



PROGRAMME AND ABSTRACTS

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WELCOME!

PREFACE

From humble beginnings in 1967, and with just a handful of students, Bob Hunter and Tom Healy have created a juggernaut of Australian Colloid Science. This student conference has now become an integral part of the Australian scientific calendar.

This year the conference is hosted for the first time by Swinburne University of Technology and is located, also for the first time, at the La Trobe University Bendigo Campus. The Swinburne organisers would particularly like to thank their La Trobe counterparts - John Wells, Bruce Johnson and Rod Harris - for their help with the organisation at this site.

In keeping with tradition, speakers and posters are not grouped into sessions of similar subject, university, gender or age. As always, it is hoped that students and staff alike will enjoy the informal atmosphere of the conference and actively partake of the social activities. As has been the case at previous student conferences, whatever the activities of the night before, all students are expected to meet the challenge of being present at the first talk the next morning! Also in keeping with tradition, students are encouraged to ask questions of the presenters. Chairpersons are asked to encourage this activity, and to give preference to students when accepting questions from the audience.

The number of awards available has increased this year thanks to some generous sponsorship. The Healy-Hunter Award honours the conference founders, Tom Healy and Bob Hunter, and will be presented for the third time at this conference. This year we have also introduced an award for the Most Outstanding Communicator (donated by the Centre for Applied Colloid and BioColloid Science, Swinburne). The CSIRO Division of Molecular Science and Dulux Australia have generously donated prizes for the best posters presented at their sponsored poster sessions. In addition, Nalco Australia has donated an award for the best presentation reporting the use of solid-liquid phase extraction processes.

Many traditions have developed at the conference over the years, which although are not strictly academic, foster collegiality amongst the colloid fraternity. Time has been made available on Wednesday afternoon for the "staff versus student" cricket match, although this time may also be used to explore Bendigo and its surrounds. Other activities will take place in the evenings, with a Karaoke night (Tuesday), our traditional Talent Quest (Wednesday) and the Conference Dinner (Thursday).

We trust that that you will find the conference both stimulating and enjoyable!

Marylou Molphy
(Secretary)

Lyndal Roberts

Lidia Konkol

Ian Harding
(Chairperson)

Danni Tilmanis

My Linh Ly

Russell Crawford
(Treasurer)

Choon Jek Ang

Peter Sanciolo

CONFERENCE DELEGATES

Carnegie Mellon University

John Anderson

CSIRO Division of Molecular Science

Patrick Hartley

Laurence Meagher

Patrick Vermette

Curtin University of Technology

Luke Kirwan

Dulux Australia

Matt Carr

LaTrobe University Bendigo

Mike Angove

Milena Fernandez

Rod Harris

Bruce Johnson

Kurt Lackovic

John Wells

Monash University

Dorothy Attard

Ron Beckett

Ian McKinnon

Niem Tri

Saga University

Junko Akagi

Swinburne University of Technology

Choon Jek Ang

Russell Crawford

Sarath Ekanayake

Daniel Eldridge

Kristi Hanson

Ian Harding

Lidia Konkol

Greg Lonergan

My Linh Ly

Marylou Molphy

Lyndal Roberts

Peter Sancio

Danni Tilmanis

University of Adelaide

Andrew Koh

Brian Saunders

Michael Shields

University of Melbourne

Ainul Azzah Abd. Aziz

Mike Bevan

Melanie Bradley

Craig Bullen

Steven Carnie

Jamie Chamberlain

Derek Chan

Tan Chor Sing

Justin Cooper-White

Michelle Gee

Di Goodall

Chris Green

Franz Grieser

Tom Healy

Janine Hulston

Luisa Jayme

Ivana Junatan

Won-Jong Kim

Daniel Lester

Hadi Lioe

George Maurdev

Scott McLean

Heidi Mielke

Ineke Muir

Sarah Nespolo

Simon Petris

John Phair

Boris Poliak

Briony Ruse

John Sader

Peter Scales

Anthony Stickland

Rohan Tronson

Shane Usher

Don Vicedendese

Orla Wilson

Annabel Wood
Christina Yip
Sabina Zahirovic

University of South Australia

Phil Attard
David Beattie
Eric Capelle
Toni Galea
Graham Gillies
Roger Horn
Ivan Kempson
Michael Moody
Gayle Morris
Patience Mpofu
Yongjun Peng
Clive Prestidge
Sarah Schwarz
Roger Smart
Matthew Taylor
Minh-Uyen Trinh
James Tyrrell
Terry Wilks
Haliong Zhang

University of Newcastle

Rob Atkin

Sharna Glover
Michael Habgood
Aaron Olsen
Mark Reitsma
Erica Wanless
Grant Webber
Peter Yates

University of New South Wales

Ashley Jones
Robert Lamb
Antonella Petrella
Hua Zhang

University of Otago

Steve Dickinson

University of Queensland

Ian Gentle
Benjamin O'Driscoll

University of Sydney

Bob Hunter
Miles Page
Laszlo Kovacs
Greg Warr

Australian Colloid and Surface Science Student Conferences

Location	Host	Year	Location	Host	Year
Sydney	U of Sydney	1967	Roseworthy	SAIT	1985
Melbourne	U of Melbourne	1969	Kioloa	ANU	1987
Sydney	U of Sydney	1972	Albury	U of Melbourne	1988
Blackwood	U of Melbourne	1973	Camden	U of Sydney	1990
Pretty Beach	U of Sydney	1974	Roseworthy	U of South Australia	1993
ANU	ANU	1976	Deakin U	U of Melbourne	1993
Blackwood	U of Melbourne	1977	Fairy Meadow	U of Sydney	1995
Yarrawood	U of Sydney	1978	Murramarang	ANU	1996
Kioloa	ANU	1980	Hahndorf	U of South Australia	1998
Mt Eliza	U of Melbourne	1982	Morpeth	U of Newcastle	1999
Yarrawood	U of Sydney	1983	Bendigo	Swinburne U	2001

Experiment #
1
2
3
4
5

SPONSORS

The organisers gratefully acknowledge the generous sponsorship provided by the following organisations:

Centre for Applied Colloid and BioColloid Science
Colloidal Dynamics Pty Ltd
CRC for International Food Manufacture and Packaging Science
CSIRO Division of Molecular Science
Dulux Australia
Eppendorf South Pacific
Manildra Group
Nalco Australia Pty Ltd
Royal Australian Chemical Institute



SCIENTIFIC PROGRAMME

Monday 12 February

0900	On-site Registration	
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1205	<i>Lunch</i>	
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1320	Welcome	
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1330-1445	Afternoon Session 1	Chair: Erica Wanless
1330	Sarah Nespolo	Hydrodynamic and Electrokinetic Properties of Decane Droplets in SDS Solutions
1355	Miles Page	Tail Geometry Effects in Aluminium Isopropoxide/Phosphate Ester Surfactant Organogels
1420	Yongjun Peng	Effect of Grinding Conditions on Galena Flotation and Galena Separation from Pyrite in the Control of Grinding pH

1445-1520	<i>Afternoon Tea</i>	
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1520-1700	Afternoon Session 2	Chair: Roger Smart
1520	Simon Petris	Phase Separation in De-Ionised Colloidal Systems
1545	Boris Poliak	Modelling Micellar Solutions
1610	Mark Reitsma	Friction and Wear Studies using Lateral Force Microscopy
1635	Choon Jek Ang	Treatment of Printing Wastewater using Adsorbing Colloid Flotation

1700-1730	Free Time	
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1730-1830	Pre-dinner Drinks – Common Room	
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1830-2000	<i>BBQ Dinner – Common Room Area</i>	
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31st March : WCC

Tuesday 13 February

0730-0845 *Breakfast*

0900-1015	Morning Session 1	Chair: Franz Grieser
0900	Lyndal Roberts	Extraction of Nutraceutical Components from an Australian Wood Decomposing Fungus
0925	Matthew Taylor	The Flocculant Concentration Influence on the Settling Behavior and Structure of Flocculated Kaolinite
0950	Antonella Petrella	¹ A Novel Single Source Precursor for the Growth of High Quality ZnO Films

1015-1050 *Morning Tea*

1050-1205	Morning Session 2	Chair: Russell Crawford
1050	Niem Tri	Can You <i>Still</i> Hear Me? Ultrasonic Forces for Particle Separation
1115	Minh-Uyen Trinh	Characterisation and Stabilisation of Lipid-DNA Complexes for Gene Therapy
1140	Rohan Tronson	² Multibubble Sonoluminescence from Aqueous Solutions Containing Aliphatic Alcohols and Surfactants

1205-1330 *Lunch*

13.30 1520-1700	Afternoon Session 1	Chair: Brian Saunders	
-14.45	1330	Shane Usher ³	Optimisation of the Washing and Dewatering of Flocculated Suspensions
	1355	Lidia Konkol	Contaminant Levels in Recycled PET Plastic
	1420	Grant Webber ²	Adsorption Behaviour and Solution Properties of Diblock Polyelectrolyte Copolymers

1445-1520 *Afternoon Tea*

1520-1700	Afternoon Session 2	Chair: Ian Gentle
1520	Hailong Zhang	AFM Study on Tissue and Biomaterials Interaction
1545	Hua Zhang	The Simulation of Extreme Surface Roughness
1610	Andrew Koh ¹	Thermally Induced Gelation of Oil-in-water Emulsions Stabilised by Graft Copolymers
1635	Heidi Mielke	New Methods in the Rheological Characterisation of Fluid Gels

1700-1730 *Free Time*

1730-1830 CSIRO Molecular Science Poster Session

1830-2000 *Dinner*

2000- Karaoke

Bistro
7.30pm

Wednesday 14 February

0730-0845 *Breakfast*

0900-1015 **Morning Session 1**

Chair: Robert Lamb

- | | | |
|------|-----------------|--|
| 0900 | Rob Atkin | The Adsorption of Cetylpyridinium Bromide (CPBr) at the Silica-Aqueous Interface |
| 0925 | Melanie Bradley | Synthesis of Cationic Polymer Latex by Ultrasound |
| 0950 | Annabel Wood | UV-Initiated Formation of Noble Metal Nanoparticles on Zinc Oxide Quantum Dots |

1015-1050 *Morning Tea*

1050-1205 **Morning Session 2**

Chair: Derek Chan *Mc!*

- | | | |
|--------------|--|--|
| 1050 | Patrick Vermette | Control over Pegylated-Liposome Aggregation by Neutraavidin™-Biotin Interactions Investigated by Photon Correlation Spectroscopy |
| <i>10.55</i> | | |
| <i>11.20</i> | | |
| <i>A</i> | 1115 Sharna Glover
<i>Newcastle</i> | Dual Polymer Flocculation of Alumina: Aggregate Structure and Filterability <i>11.20 - 11.45</i> |
| <i>V</i> | 1140 Michael Habgood
<i>Newcastle</i> | Dynamic Surface Tension between an Aqueous Salt Solution and a Surfactant-Containing Oil Solution <i>11.48 → 12.13</i> |

1205-1330 *Lunch*

1330-1730 Free Time/Cricket Match

1730-1830 Dulux Poster Session

1830-2000 *Dinner*

2000- Talent Quest

Sorbitan monolaurate

Thursday 15 February

0730-0845 *Breakfast*

0900-1015 **Morning Session 1** Chair: John Wells

- 0900 Kristi Hanson Effects of Surfactants on the Extraction and Activity of Phenoloxidases from Spent Mushroom Substrate
- 0925 Rod Harris Selective Adsorption of Dyes to Kaolinite
- 0950 Janine Hulston Investigation of the Effects of Flocculation on the Dewaterability of 'Red Mud': Case Study on Hematite
-

1015-1050 *Morning Tea*

1050-1205 **Morning Session 2** Chair: Roger Horn

- 1050 Luisa Jayme Time Resolved Polarised Attenuated Total Reflection Spectroscopy of Protein Films at the Silica/Solution Interface
- 1115 Luke Kirwan An *In situ* FTIR-HATR Investigation of the Adsorption of Polyacrylate onto Hematite
- 1140 Jamie Chamberlain Incipient Failure of a Yield Stress Material
-

1205-1330 *Lunch*

1520-1700 **Afternoon Session 1** Chair: Ron Beckett

- 1330 Laszlo Kovacs Cationic Surfactant Aggregate Geometries and their Induced Transformations at the Solid-Liquid interface
- 1355 Kurt Lackovic *Ben Muir CSIRO* The Adsorption of *Furandicarboxylate* Oxalate to Boehmite and Gibbsite
- 1420 Daniel Lester Multi-dimensional Dewatering of Flocculated Colloidal Suspensions
-

1445-1520 *Afternoon Tea*

1520-1700 **Afternoon Session 2** Chair: Ian Harding

- 1520 George Maurdev Interaction Forces between Surfaces Immersed in Polyelectrolyte Surfactant Mixtures
- 1545 Michael Moody Investigating the Curvature Dependence of Surface Tension using Computer Simulations
- 1610 Inneke Muir Interaction Forces between Two Layers of Adsorbed Beta-Casein
- 1635 John Phair Characterisation of Aluminosilicate Hydrogels as a Model System for Waste-based Concretes
-

