

Chapter Three: Structured Matter

Nanoengineered Particles for Cardiovascular and Alzheimer's Disease Diagnosis

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Magnetic resonance imaging (MRI) is a powerful non-invasive imaging technique currently used to detect abnormalities in living tissues. The ability to distinguish diseased cells at early stages of a disease is vital because early diagnosis is often crucial in developing effective treatments. The main limitation of commercially available contrast agents for MRI is that they are not targeted to specific cells and they do not localize at a specific area for any length of time. Thus targeted delivery of contrast agents represents an excellent way to assess the progress of a disease and the efficacy of treatments because MRI does not use harmful radiation.

An emerging technique to control the structure of particles on the nanoscale is the layer-by-layer assembly process[1]. In this process, layers of interacting polymers are deposited into the pores of mesoporous silica templates, which act like a sponge to soak up the polymer. This technique allows for fine control over the properties of the particles by altering the number of layers deposited, the material deposited at each layer, and also by controlling the assembly conditions. A porous polymer particle is subsequently formed by dissolving the sacrificial silica template. We have functionalised these porous particles with MRI contrast agents and are currently functionalising the capsules with antibodies [2,3] which will target the particles to amyloid fibrils, which are linked to the onset of Alzheimer's Disease, and to the plaque build-up in cardiovascular tissue to help with the diagnosis of heart disease.

[1] J.F. Quinn, A.P.R. Johnston, G.K. Such, A.N. Zelikin and F. Caruso, "Next generation sequentially assembled ultrathin films: beyond electrostatics", *Chem. Soc. Rev.*, **36**, p. 707, 2007.

[2] C. Cortez, E. Tomaskovic-Crook, A.P.R. Johnston, B. Radt, S.H. Cody, A.M. Scott, E.C. Nice, J.K. Heath and F. Caruso, "Targeting and Uptake of Multilayered Particles to Colorectal Cancer Cells", *Adv. Mater.*, **18**, p. 1998, 2006.

- [3] C. Cortez, E. Tomaskovic-Crook, A.P.R. Johnston, A.M. Scott, E.C. Nice, J.K. Heath and F. Caruso, "A General Approach for DNA Encapsulation in Degradable Polymer Microcapsules", *ACS Nano*, **1**(1), p. 63., 2007.



Fig. 1: Targeted delivery of nanoengineered capsules assembled using the Layer-by-Layer technique. (www.umshp.org/rs/images/mri_brain.jpg) (Photograph courtesy of the University of Missouri School of Health Professions.)

Targeted Delivery of Therapeutics using Nanoengineered Materials

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In chemotherapy cytotoxic drugs are distributed evenly throughout the body with detrimental effects on healthy cells, causing side-effects including hair loss and digestive problems. The ability to specifically target the drugs to cancer cells has the potential to greatly decrease the side-effects by delivering high doses of the therapeutic agents only to specific sites where required. Targeted delivery has the potential to revolutionize current methods of cytotoxic drug administration to improve the clinical outcomes for cancer patients. This project exploits the coupling of two innovative approaches to cancer treatment: immunotherapy and nanotechnology.

An emerging technique to deliver drugs is by immobilising the drug inside a nanocapsule [1]. The capsules are prepared by the layer-by-layer deposition of interacting polymers onto a sacrificial template particle. This technique allows for fine control over the properties of the capsule by altering the number of layers deposited, the material deposited at each layer, and also by controlling the assembly conditions. The surface of the capsules can be functionalised with signalling molecules, such as antibodies, peptides and other small molecules. We have demonstrated that antibody functionalised, nanoengineered capsules specifically bind to cancer cells and are internalised into the cancer cells [2], [3].

We are currently investigating the loading of these capsules with chemotherapy drugs, peptides and nucleic acids [4] and evaluating the release of these therapeutics in vitro and in vivo. We are also currently investigating the biodistribution of these capsules in animal models.

- [1] A.P.R. Johnston, C. Cortez, A.S. Angelatos and F. Caruso, "Layer-by-Layer Engineered Capsules and their Applications", *Curr. Opin. Colloid Interface Sci.*, **11**, p. 203, 2006.
- [2] C. Cortez, E. Tomaskovic-Crook, A.P.R. Johnston, B. Radt, S.H. Cody, A.M. Scott, E.C. Nice, J.K. Heath and F. Caruso, "Targeting and Uptake of Multilayered Particles to Colorectal Cancer Cells", *Adv. Mater.*, **18**, p. 1998, 2006.
- [3] C. Cortez, E. Tomaskovic-Crook, A.P.R. Johnston, A.M. Scott, E.C. Nice, J.K. Heath and F. Caruso, "A General Approach for DNA Encapsulation in Degradable Polymer Microcapsules", *ACS Nano*, **1**(1), p. 63., 2007.
- [4] A.N. Zelikin, Q. Li and F. Caruso, "Degradable Polyelectrolyte Capsules Filled with Oligonucleotide Sequences", *Angew. Chem. Int. Ed.*, **45**, p. 7743, 2006.
- [5] A.N. Zelikin, A.L. Becker, A.P.R. Johnston, K.L. Wark, F. Turatti and F. Caruso, "Influence of Size, Surface, Cell Line and Kinetic Properties on the Specific Binding of A33 Antigen-Targeted Multilayered Particles to Colorectal Cancer Cells", *ACS Nano*, **1**(1), p. 93, 2007.

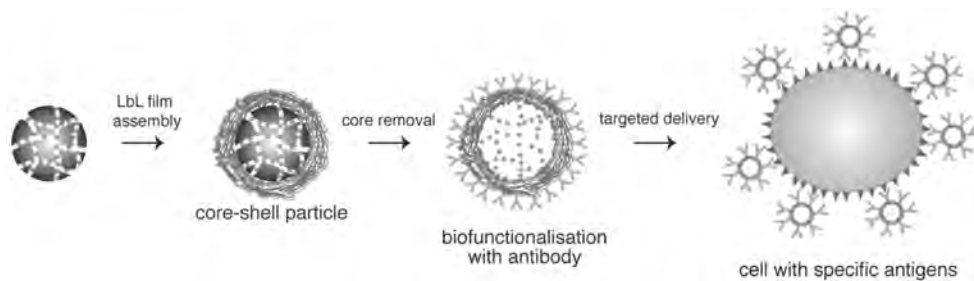


Fig. 1: Targeted delivery of nanoengineered capsules assembled using the Layer-by-Layer technique.

Study of Deformable Interfaces Using AFM

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Emulsions are made of droplets of one liquid colliding with each other in another liquid, such as oil droplets in vinaigrette salad dressing. This is a dynamic process where some droplets collide and bounce away, while others can collide and stick together or coalesce. Emulsions are prevalent in a range of applications from the purification steps in pharmaceutical and minerals processing to products such as shampoo, milk and even ice cream. Emulsions are part of a larger class of materials called "soft colloids" or solid particle with soft bio-films or polymeric coatings and are common nanotechnology, advanced materials, and bio-technology applications. In all of these cases controlling and understanding the inter-droplet or inter-particle interactions on the scale of nanometers is crucial to process improvement and new developments. Traditionally, this has been accomplished through a collection of indirect methods to predict their behaviour.

This project measures these interactions directly using a novel method employing atomic force microscopy to gain new insights into the interactions in these systems. This approach is coupled with complementary indirect methods to discern correlations between types of molecular structures and the inter-droplet interaction forces in systems with clear industrial relevance.

- [1] L.Y. Clasohm, I.U. Vakarelski, R.R. Dagastine, D.Y.C. Chan, G.W. Stevens and F. Grieser, "Anomalous pH Dependent Stability Behavior of Surfactant-Free Nonpolar Oil Drops in Aqueous Electrolyte Solutions", *Langmuir*, **23**, pp. 9335-9340, 2007.
- [2] R.R. Dagastine, R. Manica, S.L. Carnie, D.Y.C. Chan, G.W. Stevens and F. Grieser, "Dynamic Forces between Two Deformable Oil Droplets in Water", *Science*, **313**, pp. 210-213, 2006.

Dynamics of Adsorbed Polymer-surfactant Complexes

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This project focuses on the development and use of novel methods to study the dynamic behaviour of adsorbed polymer-surfactant complex layers using atomic force microscopy. The research will quantify the dynamics of adsorbed polymer-surfactant complex layers with a number of variables including ionic strength, surfactant concentration and the type of polymer. These results will be integrated into product and process developments with an industrial partner.

Visualizing the Water Uptake and Growth of Aerosol Particles on Multiple Length Scales

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Greenhouse gases are commonly perceived as the main cause of global climate change, yet aerosol particles are just as important. These tiny particles range from a few nanometers to microns in size and are always present in our atmosphere and come from both natural and anthropogenic processes. Aerosols play a large role in the climate by adsorbing or reflecting solar radiation or by taking on water to form clouds, fogs, hazes or smog. The water uptake and growth of aerosol particles is still poorly understood in cloud formation and remains the largest uncertainty in global climate models. This study focuses on visualizing this process on multiple length scales using two different techniques. A novel approach employing environmental scanning electron microscopy (ESEM) to directly observe the condensation of water droplets on micron size aerosol particles is used at Bucknell University lead by Prof. Timothy Raymond. Atomic Force Microscopy (AFM) is used to image aerosol particles on the nanometer scale as a function of relative humidity at the University of Melbourne. The combination of these two techniques (ESEM and AFM) as well as the ability to measure physical properties using the AFM will provide new information on aerosols across a large size range.

Forces in Colloidal Systems in High Salt

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Why proteins crystallize, drops coalesce and mineral particles flocculate in high salt concentrations are all examples of how the forces between particles and droplets play an important role in the Australian food, pharmaceutical and mining industries. The physical origins behind these forces are crucial to control particle and droplet stability. Yet, an understanding of these forces in concentrated salt solutions is still an uncharted area despite the prevalence of these systems. Through a novel development of a highly sensitive experimental technique, total internal reflection microscopy, this study will identify the physical origins of these forces. This fundamental study will help connect colloid science to high salt conditions relevant to both industry and biology.

