$

Here  $c$  is the concentration,  $R(\theta, c)$  is the excess Rayleigh ratio,  $K$  is the magnitude of the scattering vector, and  $H$  is an optical constant. Scattered light intensities are measured at several angles for each solution concentration and the pure solvent. It is then possible to determine the molecular weight,  $M_w$ , the radius of gyration,  $r_g$ , and the second virial coefficient,  $A_2$ , for the species under investigation.

*Summary provided by Roland Keir*

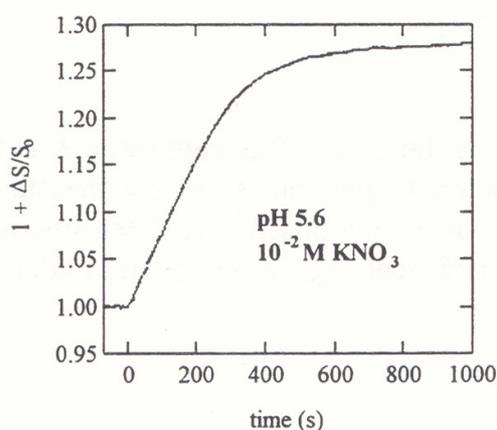
## Reflectometry

This technique can be used to determine the kinetics of adsorption of polymers and nanoparticles at the solid-liquid interface. It is a simpler variant of ellipsometry and is readily combined with a stagnant point flow cell to measure adsorption under hydrodynamically well defined conditions.



*Schematic of reflectometry in stagnant point flow*

The surface of interest, usually a thin film (20-200nm thick) on a silicon wafer, is irradiated with a linearly polarised monochromatic and collimated beam (a He-Ne laser is often used). The refractive index difference between the film and wafer changes the polarisation of the incident beam. Passage of the reflected beam through a polarising beamsplitter cube allows detection of the intensity of the parallel and perpendicular polarised components. Adsorption of molecules or particles at the surface will change the refractive index immediately adjacent to the film and consequently, the ratio of the parallel/perpendicular components ( $S$ ). It is the measured change in this ratio ( $\Delta S/S_0$ ) with time that provides the desired kinetic information



*A typical reflectometer trace obtained for 90nm silica particles adsorbing on an aminosilane treated silicon wafer*

Adsorption processes, involving polymer and particles, that occur on timescales of a minute or longer are readily monitored. To convert the raw optical data into adsorbed amount (calibration) an optical model, which treats the system as a series of flat, parallel layers of uniform refractive index is used. The method is not sensitive to the confirmation of the adsorbed layers, unlike ellipsometry. However, its simplicity lends itself to kinetic studies in a range of liquids and particularly to sequential adsorption processes.

### Suggested Reading:

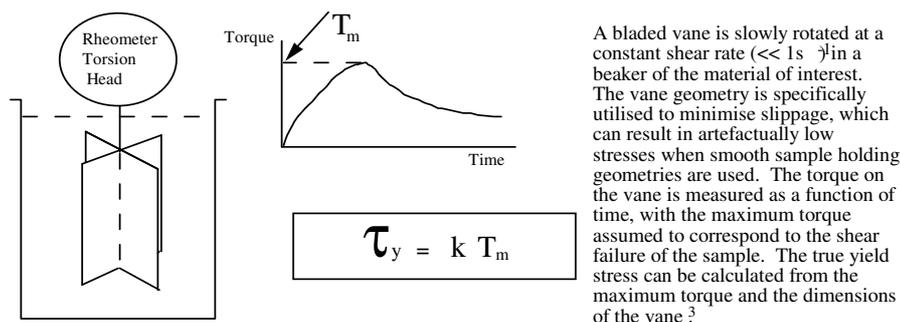
Dijt, J.C. Chohen Stuart, M.A., Hofman, J.E. and Fler, G.J., Kinetics of polymer adsorption in stagnation point flow, *Colloids and Surfaces*, **51**, 141 (1990)