1700-1730 Free Time

1730-1830 Pre-Dinner Drinks

1830- *Conference Dinner*

Friday 16 February

0730-0845 *Breakfast*

0900-1020 Plenary Session

Chair: Marylou Molphy

0900 Dr Justin Cooper-White Solution Dynamics and Drops

0940 Dr David Beattie In-situ Vibrational Spectroscopy of Confined Organic Films

1020-1030 Conference Close

1030-1100 *Morning Tea*

POSTER SESSIONS

Tuesday 13 February

CSIRO Division of Molecular Science Poster Session

T1	Craig Bullen	De-Phi-ing the Odds: The Quest for Super-Luminescent Quantum Dots
T2	Eric Capelle	Alkyl Phenyl Siloxane-Copolymer Adsorption onto Titanja Pigments
T3	Steve Dickinson	Modelling Biomineralisation with Simple Organic Molecules
T4	Sarath Ekanayake	The Characterisation of Turbidity in Unfilterable Potable Water Supplies
T5	Daniel Eldridge	The Adsorption of Aqueous Heavy Metals onto Titanium Dioxide
T6	Toni Galea	Determination of Shear Viscosity of a Simple Fluid via Molecular Dynamics
T7	Graeme Gillies	The role of Deformation on the Interactions of a PDMS Sphere
T8	My Linh Ly	Water Resistant Coatings from Recycled PET
T9	Scott McLean	Protein Adsorption onto a Biomaterial
T10	Patience Mpofo	Interfacial Chemistry, Particle Interactions and Improved Dewatering of Clay Dispersions
T11	Ivana Junatan	Gelation of Biopolymer Systems under Shear

Wednesday 14 February

Dulux Poster Session

W1	Benjamin O'Driscoll	Grazing Incidence X-Ray Diffraction Study of Nanoparticle Formation in Cadmium Arachidate and Dimethyldioctadecylammonium Bromide LB Films
W2	Aaron Olsen	Effect of Shear on Flocculation of Latex with Polyacrylic Acid Dual Polymer Flocculation of Alumina: Aggregate Structure and Filterability
W3	Danni Tilmanis	Extraction of Anti-tumour Polysaccharides from Liquid Cultured <i>Agaricus blazei</i>
W4	Briony Ruse	The Environmental Impact of Mineral Processing in Australia
W5	Sarah Schwarz	Particle Transport Mechanisms within Flotation Froths
W6	Tan Chor Sing	Dynamic Interfacial Tension and Dilational Properties of C12E8 and Beta-Casein at the oil-Water Interface
W7	Michael Shields	A Study of the Effect of Surface Modification on the Stability of Poly(dimethylsiloxane) Emulsions
W8	Sabina Zahirovic	A Rheological Characterisation and Dynamic Interfacial Tension Study of Highly Concentrated Water-in-Oil Emulsions
W9	Ainul Azzah Abd. Aziz	The Effect of Pre-shear on the Dewaterability of Flocculated Suspension
W10	Christina Yip	The Effect of Size Distribution of Granulated Blast Furnace Slag on the Dissolution of Calcium
W11	Junko Agaki	The Acid-Dissolution Equilibria of Hydrous Ferric Oxides (HFO) in Various Supporting Electrolyte Solutions
W12	Anthony Stickland	Development of Synthetic Sludges for the Measurement of the Dewatering Characteristics of Sewage Sludges

CONFERENCE AWARDS

Some generous industry sponsorship has allowed several awards to be made available. These awards will be presented in addition to the traditional Healy-Hunter Award for the most outstanding oral presentation.

In each registration bag, there is a voting slip for the relevant awards, as detailed below. By ranking in order of merit the oral presentations and posters in each session, an overall winner for each award will be decided. The committee will correlate the votes and the results will be announced on Thursday evening at the Conference Dinner.

Healy-Hunter Award

The most outstanding oral presentation will be awarded the Healy-Hunter Award. This award is a prize of a \$1,000 travel grant and is voted by staff.

Most Outstanding Communicator Award

Part of the purpose in presenting papers at a student conference is to learn, by experience, effective ways of communicating scientific research to a wide diversity of audience. Ideally, each talk should be clearly presented, understandable, enjoyable and informative to both an expert and novice in the field. To encourage this, the Centre for Colloid and BioColloid Science (Swinburne) is offering an award (\$250) to the student that exhibits exemplary communication skills during their oral presentation, as voted by the students.

Nalco Australia Presentation Award

The student that presents the most outstanding presentation (oral presentation or poster) in the area of "Solid-Liquid Separation" will be awarded the Nalco Australia Presentation Award. This staff-voted award is a prize of \$500 cash.

CSIRO Molecular Science Best Poster Award

The most outstanding poster presentation in the CSIRO Molecular Science Poster Session (Tuesday evening) will be awarded the CSIRO Molecular Science Best Poster Award. This award is a prize of \$200 cash (staff voted).

Dulux Best Poster Award

The most outstanding poster presentation in the Dulux Poster Session (Wednesday evening) will be awarded the Dulux Best Poster Award. This award is a prize of \$200 cash (staff voted).

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!

ORAL PRESENTATIONS

Hydrodynamic and Electrokinetic Properties of Decane Droplets in SDS Solutions

Sarah Nespolo, Mike Bevan, Derek Chan, Franz Grieser, Geoff Stevens

*Particulate Fluids Processing Centre
Department of Chemical Engineering
The University of Melbourne
Parkville 3010, Australia*

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The interpretation of an oil droplet's surface potential from its mobility in an electric field is the same as that for a hard particle, except that the effect of slip on the droplet drag coefficient must be considered. Although the solution for a fluid droplet's drag coefficient is well known, its experimental measurement is difficult and its interpretation is complicated because of adsorbed surfactant and the possibility of deformation.

This work interprets measured electrophoretic mobilities as zeta potentials for SDS stabilized decane droplets by using light scattering to measure the oil droplets' drag coefficients. Static and dynamic light scattering were used to measure droplet size, shape, and diffusion. The results indicate monodisperse spherical droplets, which display an increasing radius with increasing SDS concentration. For all SDS concentrations used here between 0.01 mM and the SDS cmc, the droplet's drag coefficient was identical with that of a hard sphere indicating no momentum transfer at the droplet surface into the interior fluid. The zeta potentials for all SDS concentrations were found to be near 100 mV. The present ionization of the decane droplets was then considered by comparing surface charge with the SDS adsorbed amount inferred from static interfacial tension data.

Tail Geometry Effects in Aluminium Isopropoxide/ Phosphate Ester Surfactant Organogels

Miles Page and Gregory G Warr

*School of Chemistry
University of Sydney
Sydney 2006, Australia*

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The gel formed by the mixture of didodecylphosphate and aluminium isopropoxide in a non-polar solvent is an example of a self-assembled surfactant organogel. The polymer-like particles formed in such systems have the ability to break and reform with time, such that their properties depend primarily upon micellar dynamics, and thus they have been dubbed 'living' or 'equilibrium' polymers.

When didodecylphosphate and aluminium isopropoxide are mixed in a non-polar solvent, it is observed that the behaviour of the resulting self-assembled organogel is strongly dependent on the aluminium to surfactant ratio, allowing the system properties to be fundamentally altered in both phase stability and viscoelasticity. Further control of the system can be obtained by substituting (mono)dodecyl-phosphate (single tail) or bis-(2-ethylhexyl) phosphate (bulky double tail) surfactants into the system.

The effect of the altered surfactant tail on particle structure is examined. Oscillatory shear rheology is used to determine gel relaxation times and elastic moduli in order to examine implications with respect to the evolution of particle structure in the pure and mixed surfactant systems.

Effect of Grinding Conditions on Galena Flotation and Galena Separation from Pyrite in the Control of Grinding pH

Yongjun Peng, Stephen Grano, John Ralston and Daniel Fornasiero

*Special Research Centre for Particulate and Material Interfaces
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During the grinding of sulphide minerals, galvanic interaction occurs between minerals and grinding media. pH has an important influence on the redox reactions occurring on the surfaces of minerals and grinding media. In this study, a specialised mill was designed to control pH continuously during grinding. The effects of types of grinding media (mild steel and chromium) and gas purging (nitrogen, air and oxygen) on the amount of oxidation products on the surface of galena (PbS), and consequent influence on galena flotation and its separation from pyrite were investigated at pH 9.0.

By flotation tests, EDTA extractions, XPS and TOF-SIMS measurements, it was found that iron oxidation products on galena surface played a dominant role in depressing galena flotation. Therefore, the grinding condition with chromium grinding medium and nitrogen purging produced the highest flotation recovery of galena. Lead contamination from galena oxidation on pyrite surface activated pyrite flotation. The activation was decreased by the competitive adsorption of iron oxidation species. The best galena selectivity against pyrite was achieved with the grinding condition of chromium grinding medium and oxygen purging, in which iron depression of galena and lead activation of pyrite were reduced to a minimum.

Phase Separation in De-ionised Colloidal Systems

Simon Petris, Derek Y. C. Chan, and Per Linse

*Particulate Fluids Processing Centre
Department of Chemical Engineering
The University of Melbourne
Parkville 3010, Australia*

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The coexistence of a gas and liquid phases, in experiments and Monte Carlo simulations of dilute charged colloidal dispersions, cannot satisfactorily be explained in terms of classical DLVO theory. In such a system of colloids and counterions, the van der Waals interaction between colloids is negligible, and the effect is purely electrostatic. Traditional wisdom dictates that a gas-liquid phase transition can only occur with an attractive pair interaction.

Using an extension of the Debye-Hückel theory for strong electrolytes, the thermodynamics, phase behaviour, and effective pair colloidal potentials of de-ionised charged dispersions have been investigated. With the inclusion of colloid size effects, this model predicts the possibility of the existence of a two critical points, one of which is thermodynamically metastable but can exhibit interesting behaviour at high colloid charges. This analytic model also serves as a pedagogic demonstration that the phase transition is driven by cohesive Coulomb interactions between all charged species in the systems and that this cohesion is not insistent with a repulsive effective pair potential between the colloidal particles.

Modelling Micellar Solutions

Boris Poliak

*Department of Mathematics and Statistics
The University of Melbourne
Parkville 3010, Australia*

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A theory to interpret atomic force microscope measurements of the force between a mica plate and a silica colloid probe immersed in a micellar solution will be presented. The force is calculated on the basis of the micelle distribution between the macrobodies, which is obtained using an integral equation approach from the statistical mechanics of fluids.

Friction And Wear Studies Using Lateral Force Microscopy

Mark G. Reitsma¹, Robert G. Cain², David Smith¹, Simon Biggs³, and Neil W. Page²

¹*Dept. Civil Engineering*

²*Dept. Mechanical Engineering*

³*School of Biological and Chemical Sciences*

University of Newcastle

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Tribology is the study of adhesion, friction and wear between two or more interacting surfaces. The fundamental difference between macroscopic friction and friction between surfaces that are in perfect contact is surface roughness. Surface roughness is the result of asperities at the interface. Asperities are nanometer sized hills and troughs on a surface, and are the reason that most real surfaces are not perfectly smooth. Nanotribology, attempts to scale out the multiple asperity contact that describes tribology and the classical laws of friction. We have investigated friction as a function of normal applied load for a silicon AFM tip in contact with a quartz surface at stresses likely to be experienced by quartz particles in a soil. At a constant sliding speed, friction was measured while the surfaces were subject to progressively increasing load. At low loads, the frictional force varied with stress according to an interfacial Hertzian contact area. However, at loads equivalent to stresses of ~2.5GPa, the data become scattered relative to the Hertzian model, indicating the onset of surface wear. At stresses exceeding ~3GPa, a reduced friction compared to that of the Hertzian model is obtained with increasing applied load. Scanning electron microscope images of the AFM tip used in this work reveal extensive plastic deformation, wear and possible melting of the tip contact region. It is thought that these processes may have produced a flow in the material that acted to self lubricate the tip during sliding, and thus contribute to a significantly reduced friction at high contact pressures.

Treatment of Printing Wastewater Using Adsorbing Colloid Flotation

Choon Jek Ang, Russell J. Crawford, Peter Sanciolo

*Centre for Applied Colloid and BioColloid Science
Swinburne University of Technology*

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Printing wastewater is characterised by high levels of chemical oxygen demand (COD), biochemical oxygen demand and colour. It contains a combination of heavy metals, pigments, suspended solids as well as organic solvents and hence, conventional sedimentation treatments are unsuitable. The main contaminant in the wastewater, pigment molecules are highly structured polymers and are toxic to microorganisms, biological treatment of these waste waters will not remove all organics, resulting in high COD values.

The aim of this project is to use a novel development in adsorbing colloid flotation (ACF) to treat printing wastewater. As the wastewater characteristics change with time, the ultimate objective will be to allow flexibility in the wastewater treatment process to accommodate for these changes.

Adsorbing colloid flotation is a flotation process that involves adsorption and/or coprecipitation of contaminants onto a metal hydrous oxide colloid. The surfactant will adsorb onto the colloid to render it sufficiently hydrophobic to be collected at the liquid/bubble interface and to establish a solids stabilised foam. Clean liquid drains from the foam, leaving contaminants still adhering to the foam. This is unlike conventional adsorbing colloid flotation where clean liquid remains in the flotation cell. The aim of this process is to concentrate as many of the contaminants as possible onto a small volume of liquid, leaving the bulk of liquid relatively clean.

Preliminary work has concentrated on obtaining the analytical methods and procedures to quantify the efficiency of the removal process. This involved studies on printing wastewater and the various primary coloured pigment solutions that made up the bulk of the wastewater. Batch mode flotation studies were performed on printing wastewater, which was dosed with single or mixed adsorbing colloid metals and CTAB. Adsorbing colloid metals to be investigated were Fe(III), Fe(II) and Al(III). The influence of pH, different ratios and concentration of adsorbing colloid metals on the removal of contaminants were investigated. The precipitation pH of these metals in the printing wastewater environment was also investigated.

Extraction of Neutriceutical Components from an Australian Wood Decomposing Fungus

Lyndal M. Roberts, Russell J. Crawford and Greg T. Loneragan

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Centre for Applied Colloid and Biocolloid Science
Swinburne University of Technology
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Certain *Garoderma* species of fungi have been shown to possess bioactive compounds that have neutriceutical properties, in that they can induce antibacterial, antiviral and cancer treating behaviour in animals. It has also been identified as an aid in immune system enhancement. An Australian *Garoderma* species of wood-decomposing fungus isolated from northern Queensland is being studied to determine whether it exhibits these neutriceutical properties.