Controlling Clay Behaviour in Suspension: Developing a New Paradigm for the Minerals Industry

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The Australian Mineral Science Research Institute (AMSRI) was formed in 2006 to conduct research into fundamental phenomena that have an influence on mineral processing. The Institute is composed of researchers from the University of Melbourne, the University of South Australia, the University of Newcastle and the University of Queensland. The Institute is jointly sponsored by the government (Australian Research Council) and a consortium of industry partners. The aim is to investigate research areas where quantum leap changes in mineral processing can be realised and to develop technologies to enable the new ideas to be taken up by industry.

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

The classical way to tackle behavioural problems in clay suspensions is to attempt post-dispersion remediation, usually only at the point of tailings dewatering and disposal. However in view of current indications that up-front control of initial clay dispersion during wetting is significantly more effective at improving clay behaviour than any post-dispersion treatment, implementation of a holistic approach to dealing with clay issues makes more sense. To this end, any new approach requires not just a chemical and engineering solution but a systems overview of the problem, where the nature and cost of problematic clay behaviour across all aspects of a minerals processing operation are considered.

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

Selective Adsorption of Chiral Molecules at Solid–Liquid Interfaces

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The discrimination between optical isomers by solids through selective adsorption is critical to the purification of drugs. The aim of this project is to establish the fundamental basis of this selectivity. Chiral molecules are tethered to solids and the selectivity of adsorption is examined as a function of structure and orientation. The current methods for determining enantiomeric excess rely on differences in chromatographic retention times; we are developing new optical methods for determining selectivity.

Lubrication Forces and the No-slip Boundary Condition

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The Navier–Stokes equations provide the theoretical basis for the accurate description of many problems in fluid mechanics. Solution of these equations requires knowledge of the boundary conditions, and it is customary to assume a continuity of fluid velocity. Included in this assumption is continuity of fluid velocity across a solid–liquid interface, i.e. the no-slip boundary condition. The intuitive basis is that intermolecular forces cause the fluid molecules immediately adjacent to the solid surface to ‘stick’ to the solid and therefore adopt the same velocity as the solid. However, the no-slip boundary condition has not been derived from fundamental principles; it is justified through agreement with experiment and has been reported to fail in sufficiently sensitive experiments. We are accurately measuring the lubrication forces acting on small particles to determine whether the no-slip boundary condition is accurate at high shear rates and for nanometre-thick films.

[1] C.D.F. Honig and W. Ducker, “No slip hydrodynamic boundary condition for hydrophilic particles”, *Physical Review Letters*, **98**, 2007.

The Adsorbed Gas State

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The discipline of colloid and interface science has widespread application in areas of minerals processing, emulsion preparation and food preparation. Recently it has been claimed that many hydrophobic solids become coated in tiny interfacial nanobubbles when immersed in water. If this is true, it would have far reaching implications on our understanding of interfaces, and on implementation of industrial processes that rely on interfacial properties. In this project, we study the formation conditions of interfacial nanobubbles, characterise the properties of the nanobubbles, and examine the use of nanobubbles for lubrication.

[1] X.H. Khan and W.A. Ducker, "A Nanoscale Gas State", *Physical Review Letters*, **98**, 2007.

Control of Crystal Morphology

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Our aim is to determine the general principles by which the morphology of crystals can be controlled through the selective adsorption of molecules to crystal faces. We plan to examine a variety of metal oxides, beginning with ZnO, which is valuable because of its use in light emitting diodes and as piezoelectric transducers for motion control and pressure sensing. Control of crystal shape will allow the growth of crystals in bulk and on surfaces that optimise their use as transducers and LEDs.

Nano-assembly of Light Emitting Polymer Films

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Since the invention of luminescent polymers, considerable effort has been made to produce viable flexible displays using the polymers in thin films. The luminescent properties of these films depend on the processing conditions of the polymers, and it has been established that the conformation of the luminescent polymer is directly related to the light emitting properties. This project studies the properties of MEH-PPV, a common luminescent polymer, by molecule orientation and single molecule spectroscopy, in order to gain a better understanding of how an ideal light emitting film can be produced.

This research will assist Australian industries to further advance these processes and devices leading to better quality, cheaper, more efficient products. The Australian community will benefit through economic and technological advances. These advanced materials will promote health and environmental wellbeing.

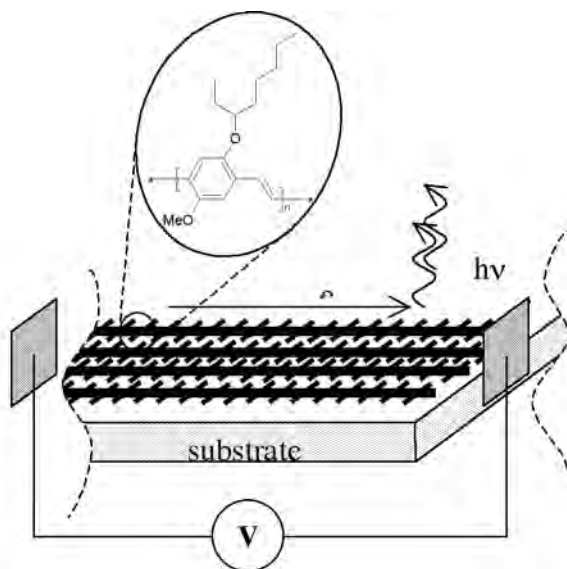


Fig. 1: Device for the conversion of light into electrical energy or visa versa. The insert shows the chemical structure of the light emitting polymers used.

- [1] E.K. Hill, K.L. Chan, A.B. Holmes and D.E Dunstan, "Rheofluorescence studies of poly(p-phenylenevinylene) derivatives in simple shear flow", *Synthetic Met.*, **153**, pp. 213-216, 2005.
- [2] D.E. Dunstan and Y. Wei, "Compressive Elasticity in Polymer Couette Flow", *European Physical Journal Applied Physics*, **38**, pp. 93-95, 2007.

Physico-Chemical Studies of Milk Proteins During Powder Rehydration

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Little is currently understood about the dynamics and mechanisms of establishing equilibrium during milk powder rehydration. Of particular interest are the calcium-laden casein aggregates which represent 80% of the protein in milk. This important polydisperse system of sub-micron-sized particles appears difficult to correctly reestablish from rehydrated powders. This project will employ various light scattering techniques to study the kinetics of powder rehydration and to extend current understanding of the casein aggregate system. It is hoped that this information can be used to direct process improvements resulting in powders with better rehydration properties.

[1] G.J.O. Martin, R.P.W. Williams and D.E. Dunstan, "Comparison of Casein Micelles in Raw and Reconstituted Skim Milk", accepted in *Int. J. Dairy Science*.

Compressibility and Permeability of Stimuli Responsive Suspensions: Application to Modelling Mineral Dewatering Processes

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The importance of efficient separation of water from solid particles in mineral processing, is gaining emphasis with increasing environmental regulation and economic rationalisation. High molecular weight polymers, called flocculants, are commonly used to induce aggregation and settling of slurry particles. This project investigates the development and use of flocculants that respond to stimuli such as changes in temperature or acidity, to manipulate particle-particle interactions. The approach provides a strategy for improving dewatering efficiency by producing both fast sedimentation of fine particles (by aggregation) and dense (low moisture) sediment beds. A stimulus is used to change the force between particles first to attractive. The particles then aggregate, rapidly settle and can be removed with a thickener. Then, by changing the inter-particle force back to repulsive, the particles in the sediment will undergo further consolidation resulting in additional expression of water from the solids suspension.

The primary parameters which influence the performance of dewatering operations such as thickening are the suspension compressibility and permeability. The techniques to measure these properties and the models used to predict performance of dewatering operations in industry have been developed over the past few years. The aim of the project is to measure these properties of suspensions when the stimuli responsive flocculants we have developed are used. The results of the measurements will be used to determine the optimum time to “switch” the stimulus in order to recover the most water in the least time.

- [1] G.V. Franks, C.V. Sepulveda and G.J. Jameson, “pH-sensitive flocculation: Settling rates and sediment densities”, *AIChE Journal*, **52**, pp. 2774-2782, 2006.
- [2] G.V. Franks, “Improved Solid/Liquid Separation using Stimulant Sensitive Flocculation and Consolidation”, *Journal of Colloid and Interface Science*, **292**, pp. 598-603, 2005.
- [3] G.V. Franks, Y. Yan, S. Biggs and G.J. Jameson, “Stimulant Sensitive Flocculation and Consolidation”, Patent Cooperation Treaty number WO2005021129, 10 March 2005.

Smart Polymer Development and Application as Stimulant Responsive Flocculants

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The importance of efficient separation of water from solid particles in slurries produced from mining or paper milling processes, is gaining emphasis with increasing environmental regulation and economic rationalisation. High molecular weight polymers, called flocculants, are commonly used to induce aggregation and settling of slurry particles. This project investigates the development and use of flocculants that respond to stimuli such as changes in temperature or acidity, to manipulate particle-particle interactions. The approach provides a strategy for improving dewatering efficiency by producing both fast sedimentation of fine particles (by aggregation) and dense (low moisture) sediment beds. A stimulus is used to change the force between particles first to attractive. The particles then aggregate, rapidly settle and can be removed with a thickener. Then, by changing the inter-particle force back to repulsive, the particles in the sediment will undergo further consolidation resulting in additional expression of water from the solids suspension.

There are several methods of controlling the inter-particle forces to be either attractive or repulsive. The use of pH, temperature or light sensitive “smart” polymers appears to have the potential for significant reduction in mineral tailings volume and enhanced water recovery. Preliminary results with model colloids indicate that for the pH controlled system up to 40%

reduction in sediment volume is possible within three hours, and for the temperature sensitive system up to 13% reduction in sediment volume is possible in less than one day.

The aim of the project is to synthesise novel homo- and co-polymers which respond to stimuli such as temperature and or light. The influence of polymer properties such as molecular weight, fraction of charged monomers and responsive unit chemistry on the polymer solution properties, polymer adsorption and suspension behaviour will be investigated.