*Summary provided by Rob Hayes*

## Concentric Cylinder Rheology

Rheology is the study of material flow under application of deformation. In practice, rheology is concerned with the flow, transport and handling of complex fluids such as dispersions, emulsions, foams, polymer melts and polymer solutions. Many industrial processes, including minerals processing, waste disposal, food and pharmaceutical formulation and polymer processing are highly rheologically sensitive. Rheological properties are commonly measured using concentric cylinder rheometers, which may operate in either constant stress or constant rate modes. Constant stress devices induce a stress in the sample by way of a torque induction motor and precisely measure its deformation, often with an optical encoder. Constant rate devices shear the sample at predefined shear rates and measure the torque, hence stress, by way of a transducer. Both types of instruments can be used in static or dynamic modes to measure flow or viscoelasticity. The commercially available constant stress devices generally have the advantage of a wider range of measureable shear rates ( $10^{-6}$  to  $10^4$  s $^{-1}$ ) and dynamic stresses or strains. Cone and plate is the preferred sample holding geometry, since homogeneous shear rates are experienced throughout the sample. However, suspensions are often analysed in cup and bob or plate and plate geometries for ease of handling and to avoid problems associated with particles in the gap between cone and plate.

In colloid and surface chemistry we are generally concerned with correlating rheological parameters with the colloidal micro-structure<sup>1</sup>. The yield value<sup>2,3</sup>, which is defined as the maximum stress achievable in a sample prior to flow, is commonly used to quantify the structure in a colloidal network and can be thought of as the elastic limit of a system under shear. Yield stresses are obtainable from the application of a model to a flow curve, e.g. Bingham (extrapolated) or Casson. The agreement of these values with the true yield value  $\tau_y$  is questionable and may be dependent on the range of shear rates analysed. The Vane technique is therefore the favoured method for yield value determination in highly concentrated dispersions.



*Schematic of the Vane technique for yield value determination*

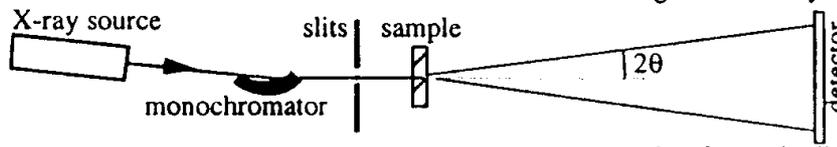
The viscoelastic characteristics of colloidal systems are also characterised by concentric cylinder rheometry, through measurement of the response to application of a sinusoidal stress or strain.  $G'$ , the storage or elastic modulus and  $G''$ , the loss or viscous modulus, are determined from the stress-strain inter-relationship and the phase angle ( $\delta$ ) between them:  $G''/G' = \tan\delta$ . For non-destructive oscillatory measurements a material should be deformed within its linear viscoelastic region, typically  $<0.1\%$  strain for aggregated suspensions. A material's viscoelastic response to frequency is generally characterised and this can then be related to colloidal interactions within the system<sup>1</sup>.

1. Tadros, Th.F., Adv. Coll. Interface. Sci. **68**, 97 (1997)
2. Cheng, D. C-H, Rheol. Acta. **25**, 542 (1986)
3. Nguyen, Q. D., and Boger, D.V., J. Rheol. **27**, 321 (1985)