The fungal strain, which is likely to be *Garoderma lucidum*, has been cultured on a range of liquid growth media in an effort to study the dependence of bioactive compound concentration on the cultivation substrate. The bioactive compounds will be isolated from both the fungal mycelium and the culture medium by solvent extraction using a range of solvents of varying polarity. These crude extract mixtures will be tested for their bioactivity, and eventually will be separated using chromatographic techniques, and the individual components identified. These isolated compounds will then be tested for their specific bioactivity.

This presentation will describe the work completed to date in this study.

The Flocculant Concentration Influence on the Settling Behavior and Structure of Flocculated Kaolinite

Matthew L. Taylor, Gayle E. Morris, Peter G. Self and Roger St. C. Smart

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

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In many minerals processing industries the flocculation and disposal of clay-based mining tailings is a major concern. Flocculation of the clay based tailings is generally achieved by the use of polymeric flocculants and it is imperative that a good understanding of the operation of flocculants is achieved in order to optimise flocculation procedures.

Kaolinite is the major component of many clay-based tailing systems. In this study the interaction of suspended kaolinite with commonly used polyacrylamide flocculants was investigated using settling experiments, cryo-vitrification-SEM, pore structure analysis and floc size / density measurements. The purpose of this study was to investigate the effect of flocculant dosage on the settling behavior and structure of flocculated kaolinite.

The results show the kaolinite suspension to have an optimum settling rate at a flocculant dosage of ~ 0.03 mg/m². The floc size, density, internal floc structure and pore distribution are all greatly effected by flocculant dosage and can be related to the settling rate and final bed height of the system.

9545 2222

A Novel Single Source Precursor for the Growth of High Quality ZnO Films

A. J. Petrella, N. Roberts, A. J. Hartmann and R. N. Lamb

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This work presents a fundamental approach to the simple fabrication of high quality ZnO films based on the single source chemical vapour deposition method. The synthesis and characterisation of $Zn_4O(O_2CNEt_2)$ will be discussed which was found to be a useful single source precursor for ZnO film growth.

Film growth was performed in a high vacuum deposition chamber. The crystallographic order, chemical composition and topography of the resultant films were then examined using X-ray photoelectron spectroscopy as well as diffraction and electron microscopy techniques. The films were found to be of self-textured polycrystalline structure with preferred c-axis orientation and relatively low bulk carbon concentration. Even though the film columns appeared to be closely packed, the films are basically stress free. Piezoelectric coefficients of the films were tested and films with piezoelectric coefficients as high as 10 ± 2 pm/V were found (single crystal literature value = 12pm/V). The excellent properties of as grown films are discussed with reference to precursor composition, structure and decomposition chemistry.

Can You *Still* Hear Me? Ultrasonic Forces for Particle Separation

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" Throwing out
 points "
ethics

Split-flow thin (SPLITT) channels are versatile and readily adaptable to new force fields. In the current study a relatively novel field, caused by acoustic pressure is considered. Consider a SPLITT channel where one wall is attached to a piezo ceramic transducer capable of generating ultrasonic frequencies. Further, consider the situation where the frequency is tuned such that a single standing wave is generated across the thickness of the channel.

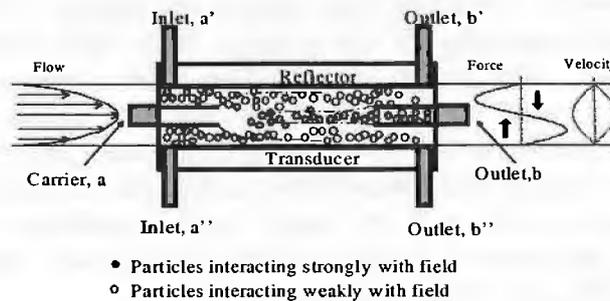


Figure 1 Dual SPLITT thin channel separation achieved using an ultrasonic standing wave.

Unlike conventional SPLITT where the force across the channel is constant, particles in the standing wave will experience an acoustic force (F) depending on its position, x given by:

$$F = 4\pi r^3 \kappa E_{ac} A \sin(2\kappa x) \tag{1}$$

where r is the particle radius, κ the wave number, E_{ac} the time averaged acoustic energy density and A the acoustic contrast factor and is given by

$$A = \frac{1}{3} \left[\frac{5\rho_p - 2\rho_l}{\rho_l + 2\rho_p} - \frac{\gamma_p}{\gamma_l} \right] \tag{2}$$

where ρ_p and γ_p are the particle density and compressibility and ρ_l and γ_l the carrier density and compressibility. Due to the nature of the acoustic fields, the distribution of the particles will depend on particle size and the compressibility and density of the particle relative to the carrier. Closer examination of the acoustic contrast factor shows that it may be negative (usually applicable to biological cells which are more compressible and less dense relative to the surrounding medium) or positive (as is in many inorganic and polymer colloids). Therefore Acoustic SPLITT (AcSPLITT) has tremendous potential in separating cells from sediments samples where separation based on compressibility is anticipated.

Yosioka, K. and Kawasima, Y. (1995). Acoustic Radiation Pressure on a Compressible Sphere, *Astia* 5: 167-173.

Characterisation and Stabilisation of Lipid-DNA Complexes for Gene Therapy

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Gene therapy is an exciting technology involving the introduction of genetic material (DNA) into cell systems in order to treat human diseases. There are many ways to do this, including lipids/liposomes, which are becoming increasingly popular as DNA delivery vehicles (Gao and Huang, 1995).

The aims of the project are to study the physicochemical properties of the complex formed between tris-conjugated cationic lipids (Cameron et al., 1999) and DNA and to relate these properties to transfection efficiency.

Dynamic light scattering measurements have shown that the size of these complexes are about 60-150 nm and are stable in the absence of NaCl. However, upon addition of NaCl at physiological conditions, the lipid-DNA complexes aggregate. Stabilising agents such as pegylated-lipid polymers were found to improve stability of the complex without impeding on transfection efficiency.

Cameron, F.H. et al. (1999) *Biochim. Biophys. Acta*, 1417(1), 37-50

Gao, X. and Huang, L. (1995) *Gene Therapy*, 2, 710-722

Multibubble Sonoluminescence from Aqueous Solutions Containing Aliphatic Alcohols and Surfactants

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This study compares the effects of surface active solutes on multi-bubble sonoluminescence (MBSL) intensity using two ultrasound frequencies, 515 kHz and 20 kHz. Unexpectedly, the response at 20 kHz is significantly different from that at 515 kHz.

The figure shows an example using propan-1-ol as a surface active solute. At 515 kHz as the propan-1-ol increased in concentration the SL intensity was almost completely quenched, at 20 kHz the SL intensity reached a limiting level. Similar differences have been found for other aliphatic alcohols and for SDS. These differences have been interpreted as being due to the different populations of transient and stable cavitation bubbles generated at the two frequencies.

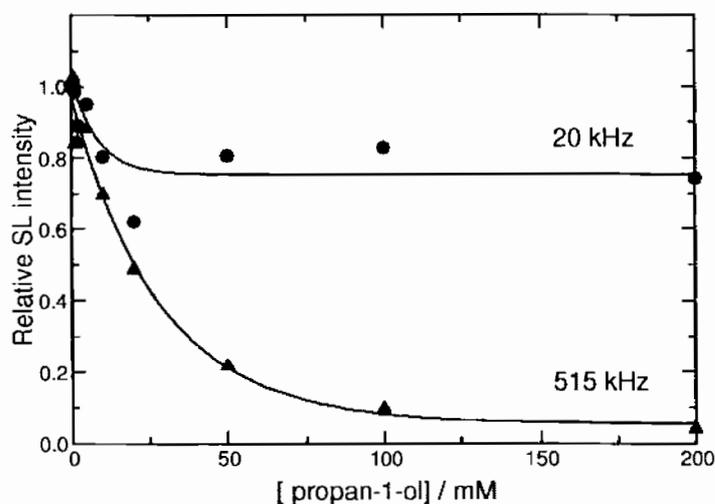


Figure 1: The relative sonoluminescence intensity as a function of propan-1-ol concentration for aqueous solutions exposed to 20 kHz and 515 kHz ultrasound.

Optimisation of the Washing and Dewatering of Flocculated Suspensions

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Optimum washing and dewatering of mineral wastes is important for the maximum recovery of expensive process chemicals and timely rehabilitation of tailings disposal areas. Washing and dewatering of waste suspensions is achieved through free settling and compressional dewatering in trains of separation equipment employing filtration and gravity thickening and subsequently in residue disposal areas. A fundamentally based mathematical theory of free settling and compressional dewatering of flocculated suspensions has been developed. The gel point, compressibility and permeability have been established as the fundamental physical properties that determine suspension dewaterability. The gel point is the critical solids concentration at which discrete flocs come into contact forming a continuous network structure, through free settling. At solids concentrations above the gel point, compressional dewatering removes liquid from suspensions through the application of a net compressive force. The compressibility expressed as a compressive yield stress, $P_y(\phi)$, allows identification of the maximum extent of dewatering for any compressive stress. The permeability expressed in terms of a hindered settling function, $R(\phi)$, determines the rate of dewatering. Techniques have now been developed to allow complete dewaterability characterisation over a wide range of solids concentrations using both batch settling and pressure filtration tests. Equilibrium and transient batch settling tests provide methods of calculating the gel point in addition to $P_y(\phi)$ and $R(\phi)$ at solids concentrations near the gel point. A newly developed stepped pressure filtration technique characterises $P_y(\phi)$ and $R(\phi)$ at high solids concentrations. Once characterised, the $P_y(\phi)$ and $R(\phi)$ data points can be fitted to continuous functions. These functions are used with fundamental dewaterability theory to predict the separation performance of thickeners, centrifuges, filter presses and residue disposal areas.

The alumina industry produces significant amounts of bauxite residue suspension that must be washed and dewatered in trains of thickeners and a residue disposal area to recover valuable alumina and sodium hydroxide. Bauxite residue dewaterability characterisation results will be presented with thickener and residue disposal area dewatering predictions. Dewaterability is strongly influenced by process variables including flocculation conditions and liquor viscosity changes due to the dissolved solids concentration in the liquor and the process temperature. These changes in dewaterability can have a dramatic influence on dewatering predictions. It will be demonstrated that dewatering predictions can be used as an optimisation tool to maximise liquor recovery through variations in process conditions.

Contaminant Levels in Recycled PET Plastic

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Consumers occasionally reuse polyethylene (PET) containers such as soft drink bottles for storing domestic and garden products. These containers pose a potential health risk if recycled and used for food purposes.

The aim of this project is to establish a chemical baseline for virgin PET and to determine chemical variability in post-consumer PET. Extraction, concentration and instrumental analysis using sensitive techniques such as GC-MS, HPLC-MS and ICP will determine contamination levels in different batches of kerbside and recycled PET. The effectiveness of the recycling process in decontaminating PET will thus be analysed.

Because of the different physical and chemical properties of organic compounds, their extraction from PET will be investigated by dissolution, static and dynamic headspace analysis, soxhlet extraction and, possibly, supercritical fluid extraction. Preliminary GC-MS analysis of kerbside PET flakes (washed and dried) reveal citrus flavour compounds and naphthalene derivatives probably derived from the solvent carriers of inks or polyethylene naphthalate contamination. The levels of these compounds were reduced after the extrusion step in the secondary recycling process.

Sorption and migration experiments of contaminants into (or from) food simulants will be performed on PET and other plastics such as high density polyethylene (HDPE) and poly(vinyl) chloride (PVC). Diffusion models and the factors influencing these diffusion mechanisms will also be investigated.

Migration into aqueous solutions will be monitored by dynamic headspace (purge and trap) GC-MS. This is a highly concentrating technique that we have applied recently for the analysis of volatile organoleptic compounds migrating from HDPE into the soft drink simulant, 10% ethanol (stored at 40°C for 10 days).

Adsorption Behaviour and Solution Properties of Diblock Polyelectrolyte Copolymers

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There has been much research into the adsorption of polyelectrolytes at the solid/liquid interface, due to the wide industrial applications of large and small polyelectrolytes. Recently, focus of such work has increasingly centred on polyelectrolyte polymers, in particular polyelectrolyte diblock copolymers. The cause of this shift has been a combination of the wider range of technological applications of the diblock copolymers and more advanced synthetic methodologies that have led to an ever increasing range of such polyelectrolytes. Amphiphilic polyelectrolyte diblock copolymers exhibit a wide range of solution properties, since the exact hydrophobic/hydrophilic nature of the diblock can be easily modified. This modification can be either through copolymer architecture or, more interestingly, via changes in the solution properties, such as pH or ionic strength.

The current study has looked at the solution behaviour and the adsorption properties of the polyelectrolyte diblock copolymer poly(2-(dimethylamino)ethyl methacrylate-*block*-methyl methacrylate) (DMA-MMA). This diblock copolymer is well known to form micelles in an aqueous solution under acidic conditions, due to proton association to the tertiary amine groups in the DMA block which renders the copolymer amphiphilic in nature. Atomic force microscopy has been used to study the adsorption, whilst dynamic light scattering has been employed to study the solution conditions, of copolymer solutions across a range of copolymer concentrations and solution pH and ionic strength.

AFM Study on Tissue and Biomaterials Interaction

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AFM (Atomic Force Microscopy) with colloidal spheres attached to cantilevers measures directly the interactions between different types of material surfaces in aqueous solution. AFM has also provided mechanistic insights into the molecular level interactions that occur at biomaterial surfaces. The performance of biomaterials is mainly dependent on the molecular interactions that take place at the interface between the implant and host in the physiological environment. Hence, AFM study of tissue and biomaterial interactions will guide improvement in the surface structure and surface properties of biomaterials.

In this report, we examine the applicability of the AFM to the study of silica surface interactions in pure water and in simulated body fluid (SBF) using anhydrous silica sphere and oxidised silicon wafer. The DLVO behavior in pure water is different from that in SBF. Similar force measurements between both hydrolysed silica surfaces were examined. A small adhesion force developed initially in SBF, however, after 18 hours there was no further change with time. Further measurements will be performed between silica probes and bioactive silica layers deposited by plasma enhanced chemical vapor deposition (PECVD).