- [1] G.V. Franks, C.V. Sepulveda and G.J. Jameson, "pH-sensitive flocculation: Settling rates and sediment densities", *AIChE Journal*, **52**, pp. 2774-2782, 2006.
- [2] G.V. Franks, "Improved Solid/Liquid Separation using Stimulant Sensitive Flocculation and Consolidation", *Journal of Colloid and Interface Science*, **292**, pp. 598-603, 2005.
- [3] G.V. Franks, Y. Yan, S. Biggs and G.J. Jameson, "Stimulant Sensitive Flocculation and Consolidation", Patent Cooperation Treaty number WO2005021129, 10 March 2005.

Advanced Ceramic Powder Processing

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Materials scientists can produce ceramic materials in the lab in small quantity with any imaginable property. These ceramics will enable emerging technologies such as advanced heat engines and electronics. The obstacle to their widespread use is the lack of low cost, reliable processes for complex shaping. Our group develops innovative processes for producing high strength complex shaped advanced ceramic components. Current research focuses on development of new and improved gelcasting binders for thick section complex shaped component production and aqueous tape casting for thin film production. Other projects include production of ceramic foams and understanding cracking in drying ceramic bodies.

- [1] G.V. Franks, D.E. Dunstan and S.B. Johnson, "Methods of Forming Shaped Articles from Suspensions", US Patent number 7,192,546, granted, 20, March, 2007. Australian Patent number 2001246249 sealed 6, January 2006. PCT number WO200176845 published 18, October 2001.
- [2] E. Santanach Carreras, F. Chabert, D.E. Dunstan, G.V. Franks, "Avoiding 'mud' cracks during drying of thin films from aqueous colloidal dispersions", *Journal of Colloid and Interface Science*, **313**, pp. 160-168, 2007.
- [3] S.B. Johnson, D.E. Dunstan and G.V. Franks, "Rheology of Crosslinked Chitosan / Alumina Suspensions Used for a New GelCasting Process", *J. Am. Ceram Soc.*, **85**, pp. 1699-1705, 2002.

Oxide Surfaces

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The surface charging properties of colloidal metal oxide particles in aqueous suspension controls the inter-particle forces between those particles. The inter-particle forces influence behaviour of suspensions of particles such as stability against sedimentation, rheology (flow) and particle packing. These suspensions behaviours are important in applications such as ceramic powder processing and solid-liquid separation in mineral processing. Oxide surfaces such as alumina, titania and zinc oxide have important applications in the production of aluminium, solar cells, photocatalysis, orthopaedic implants and blue light emitting diodes.

Our research focuses on the reactivity of these surfaces in environments where water is prevalent (such as aqueous solutions or humid air). Our approach combines experimental techniques such as zeta potential measurements, Atomic Force Microscopy, spectroscopy and Diffuse Functional Theory modelling. Understanding the relationship between surface structure and surface reactivity (such as surface charging behaviour) is a goal of the research. We hope to gain a fundamental knowledge of the factors that control crystal growth morphology and rates.

- [1] Y. Gan, E. J. Wanless, G.V. Franks, "Lattice-resolution imaging of the sapphire (0001) surface in air by AFM", *Surface Science*, **601**, pp. 1064-1071, 2007.
 - [2] Y. Gan, G.V. Franks, "Charging Behavior of the Gibbsite Basal (001) Surface in NaCl Solution Investigated by AFM Colloidal Probe Technique", *Langmuir*, **22**, pp. 6087-6092, 2006.
 - [3] Y. Gan and G.V. Franks, "High resolution AFM images of the alpha-Al₂O₃ Single Crystal (0001) Surface in water", *J. Phys. Chem. B.*, **109**, pp. 12474-12479, 2005.
 - [4] G.V. Franks and L. Meagher, "The Isoelectric Points of Sapphire Crystals and Alpha-Alumina Powder", *Colloids and Surfaces A*, **214**, pp. 99-110, 2003.
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Ion Specific Suspension and Emulsion Behaviour

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Ion specific (Hofmeister) effects produce behaviour of suspensions and emulsions that cannot be predicted with the classical DLVO theory of surface interactions. The phenomena is significant in controlling behaviour of such materials as mineral and ceramic suspensions, cosmetic products such as lotions and creams and food products such as sauces and dressings. The mechanism responsible for ion specific forces is believed to be due to either ion hydration effects and/or ion polarisability. The research focuses on elucidating the mechanism through macroscopic and microscopic measurements of suspensions and emulsions. Macroscopic measurements such as zeta potentials, rheological behaviour, droplet size, stability against sedimentation or creaming are typically conducted. Microscopic measurements of surface forces with the Atomic Force Microscope are also important to improve our understanding of the phenomena.

- [1] V. Deinz, M. Bostrom, G.V. Franks and B.W. Ninham, "Extended DLVO: Electrostatic and non-electrostatic forces in oxide suspensions", *Advances in Colloid and Interface Science*, **5**(15), pp.123-126, 2006.
- [2] G.V. Franks, A.M. Djerdjev and J.K. Beattie, "The absence of cation or anion effects at low salt concentrations on the charge at the oil/water interface", *Langmuir*, **21**, pp. 8670-8674, 2005.
- [3] G.V. Franks, "Zeta Potentials and Yield Stresses of Silica Suspensions in Concentrated Monovalent Electrolytes: Isoelectric Point Shift and Additional Attraction", *Journal of Colloid and Interface Science*, **249**, pp. 44-51, 2002.

Deformation and Flow of Networked Suspensions

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The deformation and flow of attractive particle networks is important in a wide variety of fields including nanotechnology, minerals and ceramic powder processing. Our research is aimed at improving understanding of how factors such as particle size, shape, volume fraction, and surface interactions influence the shear and compressive flow behaviour of particulate suspensions. Rheological properties such as yield stress, viscosity, elasticity and compressibility as well as permeability are typically studied for a range of particulate materials.

Aggregate-Sediment Bed Property Relationships

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The relationship between aggregate properties and flow and consolidation behaviour of sediment beds is not clearly understood. This relationship is important in developing solid/liquid separation processes that result in both rapid settling aggregates and sediment beds that dewater well. The aim of the research is to determine the relative importance of aggregate properties (such as size and structure) and inter-particle bond force in determining the attractive particle network structure, flow and consolidation behaviour.

- [1] A. Olsen, G.V. Franks, S. Biggs, and G.J. Jameson, "An Improved Collision Efficiency Model for Particle Aggregation", *J. Chem. Phys.*, **125**, 2006.
- [2] Y. Zhou, G.V. Franks, "Flocculation Mechanism Induced by Cationic Polymers Investigated by Light Scattering", *Langmuir*, **22**, pp. 6775-6786, 2006.
- [3] P.D. Yates, G.V. Franks, S. Biggs and G.J. Jameson, "Heteroaggregation with Nanoparticles: Effect of Particle Size Ratio on Optimum Particle Dose", *Colloids and Surfaces*, **255**(1-3), pp. 85-90, 2005.

Metabolic Engineering, Fermentation Processes, and Biomolecule Production

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Metabolic Engineering is concerned with the metabolism of cells. It aims to improve cellular properties or increase the production of cellular products by making directed changes to cell metabolism, either at a DNA, RNA or protein level. Research in this area typically begins with systems approaches that model the large networks involved in cell metabolism and assess potential targets for directed changes. Improvements can then be introduced by recombinant DNA techniques. This is a truly multidisciplinary area which involves chemical engineering, mathematics, biochemistry and molecular biology. It is also linked to recent breakthroughs in Metabolomics.

We have developed a new fermentation laboratory for the study of Metabolic Engineering, fermentation processes and biomolecule production. This laboratory contains four medium scale (5 L capacity) fermenters that can be used for the growth of bacterial, fungal or mammalian cells and the production of natural or recombinant biomolecules. Products include protein drugs, intracellular metabolites and other biomolecules that are useful for

research or industrial processes. The medium scale capacity of these fermenters will allow us to study the scale up and optimisation of a wide range of fermentation processes.



Fig. 1: A Biostat Aplus fermenter system
(http://www.sartorius.com/biostat_aplus/)
(Photo courtesy of Sartorius Stedim Biotech GmbH.)

Functional Foods and Advanced Dairy Technology

Staff: Sally Gras, Daniel Otieno, Sandra Kentish, Raymond Dagastine, Geoffrey Stevens

Sponsors: Department of Education Science and Training, Dairy Innovation Australia Ltd.

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Research in this area is focused on the development of functional foods and the understanding of how process parameters influence the microstructure of cheese and other dairy products.

Functional foods (also known as nutraceutical products) are foods which deliver medicinal benefits in addition to their nutritional benefits. Functional foods are a burgeoning global industry and Australia has a vibrant dairy industry which is well poised to capture a significant portion of this market, which can be captured through the development of specialised dairy ingredients for both domestic and export use.

The specific focus of our functional foods research is to investigate the enzymatic production of galacto-oligosaccharides from a number of processed milk streams using industrially relevant conditions. Work is also being conducted to develop galacto-oligosaccharide enriched dairy ingredients by purification and concentration of the enzymatic hydrolysis products. The project is an exciting example of the translation of fundamental research findings to an industrial setting and the development of novel dairy products.

Our research in cheese microstructure is a collaboration between researchers within the Particulate Fluids Processing Centre and Dairy Innovation Australia Limited. It is a preliminary study of cheese microstructure and how microstructure can be controlled on the factory floor during the curd formation process.

We are consulting with Dairy Innovation Australia stakeholders at their manufacturing sites to understand their cheese-making processes and current monitoring and control tools. We are also establishing methods to image product micro and nanostructural characteristics effectively using microscopy techniques and will evaluate this microstructure through rheological characterisation.