*Summary provided by Clive Prestidge*

## Small Angle X-Ray Scattering

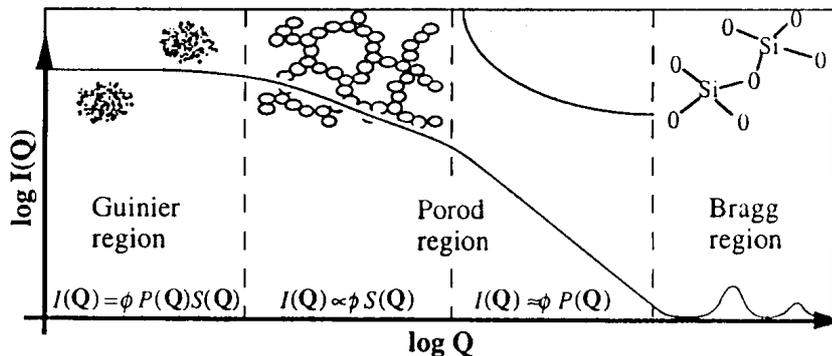
Small angle X-ray scattering allows the physical characteristics - dimensions, surface roughness and spatial arrangement - of particles ( $\text{\AA}10 - 1000\text{\AA}$ ) in solution to be studied. In practice a collimated beam of monochromatic X-rays is passed through the sample and the intensity of scattering measured as a function of scattering angle  $2\theta$  (usually  $<2^\circ$ ).



The scattering of those X-rays arises from their interaction with the electronic distribution of the scattering material, the extent of scattering is dependent on the scattering length density,  $\rho_x$ , of the material given by;

$$\rho_x = \frac{n\rho N_A b_x}{MW}$$

where  $n$  is the number of electrons in the molecular unit of the scatterer,  $\rho$  is the physical density of the scatterer,  $N_A$  is the Avogadro's number,  $b_x$  is the scattering length per electron and  $MW$  is the molecular weight of the scatterer. The intensity of the scattering signal is proportional to the square of the contrast,  $(\rho_1 - \rho_2)$ , where  $\rho_1$  and  $\rho_2$  are the scattering length densities of the particles and the surrounding medium respectively. The intensity of small angle scattering,  $I(Q)$ , is given by the general equation;  $I(Q) = \phi P(Q)S(Q)$ ;  $\phi$  is the number density of particles in solution and  $Q$  is momentum transfer,  $Q = (4\pi/\lambda)\sin\theta$ . The form factor  $P(Q)$  which contains the  $(\rho_1 - \rho_2)^2$  term, reflects the distribution of scattering material in the scattering particle and the structure factor.  $S(Q)$  is related to the spatial distribution of the scattering particles in the solvent.



At a large scattering angle, information on the atomic scale is obtained with Bragg diffraction. On the low- $Q$  side of the Bragg region information regarding the surface texture of the primary scattering particles is obtained. At slightly lower  $Q$  again information regarding the physical density of scattering material within the aggregate is accessible. In the lowest  $Q$ -region depicted here, the Guinier region, the overall dimension and shape of the aggregates can be determined.

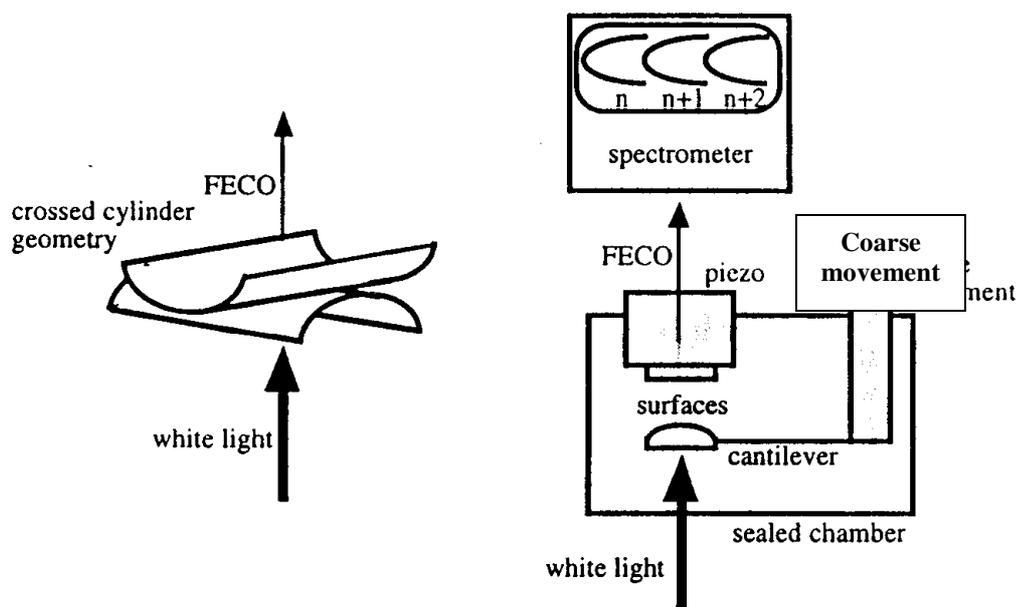
### Suggested reading:

Glatter, O. and Kratky, O. (eds), Small angle X-ray scattering, Academic Press, Sydney (1982).

*Summary provided by Julieanne Dougherty*

## Surface Force Apparatus

The Surface Force Apparatus has been the main-stay technique in the measurement of surface force for close to 30 years. Typically it is comprised of two partially silvered, thin ( $O(\mu\text{m})$ ) mica crystals, one surface supported on a piezoelectric ceramic for fine movement control, and the other on a cantilever. When white light is passed through the two opposing silvered mica surfaces the optical cavity formed transmits light of discrete wavelengths (FECO, Fringes of Equal Chromatic Order). These wavelengths are known for a given separation of the mica surfaces and refractive index of the intervening medium. By analysing the transmitted light in a spectrometer the surface separation may be determined directly (cf. force microscopy).



*Schematic of SFA with detail of partially silvered mica surfaces (left).*

In the absence of any interactions between the surfaces the separation between the two surfaces reduces at the same rate as the piezo is displaced. However, when a force acts between the two surfaces, the cantilever deflects and the separation changes by a sum of the piezo displacement and the spring deflection. As the surface separation is directly measured the deflection of the spring is taken as the difference between the measured separation and the separation expected when no force is present for a given piezo displacement. Hooke's law then gives the spring restoring force, which is equal and opposite to the measured surface force. {force  $O(0.1\mu\text{N}-\text{mN})$ , distance  $O(\text{\AA}-\mu\text{m})$ }.

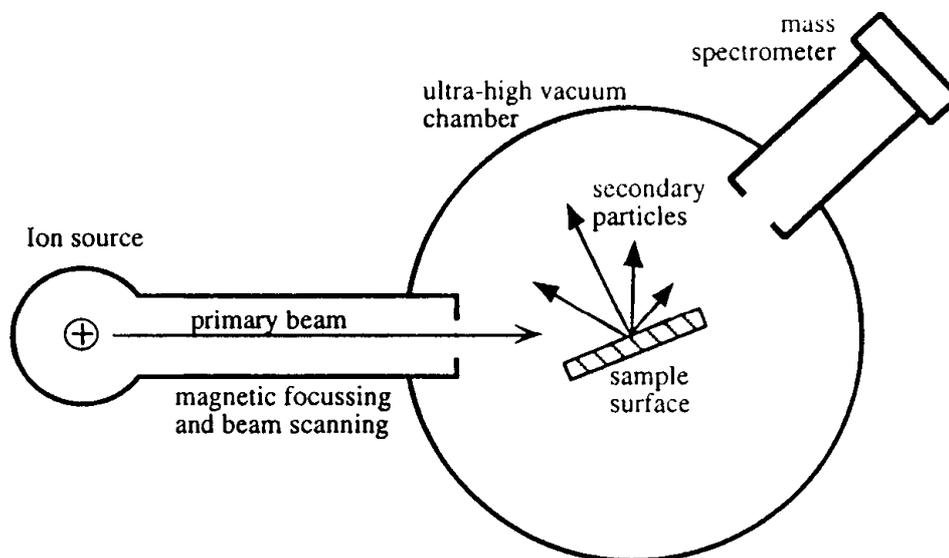
The crossed cylinder geometry approximates well as a sphere, with a radius equal to the geometric mean curvature of the two cylinders, interacting with a plane. Surfaces are restricted to those that can easily form transparent, thin smooth films, e.g. silica, sapphire, mica. Alternatively the interferometer may be formed between one reflective and one partially transmitting surface, e.g. mercury and mica.