The Simulation of Extreme Surface Roughness

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The extreme roughness of many new types of hydrophobic surfaces plays an important role in determining the extent of such hydrophobicity. However current theory applied to situations at the upper limits of hydrophobicity (ie. contact angle greater than 150°) cannot adequately explain this behaviour. A model, based on capillarity theory, has been developed in which the nature of the surface roughness is modelled as discrete bundles of capillaries. However, it is somehow difficult to estimate the roughness of an irregular surface. Fractal geometry offers mathematical models and tools to solve the problem.

Atomic force microscope (AFM) and scanning electron microscope (SEM) of high water contact angle ($>150^\circ$) surfaces have been measured and various experimental parameters have been compared with the results calculated from the model. The fourier transfer of the topographic three-dimensional images was used to estimate the fractal dimension of the rough surfaces.

The results indicate that this new theory predicts the wettability reasonably well and only requires an experimental value of roughness and readily available contact angle data for each chemical component contained on the surface.

The calculated contact angle is found to be strongly dependent on the chemical nature of the surface of the capillary as well as the nature and arrangement of these within the three phase contact line.

Thermally Induced Gelation of Oil-in-water Emulsions Stabilised by Graft Copolymers

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This work involves the synthesis of thermally sensitive graft copolymers and their utilisation in the preparation of thermally responsive oil-in-water emulsions. The copolymer consists of a poly(N-isopropyl acrylamide) (NIPAM) backbone and poly(ethylene glycol methacrylate) (PEGMA) as the side chains. It was found that emulsions prepared in the presence of poly(NIPAM-MPEG) copolymers exhibited thermoresponsive behaviour, i.e., above a critical temperature the fluid emulsion gelled. This gelation of the emulsion could be reversed by agitation (above the gelation temperature) or cooling to room temperature in the absence of agitation. The mechanism by which reversible emulsion gelation occurs was investigated using light scattering and rheological measurements. The data indicate that the temperatures at which the emulsions gel are higher than the lower critical solution temperature (LCST) of the stabilising copolymers. This suggests that the onset of gelation is not solely due to the collapse of the adsorbed copolymer chains present in the continuous phase, but other factors including the nature of the adsorbed copolymer layer are involved. These factors are discussed. This work should have significant technological importance in the field of emulsion stability as the thermally induced gelation results in a reversible transformation of a liquid emulsion into a highly viscous gel within a short period of time upon application of modest heating.

New Methods in the Rheological Characterisation of Fluid Gels

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The rheological characterisation of fluid or weak gels is of benefit to food technologists and scientists in that it assists in establishing a relationship between product performance and physical properties of the gels. Low-viscosities, heterogeneities and strongly pseudoplastic behaviour of these gels makes rheometrical measurements a difficult task. Although some rheometers performing at very low stresses are capable of measuring the properties of fluids with viscosities as low as 1 mPa s, there is still uncertainty in the existence of an apparent yield stress in some of these fluid gels.

To this end we have suggested that bubble rise measurements will help to elucidate this problem for the extracellular polysaccharide Xanthan in solution. Alkane droplets are pushed into a column filled with the fluid gel and allowed to rise. The path of the drop is monitored using digital video analysis techniques. In this way a velocity profile can be acquired for the rising bubble. Together with measuring changes in the bubble shape, a terminal velocity for the bubble can be established. A plot of terminal velocity as a function of bubble size has an x-axis intercept that correlates to the yield stress of the solution.

The path of the bubble is of interest in that heterogeneities within the system can be defined through the horizontal deviations the bubble takes. Interesting effects have also been noted in the shape of the bubbles with time and viscoelastic fluid properties. Results for a range of systems will be discussed.

The Adsorption of Cetylpyridinium Bromide (CPBr) at the Silica-Aqueous Interface

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The adsorption of Cetylpyridinium Bromide (CPBr) to the silica-aqueous interface has been studied using optical reflectometry and atomic force microscopy (AFM). The effect of pH, electrolyte and surface preparation on the surface excess and adsorption kinetics is reported. AFM imaging above the critical surface aggregation concentration (CSAC) elucidates spherical surface structures in the absence of electrolyte, and elongated cylindrical structures with added electrolyte. At concentrations around the CSAC, adsorption proceeds slowly in the absence of salt and takes hours to reach an equilibrium value. At all other concentrations and even at the CSAC when electrolyte is present, the adsorption is complete within minutes. The concentration range for which slow adsorption is apparent has been termed the slow adsorption region (SAR) of the adsorption isotherm. AFM imaging of surfactant adsorption in the SAR suggest that the slow adsorption kinetics is due to the gradual formation of surface structures in this region. The effects of pH and added electrolyte on surface excess and adsorption kinetics have also been studied. At moderate to high surfactant concentration with added electrolyte, pH increases have little effect on surface excess. In the absence of electrolyte the surface excess increases with pH as expected, but it is suggested that these increases are primarily due to increased solution ionic strength, not increased charge on the substrate. At low surfactant concentrations, cations associated with the electrolyte compete effectively with the surfactant for adsorption sites, resulting in no detectable adsorption until a pH of 8 is reached.

Synthesis of Cationic Polymer Latex by Ultrasound

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Cationic latices of polymethylmethacrylate and polybutylacrylate have been synthesised in an emulsion polymerisation process using ultrasound as the initiating source. The polymerisation was carried out at 300°C and produced particles of around 40 nm in diameter with a high degree of monomer conversion. Indications are that the process involves a miniemulsion system, produced by the shear forces generated by the ultrasound, in which continuous nucleation of particles takes place throughout the monomer conversion.

UV-Initiated Formation of Noble Metal Nanoparticles on Zinc Oxide Quantum Dots

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Quantum dots (nanosized semiconductor particles) are a relatively new phenomenon. They exhibit unusual properties as a result of spatial electron confinement within the particles, including an increased band gap energy and blue-shifted fluorescence. Quantum dots and nanoparticles have attracted a lot of academic and industrial interest because of their special properties, including small size and potential as catalysts, 'tunable' fluorescence, and potential use in biomedical applications. Still, there are many properties of quantum dots that need further investigation if they are to be fully utilised. The interaction between nanosized noble metal colloids and zinc oxide quantum dots (Q-ZnO) under UV-irradiation provides valuable information about the electronic structure of Q-ZnO. In a sample containing Q-ZnO and Pt^{6+} , Au^+ or Ag^+ , electrons from excited Q-ZnO were transferred to the metal ions, and consequently, metal particles were reduced onto the Q-ZnO particles. The processes that occur can be followed spectroscopically. The results will be discussed during the presentation.

Control over Pegylated-Liposome Aggregation by Neutravidin™-Biotin Interactions Investigated by Photon Correlation Spectroscopy

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Lipid vesicles (commonly called liposomes) have been extensively used for cancer treatment to decrease drug toxicity and increase targeting. Liposome aggregation through specific biological interactions is attracting increasing attention as a novel self-assembly method for building complex nano-structures and drug delivery systems. Limited numbers of reports are available on ligand-receptor mediated aggregation of lipid vesicles. To our knowledge, Chiruvolu et al. were the first to report on liposome agglomeration by streptavidin-biotin cross-linking. Only phenomenological observations were reported, however. Very recently, Kisak et al. reported a mechanistic model of liposome aggregation by streptavidin-biotin interactions. Although it is the first to report a mechanistic study of the controlled aggregation of liposomes, the hypotheses made to support the model were oversimplified.

The aim of the current study was therefore to investigate the self-aggregation of liposomes composed of phosphatidylcholine (DSPC), cholesterol and lipid-PEG-biotin (DSPE-PEG (2000)-biotin). Briefly, the liposomes were produced by filtration through polycarbonate membranes (100, 200, 400, 600 nm). Aggregation was induced by adding appropriate amount of Neutravidin™ solution. Liposome aggregation was followed by photon correlation spectroscopy (PCS). The liposome aggregation has been investigated as a function of the initial size of the liposomes, the total lipid concentration, and the amount of DSPE-PEG (2000)-biotin. The kinetics of liposome aggregation was also assessed.

Control over the size and shape of liposomal aggregates can be achieved by using specific ligand-receptor interactions to link the particles.

Chiruvolu, S.; Walker, S.; Leckband, D.; Israelachvili, J.; Zasadzinski J. *Science* 1994, **264**, 1753-1756.

Kisak, E.T.; Kennedy, M.T.; Trommeshauser, D.; Zasadzinski, J.A. *Langmuir* 2000, **16**, 2825-2831.

Dual Polymer Flocculation of Alumina: Aggregate Structure and Filterability

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The separation of particulate solids from liquids by filtration constitutes an important and often controlling stage in many industrial processes. Some solid-liquid systems defy easy separation and therefore, it is common practice in many applications to use chemicals to alter the surface properties of the particles. The use of polymers to control the stability/flocculation behaviour of dispersions is now an everyday practice.

In some industrial instances, it has been found that the use of two polymers in combination has a synergistic effect on the flocculation of a dispersion. The aggregates formed exhibited a higher permeability and were more resistant to shear. The practical experience of dual polymer flocculant systems is large; however, fundamental investigations of the flocculation and de-watering mechanisms of these systems are scarce.

This work examines the effect of the flocculation mechanisms in dual polymer systems on the compressibility and permeability of the aggregated suspensions. Small-angle static light scattering was employed to determine the mass fractal dimension (density) of the primary aggregates, which were formed using polyacrylic acid. A series of polyacrylic acid polymers varying in molecular weight from 1,200 to 250,000 g mol⁻¹ were investigated and mass fractal dimensions varying from 2.3 to 2.45 were achieved, respectively. A cationic polyacrylamide was then employed as the second polymer. The effect of the cationic polymer charge density and molecular weight on the de-watering properties of this dual polymer-flocculated system was investigated.

Dynamic Surface Tension between an Aqueous Salt Solution and a Surfactant Containing Oil Solution

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In emulsion production, droplets need to be stabilised within very short time scales. Dynamic measurements of surfactant adsorption are therefore of fundamental importance. Dynamic interfacial tension measurements have been performed using a pendant drop method on a variety of systems consisting of 0 to 0.5M CaCl₂ aqueous salt solution and 0 to 5 % w/w sorbitan mono oleate (SMO) in decane. Interfacial tensions obtained ranged from 1 to 51 mN/m and were measured over a range of drop (surface) ages from 0.5 to 1000 s.

Dynamic interfacial tension measurements in salt free surfactant containing systems were observed to decrease in value with increasing surface age towards an equilibrium surface tension value. At 5% w/w surfactant concentration and low salt concentration, interfacial tension decreased towards an equilibrium value and at 5% w/w surfactant and high salt concentrations an initial depression in interfacial tension was observed followed by an increase to a similar equilibrium value. At 0.5% w/w surfactant concentrations results were similar to those of the 5% w/w concentration case, although the dynamic effects were further exaggerated. The results suggest the possibility of an interesting dynamic interplay between the salt and surfactant molecules from either side of the interface.

Effects of Surfactants on the Extraction and Activity of Phenoloxidases from Spent Mushroom Substrate

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Spent mushroom substrate (SMS) consists of composted organic material heavily colonised with *Agaricus bisporus* mycelium. This fungal species produces a variety of extracellular oxidative and hydrolytic enzymes, the most abundant of which is laccase, a polyphenoloxidase. Laccase exhibits broad substrate specificity and has received considerable research attention due to its potential use in a variety of biotechnological applications. SMS is available cheaply and in large quantities as a byproduct of the mushroom industry and is therefore being investigated as an alternative source of laccase for biotechnological application.

As part of an overall project aimed at optimisation of the laccase extraction process, the present study examined the effects of surfactants on both the extraction and stability of laccase from SMS in aqueous buffer extraction systems. Relative extraction efficiencies were determined as a function of surfactant concentration for a variety of nonionic, anionic and cationic surfactants. The effect of each surfactant on the catalytic properties of pre-extracted laccase was also evaluated across the relevant concentration range in order to differentiate between surfactant effects on enzyme activity and those on enzyme release from the solid compost matrix. Results have been interpreted in terms of potential microenvironment effects on enzyme and substrate.

Selective Adsorption of Dyes to Kaolinite

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We have previously demonstrated strong selective adsorption of certain dyes (3,6-diamino acridine, 9-amino acridine, azure A and safranin-O) to the kaolinite surface. While adsorbing in large amounts to kaolinite over a wide pH range, they barely adsorb at all to oxide surfaces such as silica, amorphous alumina and gibbsite.

Dyes showing strong selectivity have a number of structural features in common, and further investigation into the mechanism of adsorption has been carried out to gain a better understanding of how these features effect adsorption. This has included experiments involving competitive adsorption between the dye and Cd cations (the adsorption of Cd to kaolinite is well characterised), the use of kaolinite samples with differing aspect ratios, ATR-FTIR spectroscopy, and surface complexation modelling of adsorption data.

The results strongly suggest that the dyes adsorb to the flat, permanently charged kaolinite face via a pi-stacking mechanism. The chemistry of the kaolinite face is quite different from that of the oxide surfaces, accounting for the difference in absorption characteristics.

Data supporting this conclusion will be presented.

Investigation of the Effects of Flocculation on the Dewaterability of 'Red Mud': A Case Study on Hematite

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The Bayer process is used to extract alumina from bauxite. In this process gibbsite present in the bauxite is extracted with concentrated sodium hydroxide to form aqueous sodium aluminate (pregnant liquor), leaving behind an insoluble residue known as 'red mud'. The red mud is separated from the pregnant liquor, with the aid of flocculants, in a clarification vessel known as a thickener. The red mud fraction is then washed in a five or six stage counter-current washing circuit to remove residual sodium hydroxide. Flocculants are again utilised to obtain the required settling rates, overflow clarities and underflow concentrations.