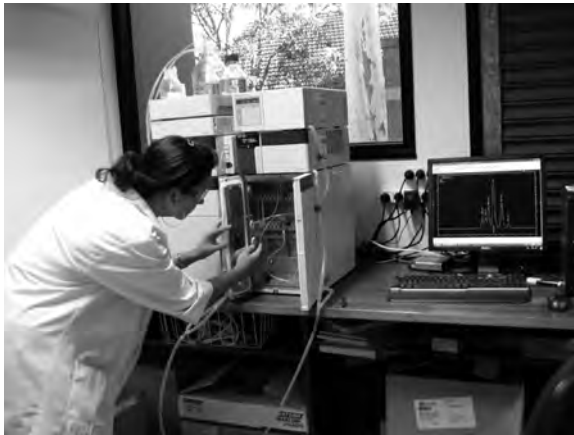


Fig. 1: A research student analyses functional food products by chromatography.

Protein Misfolding and the Self-assembly of Non-native Protein Nanostructures

Staff: Sally Gras, Upulie Divisekera

Bio21 Laboratory

Students: Yung Kei Ho

Sponsors: The University of Melbourne Early Career Researcher Scheme, Australian Academy of Science, Selby Scientific Foundation

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We are currently developing novel nanobiomaterials. Our research spans several disciplines ranging from peptide synthesis and microscopy, to spectroscopy and protein structural studies. Our studies are centred around a theme of protein or peptide self-assembly and the formation of non-native protein structures, such as amyloid fibrils. These fibrils are found in a number of diseases (e.g. Alzheimer's and Type-II diabetes) but are also associated with positive functions, can be made from generic proteins and have outstanding properties

including strength and stability in a wide range of environmental conditions. We examine how amyloid fibril-like structures made from synthetic precursors can be used to make new materials. We also seek to determine their structure and to extend their properties for biotechnology and nanotechnology applications.

A second goal is to understand how cells interact with their immediate environment, including nanomaterials, both outside and inside the body. We are currently developing nano-structured surfaces which can be used to examine and exploit cell behaviour.

We use peptide synthesis (microwave assisted and manual) to make the starting materials for building fibrils and other protein-based materials. We monitor protein aggregation and self-assembly (light scattering, dye binding), and characterise the properties (Fourier transform infrared spectroscopy, circular dichroism), structure (fibre X-ray diffraction using Wide and Small X-ray sources such as the synchrotron) and appearance of samples (microscopies including Transmission Electron Microscopy, Scanning Electron Microscopy and Atomic Force Microscopy). Cell lines are also cultured and used to study cell adhesion, cell migration and cell behaviour (confocal microscopy) in response to new nanostructured surfaces or nanofibers and to examine the potential toxicity of these novel materials.

- [1] S.L. Gras, "Amyloid Fibrils: From Disease to Design. New Biomaterial Applications for Self-Assembling Cross-beta Fibrils", *Australian Journal of Chemistry*, Special Research Front in Bionanochemistry, **60**(5), pp. 333-342, 2007.

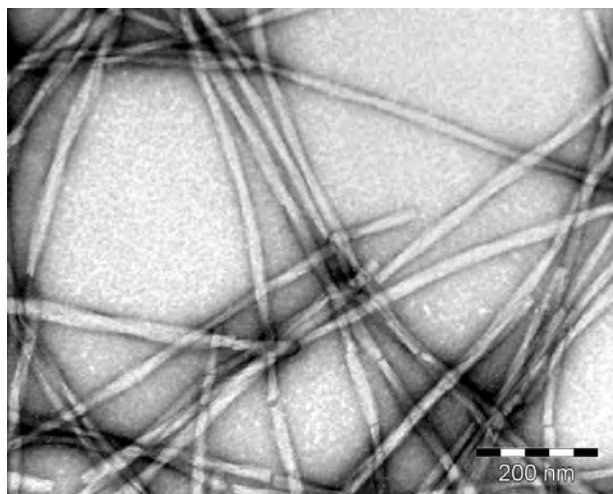


Fig. 1: A transmission electron micrograph image of a protein nanofibre. The scale bar is 200 nm in length.

Surfactant Effects in Sonoprocessing

Staff: Sandra Kentish

Collaborators: Muthupandian Ashokkumar (Chemistry)

Sponsors: ARC

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This project will provide the fundamental science required to further develop a range of ultrasonic applications within the Australian food industry, for wastewater treatment and in medical science. In particular, it will assist more applied research currently sponsored by both the Victorian government Science Technology and Innovation (STI) initiative and the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Food Futures Flagship, which considers the use of ultrasound to assist in bioactives separation, food emulsification and membrane operations. The development of ultrasound contrast agents (surfactant coated microbubbles) also has the potential to increase both the length and quality of life for many Australians. The work addresses both National Research priorities and the CSIRO Food Futures Flagship goals.

Ultrasonic Processing of Dairy Ingredients to Control Aggregation and Promote Heat Stability

Staff: Sandra Kentish, Judy Lee

Collaborators: Muthupandian Ashokkumar (Chemistry), Franz Grieser (Chemistry), Food Science Australia

Sponsors: ARC, Dairy Innovation Australia, Particulate Fluids Processing Centre

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It has been shown that the high temperatures and pressures associated with acoustic cavitation can generate free radicals and large turbulence in fluids. The aim of this research is to use these acoustically generated chemical and physical effects to modify and improve the functional properties of dairy proteins. These modified dairy proteins can also be analysed for their potential as cross linked products for medical purposes such as hydrogels for bioactive carriers and protein microspheres for medical imaging and drug delivery. Results will have significant benefits for the Australian dairy processing industry.

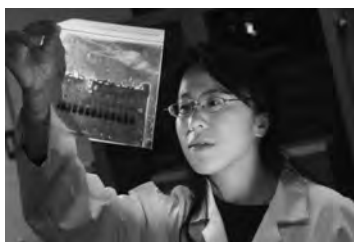


Fig. 1: Postdoctoral research fellow Judy Lee examining the effect of ultrasonic processing on dairy proteins.

Modeling the Fracture of Heterogeneous Disordered Media

Staff: Petar Liovic

Australian Mineral Science Research Institute (AMSRI)

Collaborators: Derek Chan (Mathematics and Statistics), Tim Napier-Munn (University of Queensland)

Sponsors: Australian Mineral Science Research Institute, ARC, AMIRA International BHP/Billiton, Rio Tinto, Anglo Platinum, Phelps Dodge Mining, Xstrata Copper, Orica Australia

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Major improvements in the size reduction (comminution) of mineral ores are sought by the minerals industry. The manner in which energy inputs are used and wasted is key to informing these efforts for improvement. One proposal being investigated within AMSRI is the increased use of explosive blasting, for rock fragmentation and softening, to reduce the load on subsequent crushing and grinding operations.

Fracture resulting from blasting is a challenging mathematical problem, featuring multiple coupled physical processes, and broad spectra of prevailing length- and time-scales. While models for fracture exist at various ends of the length-scale spectrum, no modeling to date has adequately coupled small- and large-scale models across the mesoscale range of heterogeneous rock composition, grain structure, defects and material damage.

The proposed project envisages the development, testing and application of computer simulation fracture models to rock breakage. There is some degree of flexibility with regard to the modelling techniques that can be used. Options include combinations of (in no order of preference, and among others): DEM, FEM, level-set methods, stochastic network models, MD, multiscale modeling.

Multi-physics Models for Drop Coalescence featuring Mass Transfer

Staff: Petar Liovic

Collaborators: Derek Chan (Mathematics and Statistics)

Sponsors: Australian Mineral Science Research Institute, ARC, AMIRA International BHP/Billiton, Rio Tinto, Anglo Platinum, Phelps Dodge Mining, Xstrata Copper, Orica Australia

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The engineering of reliable droplet coalescence or repulsion (if doable) is an attractive means of handling emulsified materials in a range of processing and waste applications, including the minerals industry. The large experimental program within the Department of Atomic Force Microscopy (AFM) is complemented by mathematical modeling efforts. These efforts

are aimed at describing the dynamic interactions witnessed under the AFM, and applying the dynamic interfacial interactions modeling capability to engineering problems.

A new problem of mathematical modeling interest in this area, is drop coalescence involving solute mass transfer. Solute mass transfer introduces new phenomenology into the coalescence problem, including possibilities ranging from enhanced drop repulsion to enhanced coalescence, enhanced mass transfer rates, and the intriguing phenomena that makes up “interfacial turbulence”.

Relevant length scales in the problem range from mm-scale drop deformations and bulk flow currents, to atomic-scale interfacial interactions and thermodynamics-driven droplet formation. Theoretical modeling has been most successful in bridging between length scales with ease, but mass transfer and interfacial turbulence represent major challenges requiring significant model upgrades. This project, therefore, embraces both theoretical and (increasingly) computational efforts.

Design of Advanced Geopolymeric Materials Based on Nanostructural Characterisation and Modelling

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Geopolymer technology utilises natural and waste materials to form environmentally sustainable advanced materials for use as a cement replacement in the building products industry. Australian researchers are leading the world in this field, and this project will provide fundamental advances in understanding the science of geopolymerisation. Development of a conceptual and mathematical model of geopolymeric structure and its formation will be undertaken, utilising data from a variety of advanced experimental and computational techniques. This will be the first detailed nanostructural investigation of these materials, and will provide information essential to the future commercial development of geopolymers.

The Removal of Mercury from Solution by Polymer Inclusion Membrane Extraction

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Students: Patrick Mornane

Collaborators: Spas Kolev (Chemistry), Bob Cattrall (La Trobe University), Ian Potter (La Trobe University), Yoshinari Baba (University of Miyazaki, Japan)

Sponsors: ARC Particulate Fluids Processing Centre (PFPC) Special Research Centre

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Solvent extraction is used extensively in the hydrometallurgical industry as a means of separating metals from their pregnant liquors and also refining them by selective removal of impurities. Generally large quantities of flammable and toxic solvents and extractants are

required making this process environmentally unfriendly and potentially unsafe. An alternative to solvent extraction is polymer inclusion membrane extraction. In this case polymeric membranes (see figure 1) have extractants (or carriers) incorporated into them, which facilitate the transport of metals through them. In this configuration the free carrier is continuously regenerated allowing for the reagents to be used more efficiently [1].