### Suggested reading:

Israelachvili, J.N., *Intermolecular and Surface Forces*, 2nd Edition, Academic Press, San Diego (1992).

## Secondary Ion Mass Spectroscopy

SIMS is defined as the bombardment of a sample surface with a primary ion beam followed by mass spectrometry of the emitted secondary ions.



*A (very) simplified schematic of a SIMS setup.*

Primary beam species useful in SIMS include  $\text{Cs}^+$ ,  $\text{O}^{2+}$ ,  $\text{O}$ ,  $\text{Ar}^+$ , and  $\text{Ga}^+$  at energies between 1 and 30 keV. Primary ions are implanted and mix with sample atoms to depths of 1 to 10 nm. The bombarding primary ion beam produces monatomic and polyatomic particles of sample material and resputtered primary ions, along with electrons and photons. The secondary particles carry negative, positive, and neutral charges and they have kinetic energies that range from zero to several hundred eV. The SIMS primary ion beam can be focussed to less than 1 micron in diameter. Scanning where the primary ion beam strikes the sample surface provides for microanalysis, and the measurement of the lateral distribution of elements on a microscopic scale.

During SIMS analysis, the sample surface is slowly sputtered away. Continuous analysis while sputtering produces information as a function of depth, called a depth profile. Sputter rates in typical SIMS experiments vary between 0.5 and 5 nm/s. Sputter rates depend on primary beam intensity, sample material, and crystal orientation.

When the sputtering rate is extremely slow, the entire analysis can be performed while consuming less than a tenth of an atomic monolayer. This slow sputtering mode is called static SIMS in contrast to dynamic SIMS used for depth profiles.

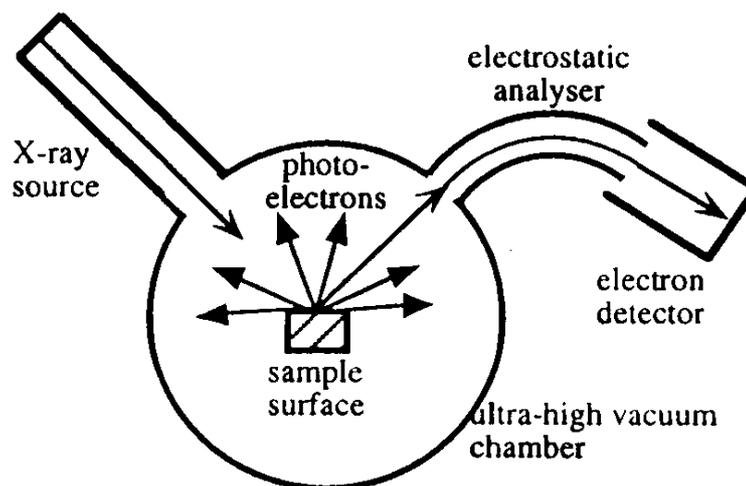
Mass spectroscopy not only provides isotopic discrimination, but both negative and positive species can also be analysed.

### Suggested reading:

Benninghoven, A., Rüdener, F.G. and Werner, H.W., Secondary Ion Mass Spectrometry; Basic Concepts, Instrumental Aspects, Applications and Trends. Wiley, New York, (1987).

## X-Ray Photoelectron Spectroscopy

XPS, also called ESCA (Electron Spectroscopy for Chemical Analysis), exploits the photoelectric effect to obtain information about the chemical composition and structure of a surface. The technique uses soft X-rays to eject electrons from core levels within the atoms. The energies of these core levels (binding energies) are characteristic of a particular element and its chemical environment.