The refining of West Australian bauxite, considered of low grade by world standards, results in the production of two dry tonnes of red mud for every tonne of alumina produced. This red mud is highly alkaline and potentially hazardous to the environment. Consequently, over the last few decades there has been an emphasis on producing high solids content, red mud and improving sodium hydroxide recovery.

It has been proposed that disposal can be further improved by optimisation of the washing, thickening and disposal stages of the Bayer process. This is to be achieved by gaining a clearer understanding of the effects of floc structure on compressibility, permeability and ultimately dewaterability. In addition, factors affecting floc structure, like mixing conditions and the inter-relationship between the red mud particle surface and the flocculant, need to be investigated.

A baffle reactor has been built to reproducibly synthesise different floc structures and the performance of different flocculants is measured in terms of settling rate, supernatant turbidity, compressibility, permeability and ultimately dewaterability. In addition a floc density analyser is being built to analyse floc structures.

Initial experiments on high molecular weight flocculants and starch have been performed. Trends in the flocculation and dewaterability of hematite suspensions will be presented.

Time Resolved Polarised Attenuated Total Reflection Spectroscopy of Protein Films at the Silica/ Solution Interface

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Protein adsorption is an important phenomenon in a wide range of industries including the food and pharmaceuticals. While numerous studies have been performed in order to elucidate the kinetics of adsorption for a number of protein systems, little attention has been paid to the kinetics of conformational reorganisation at the interface.

Time resolved polarised attenuated total reflection (TRATR) experiments provide in-situ measurement of both the adsorption kinetics and the rate of conformational evolution at the interface. Dichroic ratio analysis formulated for IR spectroscopy has been extended to UV spectroscopy to allow its use for larger molecules with known tertiary conformations. The technique and interpretation will be discussed specifically to the solid/liquid interface, and its application to a well-characterised protein system, hen egg white lysozyme (HEWL).

TRATR measurements of the adsorption of HEWL at the solid/liquid interface have shown that, depending on the background ionic species (which has implications on the choice of buffering salts), both the adsorption kinetics and conformational re-arrangement are dramatically affected. In a simple ionic system such as sodium chloride during the early stages of adsorption, there is an initial rapid accumulation of protein at the interface followed by some desorption. The system then settles such that there is a gradual increase in the adsorbed amount as the system approaches equilibrium. The early stages of adsorption/desorption are explained in terms of charge-charge repulsion and reorganisation of protein molecules at the surface.

An *In Situ* FTIR-HATR Investigation of the Adsorption of Polyacrylate onto Hematite

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High molecular weight water-soluble polymers (flocclulants) are commonly added to mineral slurries formed during hydrometallurgical processing to improve solid-liquid separation. Despite their extensive use and importance to many processes, mechanistic studies of the adsorption of flocclulants onto mineral substrates are limited. It is generally accepted that only a fraction of a flocclulant molecule adsorbs while the remainder of the molecule forms loops and tails that extend into solution. The effect of drying and the collapse of unadsorbed polymer onto the substrate surface complicates *ex situ* studies of flocclulant adsorption. A Fourier Transform Infrared-Horizontal Attenuated Total Reflection (FTIR-HATR) technique has been successfully applied to investigate flocclulant adsorption *in situ*, thereby eliminating the complications associated with *ex situ* examinations.

The purpose of this study was to gain fundamental information of the adsorption of polyacrylates onto hematite. Adsorption has been examined at differing solution compositions for polyacrylates of different molecular weights. It has been found that the adsorption mechanism and the rate of adsorption differ quite considerably at high and low pH.

The results from this study have been applied to show the implications they have to flocclulation of gangue material in the Bayer process.

Incipient Failure of a Yield Stress Material

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In this talk I will study the incipient failure of a concentrated suspension such as a mineral tailings slurry or fresh concrete. Two methods of analysing experiments on incipient failure of a cylinder of slurry will be discussed: the uniform stress model of Murata, and a new rigid plastic slip-line field model. In both models the slurry is assumed to behave as a yield stress material. Data on the height of incipient failure predicted by these two models will be presented and compared with experimental determination of the height of incipient failure. The incipient failure experiments can also be used to measure the yield stress of the slurry, using the theory developed for the two models above. These experiments will be compared against standard vane measurements of the yield stress. Some observations about the behaviour of a slurry past the point of incipient failure, the role of viscous effects, and the possibility of a pressure dependent yield stress, will also be discussed.

Cationic Surfactant Aggregate Geometries and their Induced Transformations at the Solid/Liquid Interface

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Quaternary ammonium surfactants show a wide variety of shapes when adsorbed at solid/liquid interfaces. The characteristics of these aggregates, including shape transitions caused by changing surfactant concentrations or by the addition of salt have been examined by several workers using Atomic Force Microscope (AFM) over the last five years. Adsorbed surfactants are capable of solubilising sparingly water-soluble organic substances. This process has been called surface solubilisation, coadsorption, or adsolubilisation. In this work naphthalene and 2-naphthol are used as model compounds, representative of typical environmental pollutants. The shape transformations induced by these additives have been imaged by AFM. These are presented with parallel quantitative determinations of surfactant and additive compositions in both the bulk aqueous phase and the adsorbed surfactant layer. These results support the existence of shape transitions observed from the AFM images. In addition, the effect of organic molecules with different chemical functional groups like hydrocarbons, alcohols (aliphatic and aromatic), azo, and bis-azo type dispersion dyes on the surfactant adsorbed layer structure will be discussed.

The Adsorption of Oxalate to Boehmite and Gibbsite

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The adsorption of oxalate to two hydrous aluminium oxides, gibbsite and boehmite, has been studied with both traditional experiments (potentiometric titrations and measurements of amount adsorbed as a function of pH) and by use of ATR FTIR spectroscopy. The results has been modelled with a surface complexation model that takes into account the spectroscopic information on the nature of the adsorbed species, and fits the macroscopic adsorption measurements. The combination of macroscopic and microscopic measurements provides strong support for the adsorption mechanism proposed.

Multi-Dimensional Dewatering of Flocculated Colloidal Suspensions

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In recent years, a theory of consolidation and sedimentation of flocculated colloidal suspensions (Buscall and White, 1987) has developed which has facilitated characterization of the dewaterability of industrial suspensions and simulation of dewatering operations. However, such analyses have been limited to one spatial dimension, which although generally valid, does not allow investigation of phenomena such as instability and recirculation in thickeners and simultaneous shear and dewatering.

Consequently, a multi-dimensional model of dewatering has been developed using the equations of two-phase flow which describe the transient fluid dynamics of settling and compression, whilst incorporating the governing physics of the original theory. Such an approach provides a more flexible environment for dewatering analysis as more complex geometries and flows can be simulated, atypical dewatering phenomena can be investigated, and some approximations of earlier theory are eliminated. Solution of the model is achieved in the commercial computational fluid dynamics package CFX 4.3, and has been verified against analytic and one-dimensional numerical results. Transient axisymmetric operation of a thickener, from feedwell to underflow has been performed as well as more detailed analysis of flow over a thickener rake including thixotropic effects. A framework of such versatility allows incorporation of shear dewatering theory, which can be quantified via a shear history formulation and represents a future body of work.

Interaction Forces Between Surfaces Immersed In Polyelectrolyte/ Surfactant Mixtures

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The interaction forces between mica surfaces immersed in cationic polyelectrolyte, and anionic surfactant mixtures of varying concentrations have been measured using the Surface Forces Apparatus (SFA). Results presented here demonstrate how the interaction forces measured between symmetric adsorbed layers are dependent on the structure of these layers. A range of surfactant concentrations is investigated at constant polyelectrolyte and background salt concentrations. The range of relative concentrations of surfactant molecules to polyelectrolyte monomer segments investigated, varies from ~1% to 10%. The results presented here demonstrate that the addition of small amounts of surfactant may result in a vast change in the close range surface forces between adjacent polyelectrolyte/surfactant layers.

the Curvature Dependence of Surface Tension Using Computer Simulations

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In 1949 R.C. Tolman predicted that the surface tension of an interface would depend upon its radius of curvature. It has proved difficult to obtain reliable experimental data for the dependence because it only becomes significant at extremely small radii. Recently several groups have used computer simulations to investigate and quantify the size of deviations from the planar surface tension values.

Here Monte Carlo simulations have been used to measure the surface tension of a planar liquid-vapour interface of a Lennard Jones fluid at several subcritical temperatures. The density profile and coexistence pressure have also been obtained. In order to examine the effects of a curved interface, a spherical cavity has been inserted into a liquid near coexistence. The solvation free energy of the cavity has been related to the density of the liquid at its surface, enabling the calculation of the curvature dependent surface tension.

It has been found that the Tolman length is small ($\delta < 0.5$ molecular diameters) and positive.

Interaction Forces between Two Layers of Adsorbed Beta-Casein

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The Surface Forces Apparatus was used to measure the interaction forces between adsorbed layers of beta-casein. Beta-casein was found to adsorb in a structured conformation on the mica surfaces. The thickness of the adsorbed layers increased with increasing beta-casein concentration, suggesting the build-up of successive layers (with similar outer profiles) onto the surface. Beta-casein is known to specifically bind to calcium, and so additional measurements were carried out using a fixed concentration of beta-casein with varying calcium concentration. The force versus distance measurements are indicative of adsorbed aggregates on the surface.

. Aluminosilicate Hydrogels As A Model System For Waste-Based Concretes.

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Process engineering of waste-based concretes is starting to turn to colloidal chemistry to provide more accurate descriptions of gel microstructure and ultimate material properties. The present work reports the utilisation of SANS to determine the neutron scattering contrast for a series of aluminosilicate hydrogels ($w\text{Al}_2\text{O}_3 : x\text{SiO}_2 : y\text{Na}_2\text{O} : z\text{H}_2\text{O}$), which when combined with a Porod fit, allows determination of the specific surface area and porosity of the aluminosilicate hydrogels as a function of composition. In addition, the observation of a Guinier regime through SAXS has allowed the determination of the radius of gyration (R_g) for the aluminosilicate hydrogels, providing a more meaningful mechanistic description of the scattering data. In combination with rheological, FTIR, and ^{27}Al MAS NMR data, a microstructural model has been proposed which allows the SANS data to be fitted to Porod-core shell model, and substantiates the differences observed in the scattering as a function of composition.

Tuesday 13 February

De-Phi-ing The Odds, The Quest For Super-Luminescent Quantum Dots

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Highly luminescent nanoparticles of semiconducting materials (quantum dots) display size-dependent, non-linear optical properties. Current interest in the field, in particular the intensively-studied cadmium selenide system, is highlighted by a number of publications in high profile journals. Applications ranging from fluorescence microscopy to quantum dot lasers have been proposed and are approaching realisation.

Huge progress has been made with the synthesis, characterisation and manipulation of CdSe quantum dots, but to date details of the behaviour of fluorescence with time in various chemical regimes are covered only sparsely in the literature.

We present an overview of the current developments in the field of highly luminescent quantum dots and report some observations on the stability of dilute quantum dot solutions in the presence of various organic functional groups which is the focus of the current study. Fluorescence and absorption spectroscopies are used to probe variations in solution optical properties with time.

Alkyl Phenyl Siloxane-copolymer Adsorption onto Titania Pigments

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Titania pigments are used in a wide range of areas including plastic, paint, papermaking and pharmaceutical industries. Previously we have investigated the adsorption of siloxanes onto E-glass fiber surfaces^{1,2}. This study focuses on understanding the adsorption of alkylphenylsiloxane copolymers onto titania pigments. Three different siloxane copolymers were synthesized and then adsorbed onto the pigments. The amount of adsorption was analyzed utilising Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFT spectroscopy) and Thermo Gravimetry Analysis (TGA).

The copolymers were prepared by using the following procedure. Polymethyl hydrogen siloxane (d.p. = 33) was reacted with styrene in toluene using H_2PtCl_6 as a catalyst under a nitrogen atmosphere (100°C/24 hrs). Precipitating from methanol purified the polymer. The pigment has an inorganic alumina surface treatment. The pigment was dispersed in a 0.5-wt % solution of each copolymer in acetone (1g coating/100g pigment). Samples were taken at designated times, centrifuged, the liquid decanted off and the pigment dried at 100°C overnight.

DRIFT spectroscopy was used to study the adsorption and interaction between the titania pigment and siloxane copolymer. The DRIFT spectroscopy spectra revealed that the copolymer had adsorbed onto the titania pigment surface. Free OH groups were observed indicating that the pigment surface was not fully covered when using a 0.5-wt % solution. DRIFT spectroscopy ratio analysis revealed that maximum adsorption was reached after 10 minutes. An oscillation process as a function of time occurs which may indicate complex adsorption processes are occurring. This is not accountable by experimental error alone.

TGA was undertaken to examine the mass change as function of the temperature (scanning mode), confirming the results obtained by DRIFT spectroscopy.

Britcher, L.G., Kehoe, D., Matison, J., Smart, R.St.C. and Swincer, A., *Langmuir*, **9**, 1609, 1993.

Britcher, L.G., Matison, J.G. and Kehoe, D.C., In: *Silanes and other Adhesion Promoters*, K. Mital (ed.), in press 2000.

Modelling Biomineralisation with Simple Organic Molecules

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Biomineralisation encompasses processes in nature where an organism nucleates and grows inorganic materials. Animals and plants are able to grow customised structures, which show organisation on many length scales. These materials show a diverse range of shapes and physical properties. This diversity comes about largely due to the tuning properties that proteins exert on the growing crystals.

The current study intends to mimic the proteins found in bioinorganic materials. Surfactants provide a useful mimic molecule as the self-organising behaviour of surfactants has been well characterised. We will also add other organic molecules to the crystal growing solution to explore the effect functionalities have on the growing crystal. With this knowledge it should be possible to construct organic-inorganic composite materials, possessing both high strength and toughness.