- [1] L.D. Nghiem, P. Mornane, I.D. Potter, J.M. Perera, S.D. Kolev and R.W. Catrall, "Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs)", *J. Membr. Sci.*, **281**, pp. 7-41, 2006.



Fig. 1: Polymer inclusion membrane.

Polymer Additives for Improving Nickel Extraction Processes

Staff: Greg Qiao, David Solomon, Kris Coventry, Pearl Lim, Derrick Ng

CRC for Polymers

Collaborators: Geoff Senior (BHP-B), Adrian Bolton (BHP-B)

Sponsors: BHP Billiton (Nickel West)

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<http://www.crcp.com.au>

The importance of the mining industry for the extraction of mineral and metals to Australia's economy has received much publicity in recent years. Nickel is one of the most significant of these metals in terms of its contribution to export. However, the process of extracting nickel from its natural ores can be complicated by the presence of unwanted gangue minerals.

The extraction process can be aided by the addition of natural polymers such as guar gum to modify the surface properties of the minerals. However, the improvements shown by this

process have proven to be somewhat unpredictable and are not well understood. Therefore, a detailed explanation of the roles of the biopolymers in this process would significantly improve its efficiency. The potential rewards to the Australian economy from improvements in nickel extraction efficiency are extensive.

The research towards this has focused on two distinct areas: (i) a detailed chemical and physical characterisation of guar, and (ii) an investigation of how these factors influence the efficiency of guar in the nickel extraction process. In addition to improving the performance of guar itself, one of the aims of this project is to synthesize a synthetic analogue of guar. The approach employed involves the development of a deep understanding of the mechanism of the guar-talc interaction so that it may be mimicked through the application of synthetic analogues. Synthetic polymers have the potential to be cheaper, more efficient and, most importantly, more consistent than their natural equivalents. So far the research conducted has shown much promise and has led to the filing of two provisional patent applications for synthetic aids to the flotation process (Fig. 1).



Fig. 1: Flotation cells used at Mt Keith (Western Australia) for nickel production (Reproduced with permission of BHP-Billiton.)

Novel Nano-particles for Advanced Automotive and Industrial Coatings

Staff: Greg Qiao, Anton Blencowe

Students: Tor Kit Goh, Jing Feng Tan

Collaborators: Jeff Johnson (DuPont)

Sponsors: DuPont, ARC

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In conjunction with our industrial partner (DuPont), this project aims to develop the next generation of automotive and industrial polymer coatings that can be integrated into existing production systems. The new coatings will be environmentally friendly and will make a significant contribution towards solving the emission issue of volatile organic compound (VOC) faced by the industry. The novel nano-particles developed in this project will possess unique rheological and film forming properties, whilst maintaining a commercially competitive price. The technologies developed in this project represent the cutting edge of macromolecular science.

- [1] A.K. Ho, P.A. Gurr, M.F. Mills, G.G. Qiao and D.H. Solomon, "Synthesis and Characterization of Star-Like Microgels by One-Pot Free Radical Polymerization", *Polymer*, **46**, pp. 6727-6735, 2005.
- [2] P.A. Gurr, M.F. Mills, G.G. Qiao and D.H. Solomon, "Initiator efficiency in ATRP: the tosyl chloride/CuBr/PMDETA system", *Polymer*, **46**(7), pp. 2097-2104, 2005.
- [3] B. Wei, P.A. Gurr, J. Genzer, G.G. Qiao, D.H. Solomon and R.J. Spontak, "Dewetting of a Star-Nanogel/Homopolymer Bled Film from an Immiscible Homopolymer Substrate", *Macromolecules*, **37**, p. 7857, 2004.

Core-crosslinked Star (CCS) Polymer and their Clusters: The Next Generation in Polymeric Particles

Staff: Greg Qiao, Luke Connal, Anton Blencowe, Marisa Spennello, Kris Coventry

Students: James Wiltshire, Tor kit Goh, Jing Feng Tan

Sponsors: ARC

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This project involves the development of a relatively new type of macromolecular architecture, termed core-crosslinked (CCS) star polymers and their clusters. As part of a research strategy to develop novel CCS polymers and their applications, the Polymer Science Group has prepared a large variety of polymeric materials based on CCS polymers. Recent developments include the production of CCS clusters, fullerene functionalised CCS, fluorescent CCS, Dendron-CCS, CCS dumbbells and CCS-quarto polymers. In addition, the group has conducted a variety of fundamental studies to determine the properties of these unique macromolecules, which is helping to establish their potential applications. These new macromolecules will not only advance polymer science into a new era, but will provide a basis for the development of technologically superior materials for coatings, drug delivery systems, organic photovoltaics, rheology modifiers and bio-molecular separations.

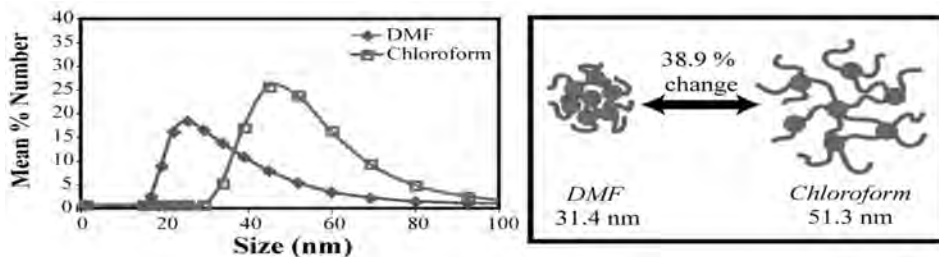


Fig. 1: Dynamic light scattering measurements (left) showing the swelling effects of CCS clusters by using different solvents, whereas CCS clusters have a mean diameter of 31.4 nm in DMF and 51.3 nm in chloroform (a 38.9 % variation) (Goh, Sulistio, Blencowe, Johnson, Qiao: 2007).

- [1] L.A. Connal, R. Vestberg, C.J. Hawker and G.G. Qiao, "Synthesis of Dendron Functionalized Core Cross-linked Star Polymers", *Macromolecules*, **40**, pp. 7855-7863, 2007.
- [2] T.K. Goh, A.P. Sulistio, A. Blencowe, J.W. Johnson and G.G. Qiao, "Synthesis and Characterization of Core-crosslinked Star Clusters by Conventional Free Radical Polymerization", *Macromolecules*, **40**, pp. 7819-7826, 2007.

Design and Synthesis of Super-macromolecular Architectures with Selectively Degradable Functionality

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Students: James Wiltshire

Sponsors: ARC

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In the past decade considerable attention has been focused on the merging fields of polymer chemistry and the biological sciences. One particular area which has attracted a great deal of interest concerns the use of polymers as potential drug delivery vehicles. Properties such as the capacity to solubilise hydrophobic drugs, target specific physiological sites such as cancerous cells, and have control over the rate of drug release have proven quite attractive for many potential applications. The use of such macromolecules can also lead to reduced dosage requirements and consequently minimise any potentially undesirable side effects associated with the drug.

This project involves the development of selectively degradable CCS polymers. The ability to control the rate at which encapsulated molecules can be released is an important factor in the design of efficient drug delivery devices. In this regard, several different techniques for incorporating degradable functionality into CCS polymers have been examined as a potential means of controlling release kinetics.

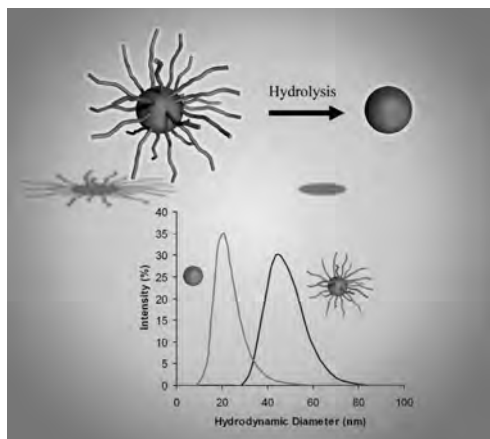


Fig. 1: Arm degradable CCS polymer was hydrolyzed to produce the core. DLS experiments indicate the size change of these nanoparticles before and after degradation.

- [1] J.T. Wiltshire and G.G. Qiao, "Selectively Degradable Core Cross-Linked Star Polymers", *Macromolecules*, **39**, pp. 9018-9027, 2006.
- [2] J.T. Wiltshire and G.G. Qiao, "Degradable Star Microgels via Ring Opening Polymerization", *Macromolecules*, **39**, pp. 4282-4285, 2006.
- [3] J.T. Wiltshire and G.G. Qiao, "Recent Advances in Star Polymer Design Degradability and the Potential for Drug Delivery", *Aust. J Chemistry*, **60**, pp. 699-705, 2007.

Flexible Honeycomb Films

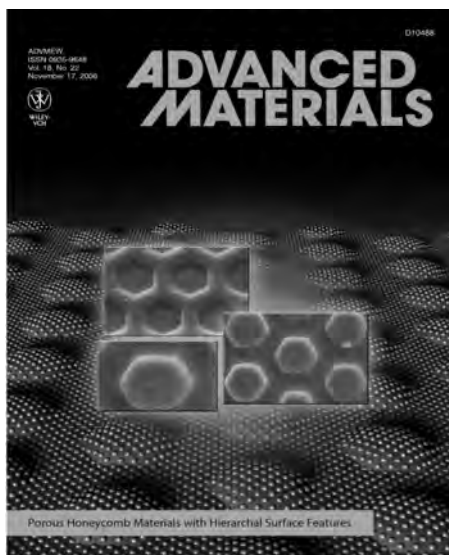
Staff: Greg Qiao, Luke Connal

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Micro-porous polymer films with self-assembled honeycomb morphology produced by the 'breath figure' technique have distinct advantages over other lithographic techniques; there is no need for expensive equipment, it is a simple and cheap process that can control pore sizes through varying casting conditions. These ordered porous films have potential applications particularly in biotechnology industries. Similar films have been made from a variety of polymers, for example, star polymers and CCS polymers.