*Schematic of XPS setup*

The kinetic energy of the emitted photoelectron,  $KE$ , is determined during the experiment,  $h\nu$  is the energy of the incident photon, hence the binding energy,  $BE$ , for the emitted photoelectron can be calculated.

$$KE = h\nu - BE - \Phi$$

where  $\Phi$  is an instrument-specific work function.

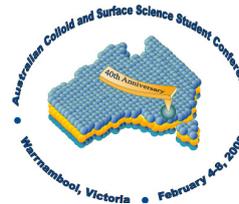
The energy of the photoelectrons emitted from an atom is also determined to some extent by the charge residing on the atom as a result of chemical bonding. Thus, a relationship between electronegativity and binding energy has been shown for many elemental systems, and a theoretical understanding of “chemical shifts” has become well-developed. From a practical point of view, it is usually possible to distinguish elemental oxidation states and sometimes other structural effects.

The kinetic energies of the photoelectrons leaving the sample are so low that, in practice, only those from the top 1-5 nm of the surface escape and arrive at the spectrometer, making it an extremely surface sensitive technique. Most elements (except hydrogen and helium) have practical detection limits of 0.02-0.2% *a/a*. This corresponds to 1-10% of a monolayer. Energy spectra are reported as binding energy against intensity. With the use of sensitivity factors, peak intensities can provide quantitative elemental surface compositions.

### Suggested reading:

Brundle, C.R. and Baker, A.D. (Ed.), *Electron Spectroscopy: Theory, Techniques, and Applications*, Vols. 1 and 2, Academic Press, London (1977).

# Index of Presenters



Robert Acres	19	Ofer Manor	72
Rory Anderson	60	Vincent Martinez	20
Linnéa Andersson	35	William McMaster	56
Joannelle Bacus	18	Donna Menzies	51
Audrey Beaussart	39	Natasa Mitik-Dineva	43
Alisa Becker	55	Anna Mularski	73
Adam Brotchie	29	Kurt Nicholson	74
Hans-Jurgen Butt	17	Zubaidah Ningsih	75
Lorena del Castillo	61	Christopher Ochs	76
Alan Chan	62	John-Paul O'Shea	49
Jayani Chandrapala	45	Shashikanth Parcha	33
Daan Curvers	63	Srinivas Parimi	50
Shyamal Das	30	Luke Parkinson	26
Terry Dermis	64	Anuttam Patra	21
Aurelia Dong	65	Luigi Petrone	38
Charlie Dong	36	Mani Paneru	22
Glenna Drisko	40	Eben Quill	77
Jason Du	41	Andrew Rapson	78
Kym Ford	66	Santanu Ray	28
Scott Fraser	67	Shoshana Rozner	44
Nasrin Ghouchi-Eskandar	52	Jan Scholz	54
Jairo Garnica	24	Iliana Sedeva	34
Mingzhao He	47	Stefanie Sham	80
Yuanhua He	53	Mandeep Jeswan Singh	81
Christine Henry	25	Rudi Spehar	79
Chris Honig	46	Andrew Stapleton	82
Shaun Howard	32	Sin Ying Tan	83
Tim Hunter	23	Boon Teo	42
Karyn Jarvis	37	Diana Tran	31
Cameron Kinnane	68	John Tulloch	84
Anat Kiviti-Manor	48	Deborah Wakeham	85
Atsushi Kobayashi	69	Stephanie Wallace	86
Anna Kogan	27	Benjamin Wong	87
Josephine Lim	70	Kai Ying Yeap	88
Jason Mann	71	Jenny Zuo	89

**The 26<sup>th</sup> Australian Colloid and Surface Science Student Conference is hosted by**



**MONASH** University  
Victorian College of Pharmacy

## ***Notes***

## **Notes**

## ***Notes***