The Characterisation of Turbidity in Unfiltered Potable Water Supplies

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Melbourne's water supply is of sufficient quality that it is not normal to filter the water at any stage from the supply in Melbourne's catchment areas to the consumer at home. Whilst this is seen as an advantage for Melbourne's water supply, it does allow the possibility of colloidal material entering the water system. In many cases, this colloidal material is not of a toxic or hazardous nature, but does cause turbidity.

South East Water has recently increased its focus towards quality assurance with respect to customer complaints concerning dirty water. One of the concerns is the occasional "turbidity spike" which is seen to move downstream through the water system. The exact origin and nature of the turbidity is not fully understood. Melbourne water is chlorinated, fluoridated and treated with lime, and the affects these have on the nature and prevalence of turbidity is also not fully understood.

This project is concerned with a full characterisation of the turbidity, which occurs from time to time in Melbourne water. It will involve chemical characterisation such as metal content (ICP), oxide content (XRF), organic content (carbon/nitrogen analyser), anion content (Cl^- , SO_4^{2-} , F^- etc.) and bacterial content. It will also involve physical characterisation such as particle size, shape, charge and number as well as direct measurement of turbidity. An interesting part of this study will be to examine the affect of, for example, Cl^- and Cl_2 , on the turbidity of model dispersions containing the components found in "real life" turbidity samples. The goal will be to model the turbidity behaviour of such "real life" samples using the data collected from model dispersions.

The Adsorption of Aqueous Heavy Metals onto Titanium Dioxide (TiO₂)

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Aqueous heavy metals are toxic to the environment and provide a health risk to humans. In the environment, adsorption onto natural organic material (humic acids etc.), marine sediments and terrestrial clay and soil provides the control for their environmental concentration. Industrially, they are a problematic waste, which cannot be degraded, and must be either reused, recycled or disposed of in a manner where it is not possible for them to leak into the environment. Their treatment generally involves adsorption as a primary step. Thus adsorption of heavy metals is a fundamental scientific area worthy of study.

It is known that the adsorption of aqueous metals ions onto simple inorganic oxides such as silica (SiO₂) is pH dependent and the pH at which adsorption starts to occur correlates to the pH at which that metal ion starts to hydrolyse. One theory used to explain this correlation is that metal ions must hydrolyse, thus lowering their charge, prior to adsorption. This lowers the change in solvation energy involved in adsorption which otherwise prevents the free metal ion from adsorbing.

TiO₂ is an unusual oxide in that it has a dielectric constant similar to that of water and thus there is little difference to the solvation energy of an adsorbed or free metal ion. For this substrate, then, there should be little solvation energy involved in adsorption and metal ions should not need to hydrolyse prior to adsorption. This theory is supported by data involving the affect of background electrolyte concentration on metal ion adsorption. Changing this value dramatically affects the adsorption of Cd(II) onto TiO₂, and onto amphoteric latex, but not onto goethite. The theory here is that electrostatic interactions are the "driving forces" behind adsorption onto TiO₂, where there is little solvation barrier to adsorption, and onto latex, where the specific interaction between metal ion and carboxylic acid functionality is so great that the solvation barrier is easily overcome. For SiO₂, however, the "driving force" is hydrolysis in solution, and this is considerably less affected by background electrolyte concentration than electrostatic interaction is.

The purpose of this project, then, is to further investigate the role (or lack thereof) of hydrolysis in the adsorption of metal ions onto TiO₂. Very simply, the pH dependent adsorption of several metal ions onto TiO₂ will be measured. If hydrolysis is crucial, as it is with SiO₂, then adsorption will be quite different from one metal to another and will reflect hydrolysis. If not, then the adsorption of all metal ions should be similar.

Determination of Shear Viscosity of a Simple Fluid via Molecular Dynamics

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The shear viscosity of a simple fluid can be accurately determined via non-equilibrium molecular dynamics (NEMD) methods. The modified homogenous shear method, specifically the SLLOD equations of motion is the most widely used method of simulating shear flow. However there is no sound basis for the derivation of such modified non-equilibrium equations of motion.

We have developed alternative non-Hamiltonian equations of motions using Gauss' principle of least constraint. The viscosity given by the various non-equilibrium approaches are compared with each other and with Green-Kubo equilibrium simulations. Shear thinning of a Lennard-Jones fluid is exhibited at high shear rates. The prospects of generalising the approach to other types of flow and to different simulation algorithms are discussed.

The Role of Deformation on the Interactions of a PDMS Sphere.

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The aim of this project is to gain an understanding of the role that the deformability of an emulsion droplet has on its interaction with other droplets and its adhesion to interfaces.

Polydimethylsiloxane (PDMS) spheres were prepared by base catalysed emulsion polymerisation. The internal rheology (and hence deformability) of the PDMS spheres was controlled with the presence of a cross-linking agent¹. The resultant colloids have been characterised in terms of their size, zeta-potential and bulk rheology.

Atomic Force Microscopy (AFM) was used to characterise the interaction forces between a silica probe and PDMS spheres immobilised on a hydrophobic surface. Using a variety of PDMS spheres with different deformability, force distance relationships were obtained as a function of pH, electrolyte concentration and approach rate. Analysis of these force distance relationships gives the repulsive force between colloids and the deviation from DLVO theory that results from deformation. Once in contact, Young's modulus is obtained from the deformation of the sphere due to the applied load; this deformation is then compared to values predicted by JKR theory.

M.I. Goller, T.M. Obey, D.O.H. Teare, B.Vincent, M.R. Wegener; *Colloids and Surfaces* **123 - 124** (1997) 183 - 193

Water Resistant Coatings from Recycled PET

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The scope of this project covers the synthesis, characterisation and subsequent evaluation of a water resistant coating for paper, using waste poly(ethylene terephthalate) (PET). The requirements of the coating are not only to render the substrate waterproof, but to also be water-redispersible in order to recycle the paper substrate.

Preliminary studies on a series of these "water resistant" polyester resins (developed in the USA by Evcote) indicated that they were effective as water repellent barriers and improved the strength of the paper marginally, without adding excessive weight.

According to the US Patents on this development, the mode of synthesis is a series of transesterification reactions that break down the PET, then modify it such that it possesses functional groups with both hydrophobic and hydrophilic properties. The kinetics for this process will be investigated by monitoring the hydroxyl values, acid values and saponification equivalents of the reaction mixture.

Once the polyester resin has been isolated and purified, its physical and chemical characteristics, both as a solid and as a dispersion, will be characterised. The techniques to be used include: thermal gravimetric analysis (TGA), modulated differential scanning calorimetry (m-DSC), gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), FTIR and Raman, photon correlation spectroscopy and electrophoresis.

Finally, the performance of the polyester resin, when applied as a coating to paper, will be assessed. This will be carried out using various paper strength test techniques (including ring crush tests, burst tests and bending resistance tests), dynamic water repellency tests and contact angle analysis.

The results obtained from the preliminary assessment of available water resistant polyester coatings will be discussed.

Protein Adsorption onto a Biomaterial

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This study has used the Atomic Force Microscope to investigate protein adsorption onto poly(ethyleneoxide), using the Pluronic F108 triblock copolymer. The pluronic was adsorbed onto a hydrophobic Radio Frequency Glow Discharge thin film. The two proteins investigated in this study were, avidin and fibronectin. The pluronic layer was characterised with the AFM, and indicated that the pluronic adsorbed in low, medium and high packing densities in different experiments. Thus between experiments the adsorption of the pluronic was quite heterogeneous. However within each experiment very reproducible results were obtained. This indicated that the packing density of the pluronic layer remained constant throughout an experiment. The interaction force data obtained showed significant adsorption of fibronectin onto a low packing density pluronic layer whereas on a high packing density pluronic layer lower adsorption of fibronectin was observed. The interaction force data obtained for avidin adsorption onto a pluronic layer indicated that only a small amount of avidin had adsorbed, but that had only been loosely associated with the pluronic layer.

Interfacial Chemistry, Particle Interactions and Improved Dewatering of Clay Dispersions

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Tailings treatment and disposal is an important technological and environmental problem confronting mining and mineral industry worldwide. Several billion tonnes per year of intractable mineral waste slimes at relatively low solids content, are produced annually as a result of hydrometallurgical processing of mineral ore. The interactions between colloidal particles dispersed in an aqueous environment as well as the chemistry of the particle-solution interface are central to the dewatering behaviour of tails. The aim of this study has been to investigate the effect of adsorbed, hydrolysable metal ions, Mn^{2+} and Ca^{2+} adsorption on the surface chemistry (electrokinetic potential), particle interactions (shear yield stress) and the dewatering behaviour of smectite and kaolinite dispersions.

It is shown that hydrolysable metal ion adsorption strongly influences the zeta potential, shear yield stress, the settling rate and consolidation of flocculated clay slurries. The magnitude of zeta potentials decreased (became less negative), with increasing ionic strength of metal ions as expected, but was pH dependent for kaolinite and pH independent for smectite. For kaolinite dispersions, the decrease in zeta potential was accompanied by a shift in iep. The metal ion mediated particle interactions reflected in shear yield stresses, which were found to be lower than in the absence of metal ions. At equivalent solids volume fraction, the smectite dispersions displayed higher yield stresses than kaolinite dispersions. The lower yield stress dispersions displayed faster settling rate and better consolidation. The findings show that clear links between surface chemistry, particle interactions and dewatering of clays exist and these may be optimised for improved dewaterability.

Gelation of Biopolymer Systems under Shear

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The flow-induced microstructure of biopolymer solutions/gels is investigated. A biopolymer solution undergoing gelation is subjected to a controlled shear flow condition such that a fluid gel is produced. The evolution of the rheological behaviour during gelation is examined using a cone-and-plate rheometer. The shearing conditions and parameters are varied to assess their effect on the microstructure formed in fluid gels using a range of compatible and incompatible biopolymer mixtures. Several experimental techniques are used to relate the rheological behavior to the microstructure, including optical microscopy and direct contact imaging using Atomic Force Microscope (AFM). Measurement of the anisotropy of the system is investigated using rheo-optical techniques. The data will then enable prediction of the dominant structure that will be produced in pipes and other flows.

Dulux Australia Poster Session

Wednesday 14 February

Grazing Incidence X-Ray Diffraction Study of Nanoparticle Formation in Cadmium Arachidate and Dimethyldioctadecylammonium Bromide LB Films

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Control of the morphology of semiconductor nanoparticles is a vital step in the development and eventual application of these materials. To this end the Langmuir-Blodgett (LB) technique has been investigated, as the formation of particles is restricted by the nature of the film. Moreover, experiments using LB films of two or more components have indicated that by altering the domain size through addition of a second amphiphile, the particle size distribution may be changed. In this study, a series of LB films consisting of cadmium arachidate and dimethyldioctadecylammonium bromide were produced and the effect on particle size determined using UV-Vis spectroscopy. Grazing incidence x-ray diffraction was used to accurately study the structure of the films both before and after nanoparticle formation. The results show that the film structure was significantly altered by the formation of nanoparticles whilst change in the size of the nanoparticles was minimal.

Effect of Shear on Flocculation of Latex with Polyacrylic Acid Dual Polymer Flocculation of Alumina: Aggregate Structure and Filterability

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The mechanisms by which polymer flocculation occurs have been the subject of many recent studies. Three mechanisms may be used to describe the flocculation caused by polymers: charge neutralisation, polymer bridging and electrostatic patch and depletion flocculation. The focus of this work is polymer flocculation that proceeds via the irreversible bridging mechanism. The polymer used is 2.5×10^5 g/mol polyacrylic acid.

Small-angle static light scattering was used to examine the effect of increasing shear rate on the aggregate mass fractal dimension. Shear rate was controlled using a constant shear cell. Studies revealed increasing shear rate coincided with an increasing aggregate mass fractal dimension.

Extraction of Anti-tumor Polysaccharides from Liquid Cultured *Agaricus blazei*

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The mushroom *Agaricus blazei* is a native fungus of Brazil. It has been the subject of research in Japan and is reported to possess medicinal properties. The medicinal properties documented arise from the presence of bioactive compounds or “nutriceuticals” contained within the mushroom fruiting bodies, mycelia and liquid culture filtrates. The main area of research has been in regard to the anti-tumor constituents of the mushroom, although other reported bioactive properties include the stimulation of the immune system and antibacterial activity. It is also thought that this fungus contains components with properties similar to Viagra.

These bioactive compounds have been isolated from the fruiting bodies, mycelia and culture filtrate by the process of solvent extraction. Anti-tumour activity has been detected in a range of isolated compounds, these being predominantly polysaccharides, either alone or with an associated protein component.

In the course of this research, the extraction methods reported in the literature will be used to extract the bioactive compounds. In addition, different culture media and growth conditions will be tested in an effort to assess growth-substrate relationships with regards to the production and yield of these bioactive compounds. The effect of different solvent extraction protocols will be studied, as well as an investigation as to whether other possible medicinal substances (such as anti-viral compounds) are present. The antibacterial activity of the bioactive compounds present will also be investigated extensively.

The Environmental Impact of Mineral Processing in Australia

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Much research has been undertaken on the subject of minimising the volume and impact of mine tailings produced in the minerals industry. Currently a large but unquantified volume of mineral waste is produced within Australia. There are many problems associated with the disposal of this waste; these problems largely arise from the high water content of tailings. The tailings are generally dilute and thus must be stored in large dams, therefore ground water contamination and land reclamation become immediate problems, followed by the risk of potential tailings dam failure through dam leakage, instability or liquefaction. Many of these difficulties may be mitigated through the dewatering of the tailings. The process of dewatering can be applied in several ways that are able to increase the solids content of tailings from 10-30% to up to 70%. However, mining companies are reluctant to adopt these methods due to the perceived prohibitive cost of installing new large-scale dewatering equipment on existing plants. The low implementation level of dewatering in large plants leads to a deficit of data for large scale dewatering, and a lack of information pertaining to the benefits of dry disposal techniques. Thus, the industrial hesitation to use new dewatering methods becomes self-perpetuating. The current work addresses this problem, developing a more lucid profile of the current state of tailings disposal within Australia. The need for minimisation solutions is highlighted, with proposals offered to raise public awareness of both the current practices within the industry and the available solutions for these tailings disposal problems.