In this project we have developed a technology to coat honeycomb films on non-flat surfaces. For example, an ordered honeycomb film has recently been coated onto the surface of non-flat TEM grids by using CCS polymers with low glass transition temperatures (T_g). The advantage of these low T_g systems is that the resulting honeycomb films have better elastic properties, which therefore leads to more robust and uniform films that are resistant to fracture. A similar system has also been developed to coat particulate surfaces, including glass microbeads, kaolin particles, salt and sugar crystals. The process is very robust and the project is now applying this technology to developed biosensor systems.



1.1



1.2

Fig. 1: Regular porous honeycomb films were produced on the surface of TEM grid (left) and particle surface (right).

(1.1 Reproduced with permission of Wiley-VCH Verlag GmbH & Co KGaA.)

(1.2 Reproduced with permission of the Royal Society of Chemistry.)

[1] L. Connal and G.G. Qiao, "Honeycomb Coated Particles: Porous Doughnuts, Golf balls and Hollow-Porous-Pockets", *Soft Matter*, **3**(7), pp. 837-839, 2007.

[2] L. Connal and G.G. Qiao, "From Replication of Complex Surfaces with a Highly Ordered Porous Poly(Dimethyl Siloxane) Based Honeycomb Coating", *Adv. Mater.*, **18**(22), pp. 3024-3028, 2006.

[3] G.G. Qiao, L. Connal and J.Wiltshire, "Porous Polymeric Materials and Polymer Particles For Preparation Thereof", (*PCT Int. Appl; AU 2006-904451; WO 2007051252*), 2006.

Investigating the Structure-Property Relationships in Micro/Nano-reinforced Thermoset Polymer Systems

Staff: Greg Qiao, Clem Powell

Students: Ranya Simons

Collaborators: Stuart Bateman (CSIRO)

Sponsors: Commonwealth Scientific and Industrial Research Organisation (CSIRO)

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Thermosetting polymers offer advantages such as light weight, high strength and excellent mechanical properties. Polymer nanocomposites are a relatively new class of polymers that

exhibit markedly superior physical and chemical properties, with low filler concentrations. In collaboration with CSIRO, this project is investigating the structure-property relationships in micro/nano-reinforced thermosetting systems, more specifically, how changes in molecular architecture surrounding the fillers impact on the overall performance of the material. New nanocomposite material are currently being synthesised, modelled and their curing kinetics evaluated. The systems will be analysed by a range of analytical and physical performance techniques, including x-ray diffraction, transmission electron spectroscopy, nuclear magnetic resonance, infrared spectroscopy, thermal and thermo-mechanical techniques to assess the structure-property relationships.

Solid-Liquid Separation: Characterisation, Modeling and Application

Staff: Peter Scales, Shane Usher, Adam Kilcullen, David Dixon, Ross de Kretser

Students: Hemadri Saha, Rudi Spehar, David Verrelli, Anat Kiviti-Manor

Collaborators: Murray Rudman (CSIRO), Dr Phil Fawell (CSIRO), Professor Simon Biggs (Leeds University), Professor Lee White (Carnegie Mellon University)

Sponsors: United Utilities, Yorkshire Water, RioTinto, AMIRA, ARC

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The industrial utilisation of many fundamental approaches to process modeling is low and the gulf between academia and operations is indeed wide in the area of solid-liquid separation modeling. A comprehensive description of suspension compressional dewatering was first published in 1987 and this theoretical description has now been complemented with the development and validation of rigorous laboratory and field characterisation methods for the extraction of material property parameters for input to process modeling. To achieve this task, test rigs and software tools for dewatering parameter estimation have been developed and licensed. Simple steady state and one dimensional phenomenological mathematical models of sedimentation, thickening, plate and frame filtration, gravity belt filtration, and batch and continuous centrifugation have also been developed. These models have proven to be successful in describing the basics of many process operations in the minerals industry and for non-biological particulate suspensions (sludges). Despite the successes, the models have proved to be inadequate in many instances. It is often not clear if this is as a result of model or parameter estimation difficulties. To this end, the aim of this work is to extend the models to two and three dimensional descriptions and to include transient rather than steady state behaviour. The modeling is based on analytical, numerical and computational fluid dynamics approaches. Application of the modeling has been to processes in the minerals, dairy and water and waste water industries and this will remain the focus of the work.

- [1] D.R. Lester, S.P. Usher and P.J. Scales, "Estimation of the hindered settling function $R(\phi)$ from batch settling tests", *AIChE Journal*, **51**, pp. 1153-1168, 2005.
- [2] A.D. Stickland, R.G. deKretser, P.J. Scales, S.P. Usher, P. Hillis and M.R. Tillotson, "Numerical modelling of fixed cavity plate and frame filtration: Formulation, validation and optimisation", *Chem. Eng. Sci.*, **61**, pp. 3818-3829, 2006.

- [3] S.P. Usher and P.J. Scales, "Steady state thickener modelling from the compressive yield stress and hindered settling function", *Chemical Engineering Journal*, **111**, pp. 253-261, 2005.
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Wastewater Sludge Dewatering

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Students: Lindsay Studer, Rachael Wall

Collaborators: Lee White (Carnegie Mellon University)

Sponsors: United Utilities, Fonterra, ARC

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The project aims to characterise the compressional dewatering properties of wastewater (biological) sludges for input into models of dewatering devices such as filters and centrifuges. These sludges show poor settling and non-quadratic filtration behaviour. As a consequence, the development of methodologies for the extraction of material dewatering parameters requires development of new laboratory techniques. A key approach in this area is to use a centrifugation approach to extract compressibility and hindered settling function information from interface height data as a function of time. Mathematical approaches for solving the inverse problem are now well advanced and it would seem that we are able to characterise and model the behaviour of biological sludges for the first time. Optimisation of the parameter extraction process is a key future aim of this work. The expected result is a predictive capacity for the dewatering of biological suspensions. Further to the materials property characterisation work, the role of membranes and fouling in biological sludge processing and dewatering can now be considered in a quantitative manner. This will be the focus of future work.

- [1] A.D. Stickland, R.G. deKretser and P.J. Scales, "Nontraditional constant pressure filtration behavior", *AIChE Journal*, **51**, pp. 2481-2488, 2005.
- [2] S.P. Usher, P.J. Scales and L.R. White, "Prediction of transient bed height in batch sedimentation at large times", *AIChE Journal*, **52**, pp. 986-993, 2006.
- [3] A.D. Stickland, P.J. Harbour, D.R. Dixon and P.J. Scales, "Scaling the initial dependencies of the time to filtration of wastewater sludge", *Water Research*, **41**, pp. 206-216, 2007.
-

Stabilisers for Nanoparticles and their use in Nanoparticle Synthesis

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Students: Rory Anderson

Collaborators: Paul Mulvaney (Chemistry), Richard Buscall (Muscat Consulting)

Sponsors: ICI

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Particles with diameters in the nanometre range are of interest for a wide variety of industrial applications but preventing such fine particles from growing or aggregating remains a challenge. The project is exploring ways of growing, measuring and improving the stability of inorganic nanoparticles dispersed in fluids of industrial interest. Of particular interest, is the growth and stabilisation of nano particles in an aqueous environment at high solids. This has required the development of novel surfactant and polymer moieties and controlled shear manufacture technologies. The particle targets of the work are metals and metal oxides that show either conducting, semi-conductor and resistive properties as potential for use in inks and as fillers.

Suspension Rheology

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Students: Jonathan Foong, Woojoo Han, Maria Kristenson

Collaborators: Kristain Keiding (Aalborg University), Richard Buscall (Muscat Consulting), Kyung Hyun Ahn (Seoul National University)

Sponsors: ARC

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The flow properties of concentrated suspensions of colloidal particles is of interest to a wide range of industries. The aim of our work is to provide a fundamental understanding of the failure of attractive colloidal networks and to establish new methodologies for the measurement of particulate suspension rheology across a wide range of solids concentrations and shear rates. To this end, new analysis techniques are being developed to understand the behaviour of colloidal networks in small and large amplitude oscillatory shear. The expected outcome is a more quantitative methodology for the interpretation of flow property data for particulate suspensions. In addition, the use of non-slip methodologies such as the vane in 'infinite' media measurement technique are being explored as an alternative to cup and bob and other techniques for the measurement of industrial particulate suspensions. These measurements are being coupled with capillary rheometry to provide a broad shear rate range for suspension characterisation. This is of particular relevance to coating flows.

[1] D.T. Fisher, S.A. Clayton, D.V. Boger and P.J. Scales, "The bucket rheometer for shear stress – shear rate measurement of industrial suspensions", *Journal of Rheology*, 2007, (in press).

Development of a Concept Inventory for Material and Energy Balances

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All students enter a course or commence a subject with certain preconceptions and misconceptions relating to the subject content. Often these misconceptions, if left uncorrected,

will have a detrimental effect on a student's grasp of the material. At the same time many different methods are available to academics to teach the material in their subjects. Which method is most effective? What measures exist that will allow the effectiveness of different methods to be assessed objectively?

The Force Concept Inventory was developed in the early 1990's to test students' understanding of the underlying concepts relating to the action of forces on bodies. The Force Concept Inventory consists of 30 multiple-choice questions designed to probe the students' understanding of the topic. The test is administered at the start of a course and again at the end. By comparing the pre- and post-tests results it is possible to gauge the effectiveness of different styles, methods and techniques of teaching. The Force Concept Inventory has been the subject of much study and its usefulness has been confirmed.

This project is aimed at developing an instrument to measure the improvement in learning and correcting misconceptions for use in a key chemical engineering subject. This is the first time such an instrument has been developed for the basic chemical engineering subject. The goal of the work is to understand the misconceptions that chemical engineering students commence their university studies with. The first version of this concept inventory has been tested at the University of Queensland and the University of Sheffield. It will also be piloted at two universities in the US. The third version of the inventory was recently released for testing.

Development of In Ground and On Site Technologies for Low Cost Metal Remediation of Remote Contaminated Sites

Staff: Geoffrey Stevens

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Sponsors: ARC

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Australia has taken a leading role internationally in promoting environmental awareness and is committed to both tackling existing pollution and mitigating future hazards. The clean-up of contaminated Australian, Antarctic and sub-Antarctic sites is seen as a national priority and research into in-situ technologies is central to meeting established remediation goals. Successful development of a low-cost in-ground remediation scheme will provide vital protection for remote Australian, Antarctic and sub-Antarctic areas. It will also do much to cement Australia as a global leader in environmental protection, offering as it does a generic remote regions metal contamination remediation solution.

Development of Low Cost In Situ Techniques for Petroleum Remediation in Cold Regions

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Internationally, Australia has taken a leading role in promoting environmental awareness and is committed to both the mitigation of future hazards, and the tackling of existing pollution. The clean-up of abandoned Antarctic sites is seen as a priority, and research into low-impact technology is central to meeting established remediation goals. Successful development of a low-cost in-situ remediation scheme will not only serve to protect vulnerable Antarctic habitats in Australian stewardship, but will do much to cement Australia as a global leader in environmental protection offering as it does, a generic cold region hydro-carbon remediation solution.

Influence of Impurities in Commercial Solvent Extraction Processes

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This project directly supports the solvent extraction industry in Australia. This industry is responsible for generating in excess of \$600M annually of export earnings for Australia. This type of technology can be applied in the recovery of base metals such as copper, nickel, cobalt, etc. and in the environmental area for the clean up of heavy metals from waste water. Solvent extraction has the advantage of high selectivity that enables metals to be recovered and recycled, thus reducing the wastage of these metals in, for example, the chromium plating process.

Next Generation of Separation Equipment for Natural Product Extraction

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The benefit to GlaxoSmithKline will be the potential to upgrade to a more efficient plant which is important for maintaining their competitive position in this global business. The benefit to other Australian processing industries will be an improved understanding of the performance of membrane contactors when used for natural product separation and more specifically, a reliable method for controlling fouling in this type of equipment, which is a currently a significant industry problem.

Development of Biocompatible, Biodegradable Composite Scaffolds for Adipose Tissue Engineering

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The aim of the research is to develop biocompatible, biodegradable composite materials (collagen/mesoporous silica) for adipose tissue engineering applications. These materials would constitute the 'constructs' onto which new vascularised adipose tissues may regenerate and repair tissue defects due to trauma (e.g. deep burns), tumour defects (e.g. breast cancer) or disease (e.g. Poland Syndrome). When realised, these scaffolds will constitute a significant advancement particularly in the field of plastic reconstructive surgery from which new clinical therapies could originate to enhance the lives of many patients afflicted by the aforementioned pathologies.

Investigation of the Coupling of Bio-active Groups to Biodegradable Polymers

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The synthesis of biodegradable polymers containing functional groups which can be utilised for further coupling reactions with bio-active molecules has uses in many different applications including tissue engineering, drug delivery and biosensors. These functional groups are incorporated into the polymer backbone through the synthesis of a functional monomer and subsequent co-polymerisation with a standard monomer. This project investigates the efficiency of several different coupling techniques in attaching various bio-active molecules before looking at different properties that can be attained and some applications.

Bioactive Tissue Engineering Scaffolds

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3D biodegradable polymeric scaffolds play an important role in the development of tissue engineering. They must provide both an optimal physical and chemical template for cell attachment, migration, proliferation and tissue generation. In this project, 3D scaffolds with large and highly interconnected pores ($> 300 \mu\text{m}$) are fabricated from poly(lactico-glycolic acid) (PLGA) using thermally induced phase separation (TIPS). Scaffolds are tested for mechanical strength and in vitro cell attachment and proliferation. The scaffolds will be modified by incorporating basic fibroblast growth factor (bFGF) for enhanced bioactive properties. The approach involves using a layer-by-layer (LbL) technique which allows the build up of multilayer films via the alternate deposition of polycations and polyanions onto charged surfaces. The bFGF release kinetics will be determined by immunoassays. The modified scaffolds will be tested in vitro for cell attachment and proliferation. Finally, the promising scaffolds will be used for in vivo animal tests towards a potential new human applicable biomaterial scaffold.

Cell Migration Models

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T cell development occurs in the thymus throughout life. The seeding of the thymus by multipotent stem cells from the bone marrow is periodic (approximately every 3 weeks), however it is well known the output rate of cells from the thymus is constant. Imaging data of the thymus show immature T cells are highly motile and are actively interacting with antigen presenting stromal elements. Immature thymocytes out-number the stromal cells 200 to 1, and this raises the possibility of competition between cells for survival and maturation signals. The maturation of cells also depends on spatial signals in the thymus. A combination of systems of ordinary and partial differential equations are used to model T cell development.

Microemulsion Templated Mesoporous Silica for Affinity Separations

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In areas such as the production of protein-based pharmaceuticals, the selective adsorption of biological macromolecules is an important step to achieving the required purities. Recently developed microemulsion templated mesoporous silica foams which consist of highly porous 3-dimensional networks, offer the potential to be adsorbents with both high selectivity and high capacity. The study has focused on the development of these materials for protein-A IgG bio-affinity separations and has involved both materials science aspects of synthesising, functionalising and characterising these materials, as well as the application side in demonstrating their use in the protein-A IgG bio-affinity separation. Significantly the work has shown that these materials have over twice the adsorption capacity of commercially available media, highlighting their potential in this area.

Development of Mesoporous Bioaffinity Adsorbents for Biological Applications

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This study investigates potential application of mesocellular foam (MCF) for industrial bio-separations application. Several techniques are being explored such as a templating method, in-situ particle enlargement, as well as post synthesis enlargement. In the templating approach, a porous template of polyacrylamide was selected for the composite MCF adsorbent to form and retain its structure. Sedimentation polymerisation of polyacrylamide coupled with optimisation of calcination temperature were directed towards controlling the enlarged particles' stability, for bio-separation application. Upon MCF particles size enlargement, reusability and adsorption kinetics of enlarged adsorbent will be studied as well as regeneration methods required to prolong the adsorbent lifetime in their application.

Use of Zeolites as Controlled Release Fertilisation Systems for Petroleum Hydrocarbon Remediation at Low Temperatures

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During the 2005/06 Casey Station Antarctic season a permeable reactive barrier was built and installed at the end of a hydrocarbon plume. The barrier contained a range of materials (zeolites, nutrient amended zeolite, granulated activated carbon, maxbac and sand), to both capture hydrocarbons and degrade them via microbial stimulation. The barrier was heavily sensed with twenty six temperature sensors, ten oxygen sensors and forty multiport strings. In addition, the barrier contained oxygen distributors and heat tracing. During the season the performance of the barrier was continually monitored and work is still continuing.

In-Situ Remediation Technologies for Cold Regions Contaminated Sites

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This research is involved in development of in-situ remediation technologies for use at contaminated sites in Antarctica, the sub-Antarctic islands and the Arctic. This includes laboratory testing of sorbent materials for removal of heavy metals and hydrocarbons from contaminated groundwater at low temperature. The aim is to investigate the ion exchange/sorption characteristics of various materials, and develop binary and multicomponent system models to predict the behaviour of these materials at low temperature and variable salinity.

The Use of Nanoporous Carbon Membranes for High Temperature Carbon Dioxide Separation

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Nanoporous carbon (NPC) membranes have tremendous, but presently largely untapped possibilities for the large scale separation of gases. The focus of this project is to investigate the viability of these membranes for the separation of carbon dioxide from both flue gas and natural gas streams. Over the past year, membranes with a CO₂/N₂ selectivity as high as 10 have been successfully synthesised from carbonising polyfurfuryl alcohol. The next phase of the project is focused on increasing the permeance of the NPC membranes whilst retaining a high CO₂/N₂ selectivity. This will be achieved by thinner unsupported membranes made from carbonising flat sheet polyimide. This project is a collaborative effort between the Particulate Fluids Processing Centre (PFPC) and the CRC for Greenhouse Gas Technologies.

Characterisation of Glassy Polyimide Gas Separation Membranes at Elevated Temperature

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In response to growing concern over increases in globally averaged surface temperatures and associated global warming phenomena, there has recently been added interest in geosequestration of carbon dioxide as a possible short/medium term solution. This project investigates the use of polymeric membranes as a possible CO₂ capture technology for geosequestration. Specifically, this project considers polyimide membranes for the separation of carbon dioxide from the flue gases of coal-fired power stations, as well as from natural gas. Several facets of glassy polyimide membranes have been investigated, including the relationship between temperature and the CO₂-induced plasticisation tendencies of such membranes. Enhancement of polyimide membrane performance with increasing temperature due to charge transfer complex formation has also been investigated. Recently completed work included examination of improved membrane stability through grafting of epoxy material into the membrane's polymeric structure. This project is a collaborative effort between the Particulate Fluids Processing Centre (PFPC) and the CRC for Greenhouse Gas Technologies.

CO₂ Recovery Using a Modified Polypropylene Gas Absorption Membrane

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Membrane contactors have significant advantages over packed columns for CO₂ separation from other gases using chemical absorption. The membrane offers a larger interfacial area between phases but must be compatible with the solvent. The extreme hydrophobicity of polytetrafluoroethylene makes this an ideal membrane material but it is expensive. While untreated polypropylene is insufficiently hydrophobic for use with low surface tension amine based solvents, polypropylene membranes that are treated may provide a cheaper alternative. Different membranes are being developed and tested using both hollow fibre and flat sheet membrane configurations. This project is a collaborative effort between the Particulate Fluids Processing Centre (PFPC) and the CRC for Greenhouse Gas Technologies.

Impact of Impurities on Polyimide Membrane Performance

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Previous studies have shown that polyimide membranes exhibit high permeabilities and permselectivities for the removal of CO₂ from both natural gas and flue gas streams. However, most of these studies have been conducted with pure gases in the absence of any contaminants. Contaminants such as hydrocarbons, water and sulphur compounds may restrict the performance of a membrane and result in premature membrane failures in the field. This research is aimed at understanding the impact of these contaminants on 6FDA-Durene and Matrimid 5218 membrane performance. Results will allow for the improved design of pre-treatment systems to remove these contaminants prior to the membrane system. The possibility of regeneration of the membrane to restore the original performance after it is exposed to contaminants will also be studied. This project is a collaborative effort between the Particulate Fluids Processing Centre (PFPC) and the CRC for Greenhouse Gas Technologies.