Particle Transport Mechanisms within Flotation Froths

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To model the flotation process, the pulp and froth phases must be separately analysed. Whilst the sub-processes of collision, attachment and stability have been identified and reasonably well modelled in the pulp phase, this is not true of the froth phase. A laboratory flotation column has been modified to allow sampling of both the pulp and froth phases via a number of compartments. Mass balances around each compartment and varying the total froth height have allowed a model to be developed that describes the particle transport mechanisms within the froth phase. This model includes parameters that describe particle entrainment, drainage, detachment and re-attachment. The froth efficiency E_{froth} can be calculated from this model.

A Study of the Effect of Surface Modification on the Stability of Poly(dimethylsiloxane) Emulsions

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Surfactant free poly(dimethylsiloxane) droplets can be prepared from single monomers (e.g., diethoxyl dimethylsilane) in water and ethanol using base as a catalyst. This discussion involves the effect of inclusion of functionalised siloxane monomers containing side groups of primary amines or secondary/tertiary amines attached to ethyleneoxide units. The strategies used to incorporate the functionalised monomers involve either incorporating the monomers on the surface of the as-made droplets or the formation of siloxane co-polymers prior to dispersion in water. Techniques employed to characterize the emulsions include zeta potential measurements, photon correlation spectroscopy, turbidity measurements and optical microscopy. Silicon and proton NMR data are considered with respect to copolymer characterisation. The effect of incorporation of these functionalised attachments to emulsion stability is discussed in terms of droplet coalescence and emulsion phase separation.

Dynamic Interfacial Tension and Dilational Properties of C12E8 and Beta-Casein at the Oil-Water Interface

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The dynamic of non-ionic surfactant (C12E8) and protein (Beta-casein) at oil (squalene)/water has been measured and studied by using the drop shape method over the long time scales. The transient relaxation studies on the non-ionic surfactant samples showed the diffusion controlled adsorption process at oil/water interface. The kinetics of adsorption of the protein is interpreted from the interfacial tension/log time plots to determine the regimes, which indicate the molecules arrangement at different time scales. Interfacial dilational or viscoelastic properties of the studied systems at different frequencies have been measured by using the same dynamic studies technique by employing a sinusoidal change in the interfacial area of the oil droplet at equilibrium state. The measured time domain sinusoidal waveforms of interfacial tension are transformed by using the Fast Fourier Transform to obtain the dilational moduli. The dilational properties are dependent on the surfactant and protein concentrations. The plots of dilational storage elasticity, G' ; and loss elasticity, G'' ; at different frequencies range, provide the information of relaxation time for both non-ionic surfactant and protein systems. The Cole-Cole plots indicate the number of reorientation process of the molecules at the liquid-liquid interface. The effect of dilational properties on the stability of oil-water system would be discussed.

A Rheological Characterisation and Dynamic Interfacial Tension Study of Highly Concentrated Water-in-Oil Emulsions

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Emulsions and emulsion technology have significant practical applications, including use in foodstuffs, pharmaceutical preparations, cosmetics and agricultural sprays. The aim of the research presented in this paper was to study the interfacial tension and rheological properties of highly concentrated water-in-oil (w/o) emulsions. Important factors affecting the bulk properties of the emulsions include surfactants, concentration, phase ratio, temperature etc.

In this work a range of highly concentrated w/o emulsions prepared using different poly-isobuteric succinic anhydrides emulsifiers have been investigated. Various stress and strain controlled rheometers were used to measure the rheological properties and a pendant drop tensionometer was used to characterize the dynamic interfacial properties. The rheology of these highly concentrated w/o emulsions has been found to suffer from "wall slip" effects in various "smooth" geometries. The roughened cone and plate geometry gave the same shear viscosity data as the vane geometry and both of these results are similar to the no-slip results from parallel plates, which have been corrected for slip velocity. The various emulsifiers show different dynamic rheological properties, indicating that there is a significant difference in the microstructure of the emulsions due the emulsifiers. These results will be correlated with the dynamic surface tension measurements on the same systems.

The Effect of Pre-shear on the Dewaterability of Flocculated Suspensions

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Dewatering is an important operation in industrial processes. Techniques including filtration, centrifugation, thickening, filter belt pressing are widely utilised. In order to optimise such processes, the use of chemical additives such as coagulants, flocculants, changing pH or changing ionic strength is employed. In addition, the performance of the additives can also be optimised by designing appropriate mixing condition.

This study aims to understand the effect of pre-shear on flocculated suspension on its dewatering properties. This work utilized a baffled mixing tank with a six flat bladed impeller to produce flocs. A pressure filtration rig was used to perform filtration experiments. A series of tests were performed on a model kaolin system flocculated using three standard industrial polymers. It was found that as the shear rate increased, the diffusivity or $D(f)$ of the material decreased. Shear was found to reduce the size the flocs and also packing in dense suspensions. Thus, the actual way in which mixing conditions has a detrimental effect on the dewaterability of a material has been elucidated.

The Effect of Size Distribution of Granulated Blast Furnace Slag on the Dissolution of Calcium

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It is well known in the cement industry that the size distribution of granulated blast furnace slag (GBFS) has a significant impact on the compressive strength of cement. In the present work, it is found that similar trends are observed when GBFS is incorporated into geopolymeric materials. Leaching tests have been conducted on GBFS using alkaline solution, and the results show that the dissolution of calcium increases with increasing specific surface area of GBFS. Scanning electron microscope (SEM) and transmission electron microscope (TEM) have been used to examine the surface of GBFS prior to, and after leaching with alkaline solution. It is postulated that the geopolymeric reaction involving calcium takes place at reactive sites on the surface of GBFS. Moreover, it is proposed that only calcium present on the surface of GBFS is leachable, thereby is responsible for the formation of colloidal calcium silicate hydrate crystalline phases within geopolymeric materials.

The Acid-Dissociation Equilibria Of Hydrous Ferric Oxides (HFO) In Various Supporting Electrolyte Solutions

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Even though the Gibbs-Donnan model has mainly been applied to the analysis of ion-binding equilibria of polyelectrolytes and ion-exchangers, the applicability to the description of ion-binding equilibria at the hydrous metal oxide/solution interface has recently been suggested by Marinsky. Since the acid-dissociation behaviors of these systems have traditionally been characterised by the electrical double layer model, a different aspect on the equilibria is expected.

In this work, the acid-dissociation behaviors of the amphoteric functionalities present in the surface gel layer of hydrous ferric oxide particles at 25°C have been investigated precisely with potentiometric titration. The effect of the degree of dissociation of acidic functionalities, the concentration level of supporting electrolyte and the kinds of anions on apparent acid-dissociation constants have been studied. The equilibria are highly dependent on the salt concentration level, indicating that they can be treated as an ion-exchange reaction between the surface layer and the bulk solution phase, and on the nature of anions. The surface gel phase volume as well as the thickness of the layer has been calculated based on Donnan's law.

Development of Synthetic Sludges for the Measurement of the Dewatering Characteristics of Sewage Sludges

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The dewatering behaviours of several synthetic sludges were investigated using a constant pressure batch filtration technique. The aim of the work was to manufacture a synthetic sludge that mimics the permeability and compressibility characteristics of real sewerage sludges. A biologically and chemically stable synthetic sludge can be used to investigate the fundamental dewatering behaviour of sewerage sludges without any of the inherent problems usually encountered with active sludges.

It was found that the nature of the extracellular polymer substitute had a significant effect on the dewatering behaviour, and that gelatine-based synthetic sludges simulate sewerage sludges better than alginate-based sludges. The role of particles in the suspensions was investigated, and it was found that an increase in the concentration of deformable yeast particles reduces the permeability and increases the compressibility.

The characterisation of the dewatering parameters of a fibre suspension was undertaken that showed that the solids diffusivity coefficient, $D(\phi)$, decreased with increasing solids volume fraction, ϕ . Thus, the fibres exhibit non-ideal behaviour, which suggests that they are the cause of the complex dewatering behaviour of sewerage sludges.

PLENARY ABSTRACTS

Solution Dynamics and Drops

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The dynamics of drop impact is relevant to many industrial processes, including spray coating, spray drying, ink-jet printing and agricultural chemical dispersion. When a drop impacts a solid surface, the drop first spreads until it reaches a maximum diameter, then it shrinks with an oscillating movement, finally reaching an equilibrium shape. The resultant spreading and recoil of the drop represents a continual trade-off between inertial centrifugal forces, capillary centripetal forces, and viscous dissipation. Research into the drop dynamics of Newtonian solutions have provided great insight into the respective contributions of inertia, viscosity, surface tension and the surface characteristics of the solid upon which the drop is impacting, that is, the hydrophobic/hydrophilic nature and roughness.

Unfortunately, most industrial formulations are not 'simple' Newtonian solutions. Polymers are often added to mixtures used in these applications to improve processibility, recently shown to be due to the associated enhancement of elasticity and extensional viscosity. Surfactants are also added to enhance wetting in some of these applications, especially in agricultural spraying, in which the efficacy of the agrochemical is enhanced by the presence of surfactants. Many solutions used in such applications in fact contain both polymers and surfactants of various types and concentrations. The addition of these components creates solutions, which have both complex fluid and surface characteristics.

Solutions may be 'tuned' to suit the particular application only when the dynamics of the polymer and surfactant within these systems are well understood. In this presentation, the results of drop impact studies of well characterised polymer, surfactant and polymer-surfactant solutions will be discussed, providing significant insight into the contributions of 'dynamic' fluid properties to their splash and rebound behaviour on hydrophilic and hydrophobic surfaces.

In-situ Vibrational Spectroscopy of Confined Organic Films

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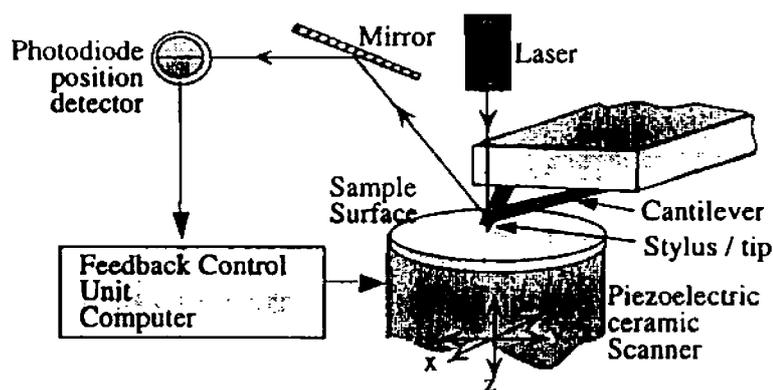
In recent years a new research area has grown out of the field tribology; micro-tribology. Micro-tribology is the study of molecular effects in friction, lubrication, and wear. Numerous indirect probes, such as the surface force apparatus (SFA) and the atomic force microscope (AFM), have been used to obtain information about lubricants confined between solid surfaces. However, the molecular structure is only *inferred* from the microscopic force measurements. Vibrational spectroscopy gives us the ability to gain direct structural information.

Raman scattering and sum-frequency spectroscopy has been used to study the structure of a Langmuir-Blodgett monolayer of Zn arachidate at the solid-solid interface. The Raman and sum-frequency spectra both show that the deposited monolayer is conformationally ordered and that the monolayer retains this order under varying pressure and shear. The behaviour of thin *liquid* films at the solid-solid interface has also been investigated. Raman scattering was used to probe the molecular structure of hexadecane and octamethylcyclotetrasiloxane (OMCTS). No evidence was seen of any 'confinement phenomena', as reported in AFM and SFA experiments on confined liquids.

EXPERIMENTAL TECHNIQUES

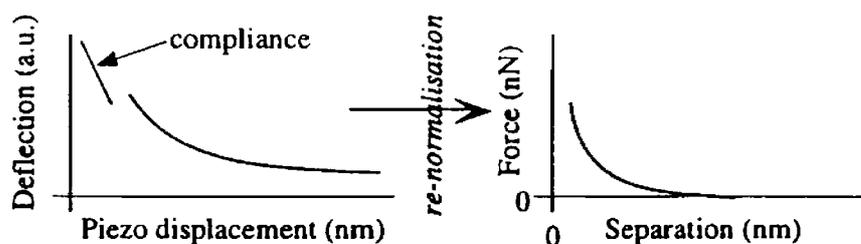
(ATOMIC) FORCE MICROSCOPY

The Force Microscope is one of a family of Scanned Probe Microscopes derived from the Scanning Tunneling 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 $O(\text{pN} - \mu\text{N})$, distance $O(\text{\AA} - \mu\text{m})$ }. Tip composition and geometry may be varied.

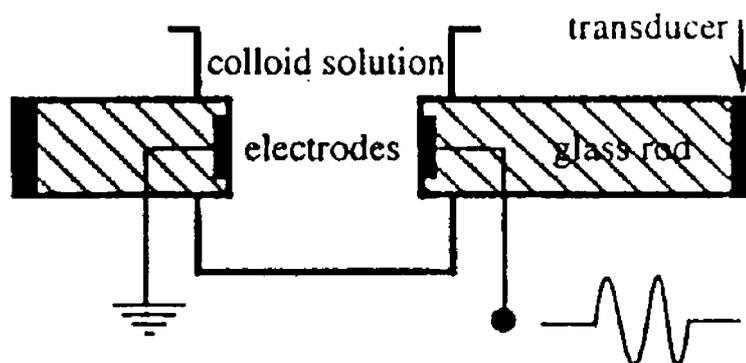


Suggested reading:

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.