Capture of Carbon Dioxide from Flue Gas using Potassium Carbonate

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The absorption of carbon dioxide in chemical solvents has been extensively utilised for the capture of CO₂. However, the capture of CO₂ from coal-fired power plant flue gas streams presents new challenges to current absorption technologies. These are due mainly to the nature of these emissions, that being extremely large volumetric flows with low total and CO₂ partial pressures. This project has been investigating various process flowsheet options and equipment designs to optimise the energy requirements of a process utilising a potassium carbonate solvent. To date, detailed process simulations, experimental verification of simulations utilising a lab scale rig and preliminary design studies have been performed. This project is a collaborative effort between the Particulate Fluids Processing Centre (PFPC) and the CRC for Greenhouse Gas Technologies.

Production of Concentrated Fresh Milk Products

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A new application for microfiltration membranes in the dairy industry is in the separation of native casein micelles from whey proteins by processing skim milk. The production of casein in its natural state is expected to be extremely beneficial. The casein concentrate should result in better texture and yield in cheese manufacture, whilst the permeate produced is better for purifying whey proteins than standard cheese whey. However, high fouling of the microfiltration membrane limits this process. This project investigated operating conditions and membrane configurations, materials and pore sizes in order to optimise the process in terms of processing flux, processing time and the separation characteristics.

Study of the Interactions between Fluorocarbon Surfaces using an Atomic Force Microscope

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Collaborators: Lucy Clasohm (Chemistry), Franz Grieser (Chemistry), Derek Chan (Mathematics and Statistics)

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Fluorocarbon liquids have been widely applied in the electronics industry for years as their unique properties (i.e. extremely stable, chemical inert and practically non-toxic) made them ideal liquids for use in manufacturing, heat transfer and testing applications. Understanding the interactions between a fluorocarbon liquid and another surface and/or between two fluorocarbon liquids is very important. In this study the atomic force microscope has been employed to directly measure the forces acting between a solid surface and a fluorocarbon liquid and between two fluorocarbon liquids, to help further our understanding of the behaviour of these fluids.

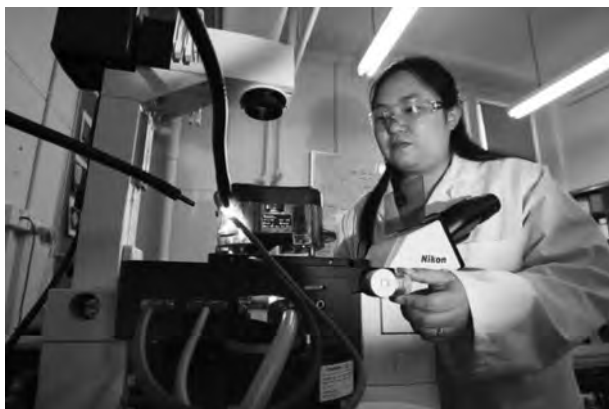


Fig. 1: Postdoctoral research fellow Lucy Clasohm is using an atomic force microscope to study the interactions between fluoro carbon surfaces.

Wetting Characteristics of Perforated Plate Columns

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Collaborators: GlaskoSmithKline

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Pulsed perforated and reciprocating plate columns have been used in the solvent extraction industry for many years. Recent studies in our group have shown that changes in the surface properties of the plates directly influence the performance both in terms of the separation efficiency and also the throughput. Although studies have been undertaken on the effect of using different plate surfaces, different phases for dispersion and the influences of changing plate geometry on the hydrodynamics of the column, no qualitative studies have been reported on how hold up is influenced by plate ageing. The scope of this work will be to investigate in detail the effect of using different plate surfaces on the drop size diameter, hold up, mass transfer performance and axial dispersion. The onset of ageing for different plate surfaces will also be investigated.



Fig. 1: Postgraduate student Ravi Arun by small scale liquid extraction columns.

Emulsion Stability in the Pharmaceutical Industry

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Emulsion stability and coalescence rates of liquid-liquid systems are an important consideration in numerous large-scale processes including solvent extraction. This project examines the mechanisms that dominate in film drainage, a process that controls droplet coalescence and emulsion stability. A novel method employing imaging ellipsometry is used to study the thin film drainage between a silica surface and oil droplet in an aqueous phase. The effects of interfacial tension and mass transfer across the liquid-liquid interface have been the focus of recent studies. This project is also aimed at developing current experimental methods to study thin films between silica and a 'free' oil droplet in a continuous phase approaching the silica surface with known velocity.

Hydrodynamic Interactions between a Silica Particle and a Deformable Oil Droplet – Effect of Particle/Droplet Size Ratio

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In many industrial applications such as froth flotation, foams and emulsions, the interactions between solid and deformable interfaces, or two deformable interfaces, is of critical importance. Understanding these micro-scale interactions is vital for the prediction and control of the macro-scale behaviour. This project specifically aims to investigate the existence, or otherwise, of a slip boundary between the two interacting surfaces. Experimental data will be collected using the atomic force microscope, and modeled using a mathematical model developed within the PFPC. This data will then be compared to the theoretical interactions, in which different slip lengths can be incorporated. The major challenge with this project is using the optimum parameter space, where the strength of the hydrodynamic interaction, and the theoretical effect of slip, are maximised. To this end, interaction profiles between large silica particles (>50µm diameter) and oil droplets of similar size or smaller have been measured, and will be compared to interaction profiles predicted by the mathematical model.

Influence of Fine Particles on Collection Efficiency in Flotation

Staff: Geoffrey Stevens, Sawsan Freij, Raymond Dagastine

Sponsors: Australian Mineral Science Research Institute, ARC, AMIRA International BHP/Billiton, Rio Tinto, Anglo Platinum, Phelps Dodge Mining, Xstrata Copper, Orica Australia

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Flotation is a major process used to separate valuable minerals from clays, silica and other non valuable materials in many mineral processing operations. The process involves the use of surfactants to attach the valuable materials to the air – water interface. This project aims to measure the colloidal and interfacial forces at the gas liquid interface using the atomic force microscope. Comparing the forces for the bare air – water interface with interfaces covered with fine dispersions of clay, for example, will help to understand the role of these fine particles in the flotation process. This information is vital to the minerals industry in controlling its water usage and its long term sustainability.

Design and Synthesis of Complex Nanostructured Materials for Enhanced Performance

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Sponsors: ARC

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This project aims to significantly enhance mechanical properties of existing light alloys including room temperature strength and ductility and high temperature creep resistance and to achieve a good combination of these properties. In particular, the microstructure will be designed using a selection of metallic, intermetallic, ceramic, amorphous and other structures. The designed microstructure will be synthesised from particles, in particular nano-sized and nano-structured particles, using the newly developed back-pressure equal channel angular consolidation process, which achieves instantaneous bonding and full density at much lower temperatures than those used in conventional sintering. This approach enables more flexible design of composition and microstructure and production of a large volume of high integrity materials for reliable characterisation and study of mechanical behaviour. The project will integrate design of microstructure, realisation of the designed microstructure through novel processing, characterisation of microstructure and mechanical behaviour, and modelling of the correlation between microstructure and mechanical behaviour.

Ultrahigh strength Al and Ti based materials have been produced. More sophisticated alloys are being designed and processed. These new materials will offer significantly enhanced properties. More importantly, the approach will usher in the era of materials by design.

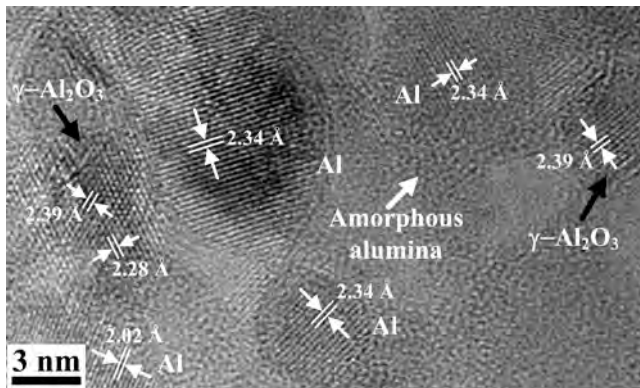


Fig. 1: Nanocrystalline Al and Al_2O_3 composite structure obtained by consolidation and severe plastic deformation of ultrafine Al particles (Xu, Honma, Wu, Ringer, Xia: 2007).

- [1] W. Xu, T. Honma, X. Wu, S.P. Ringer and K. Xia, "High Strength Ultrafine/Nano-Structured Aluminum Produced by Back Pressure Equal Channel Angular Processing", *Appl. Phys. Lett.*, **91**, 031901, 2007.

Titanium Powder Forging

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Titanium and its alloys possess good strength and stiffness as well as excellent corrosion resistance and are widely used in aerospace and biomedical applications. However, it is relatively expensive if produced by melting and casting since a vacuum is needed during processing to prevent excessive oxidation. It is therefore desirable to use Ti powder which can be produced from Ti-containing minerals directly.

To achieve the maximum benefit, it is necessary that Ti powders be formed into final shapes directly. This project will take pre-sintered Ti preform or compacted Ti powders and forge it into near-net-shape for applications. It is expected that Ti components so produced will be competitive in cost and superior in performance.

Synthesis of Organic/Inorganic Nanocomposites by Mechanical Activation

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Polymer based composites reinforced with nano ceramic and metallic particles are attracting increasing attention for their unique properties and much improved performance. These materials are traditionally melt processed, i.e. above their melting temperatures, in industry. The distribution of the nanoparticles and the bonding between the particles and matrix are often not satisfactory, resulting in failure to achieve the potential of the materials.

In this project, mechanical activation is utilised to process the nanocomposites in their solid state. In particular, ball milling and equal channel angular processing are combined to realise uniform distribution of nanoparticles and strong bonding between the particles and matrix. The approach also has potential to combine usually incompatible polymer matrix and inorganic nanoparticles to produce novel nanocomposites.