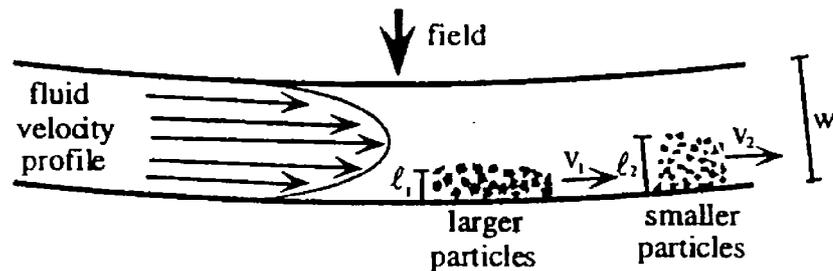
The dynamic mobility is a complex quantity equal in magnitude to the ratio of the particle velocity divided by the applied field. It is complex because there is a phase lag between driving frequency and the response of the particles to that field. As the applied field tends to zero the mobility becomes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

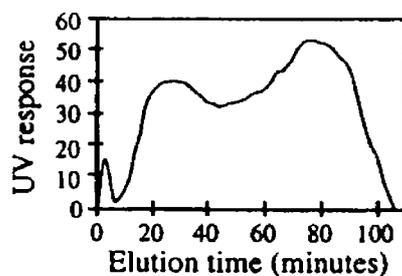


A schematic diagram of a sedimentation FFF channel.

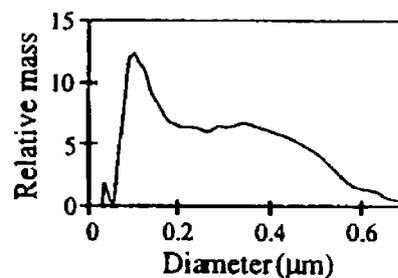
The data obtained is called a fractogram. The elution time can be converted to particle diameter using the equation;

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

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, ω is the field strength, λ 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 Fornisiero

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 η 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

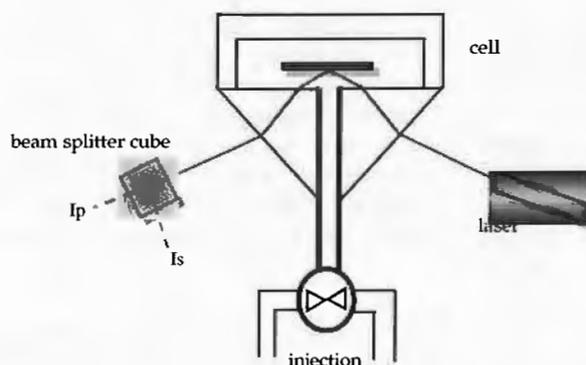
$$\frac{Hc}{R(\theta, c)} = \frac{1}{M_w} \left[1 + \frac{r_g^2 K^2}{3} \right] + 2A_2 c$$

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 K ar

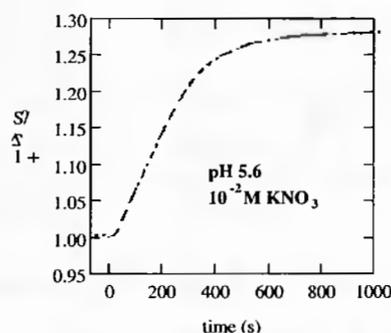
REFLECTOMETRY

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 stagnation point flow cell to measure adsorption under hydrodynamically well defined conditions.



Schematic representation of reflectometry in stagnation point flow

The surface of interest, usually a thin film (20-200 nm 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 90 nm silica particles adsorbing on an aminosilane treated silicon wafer

Adsorption processes, involving polymers and particles that occur on time scales 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 conformation 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:

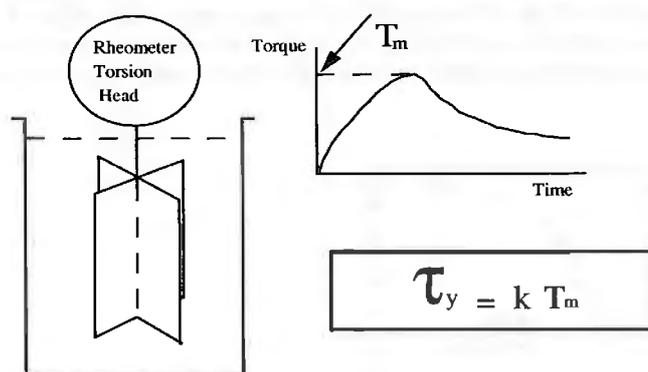
Dijt, J.C., Cohen Stuart, M.A., Hofman, J.E. and Fleer, G.J., Kinetics of polymer adsorption in stagnation point flow, *Colloids and Surfaces*, **51**, 141 (1990).

Summary provided by Rob Hayes

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 measurable 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-structure¹. The yield value^{2,3}, 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 τ_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.



A bladed vane is slowly rotated at a constant shear rate ($\ll 1s^{-1}$) in a beaker of the material of interest. The vane geometry is specifically utilised to minimise slippage, which can result in artefactually low stresses when smooth sample holding geometries are used. The torque on the vane is measured as a function of time, with the maximum torque assumed to correspond to the shear failure of the sample. The true yield stress can be calculated from the maximum torque and the dimensions of the vane³.

Schematic of the Vane technique for yield value determination

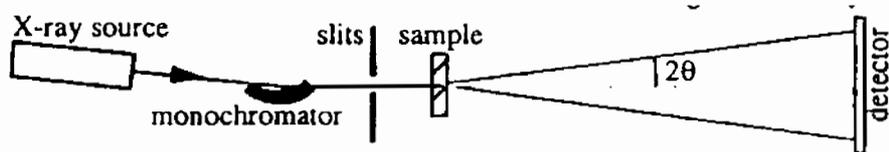
The viscoelastic characteristics of colloidal systems are also characterised by concentric cylinder rheometry, through measurement of the response to application of a sinusoidal stress or strain. G' , the storage or elastic modulus and G'' , the loss or viscous modulus, are determined from the stress-strain inter-relationship and the phase angle (δ) 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 system¹.

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

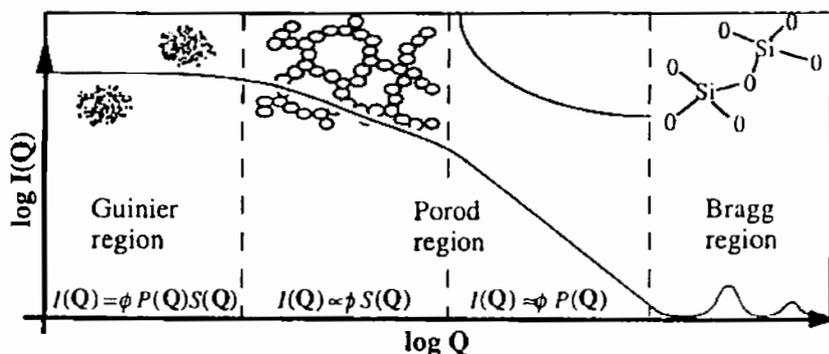
Small angle X-ray scattering allows the physical characteristics - dimensions, surface roughness and spatial arrangement - of particles (diameter 10 - 1000Å) in solution to be studied. In practice a collimated beam of monochromatic X-rays is passed through the sample and the intensity of scattering measured as a function of scattering angle 2θ (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, ρ_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, ρ 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, $(\rho_1 - \rho_2)^2$, where ρ_1 and ρ_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; $I(Q) = \phi P(Q) S(Q)$; ϕ 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.

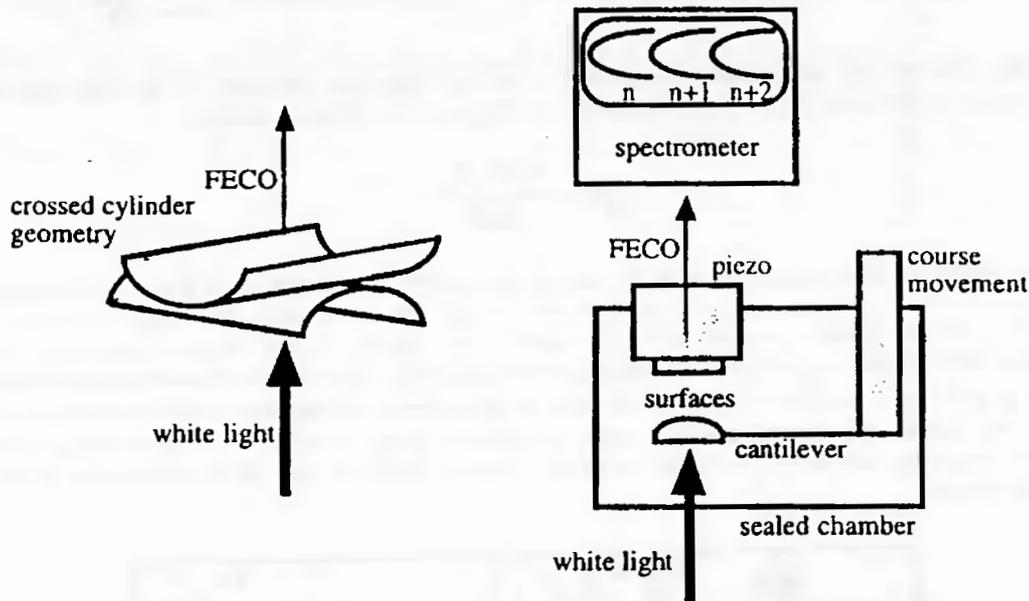
Suggested reading:

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

Summary provided by Julianne 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 $O(\text{\AA}-\mu\text{m})$ }.

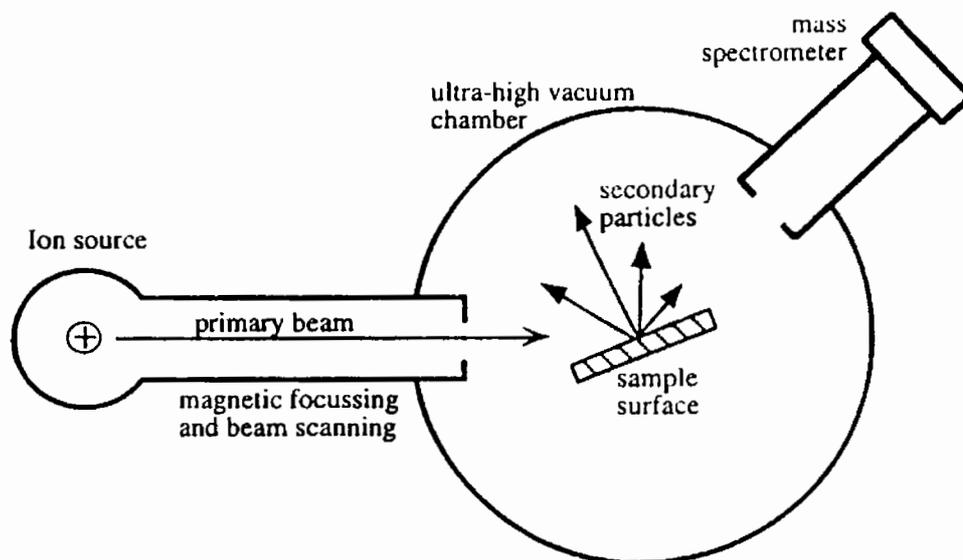
The crossed cylinder geometry approximates well as a sphere, with a radius equal to the geometric mean curvature of the two cylinders, interacting with a plane. Surfaces are restricted to those that can easily form transparent, thin smooth films, e.g. silica, sapphire, mica. Alternatively the interferometer 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 Cs^+ , O^{2+} , O , Ar^+ , and 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.

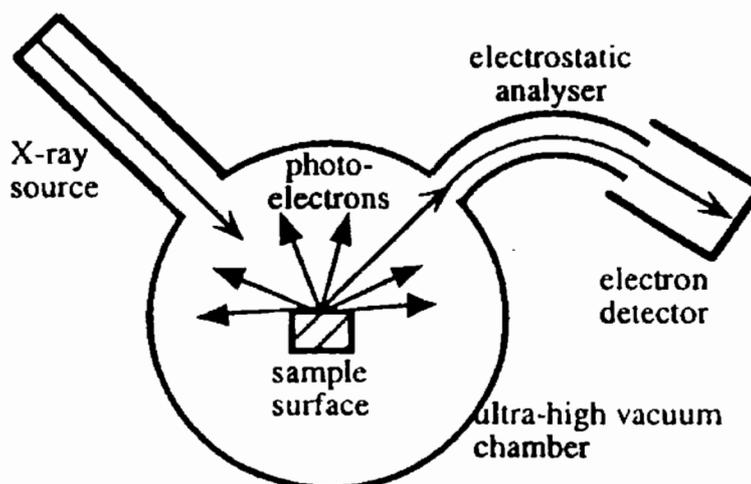
Mass spectroscopy not only provides isotopic discrimination, but both negative and positive species can also be analysed.

Suggested reading:

Benninghoven, A., Rüdenauer, 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.

$$KE = h\nu - BE$$

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.

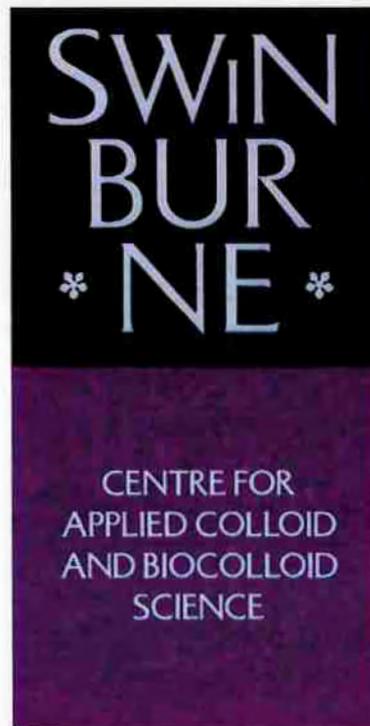
The kinetic energies of the photoelectrons leaving the sample are so low that, in practice, only those from the top 1-5 nm of the surface escape and arrive at the spectrometer, making it an extremely surface sensitive technique. Most elements (except hydrogen and helium) have practical detection limits 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).

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