

Palmerston North

9/2/21

Palmerston North – Keynote Abstracts

Emulsion Studies with Optical Tweezers

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Abstract

This talk will describe two of the adventures we have had in our Optical Tweezers research, studying emulsion droplets.

1) Optical tweezers have been used to investigate the dependence of electrostatic inter-particle forces on separation, in systems consisting of pairs of either model silica beads or emulsion droplets. Measurements were carried out as a function of ionic strength and, at salt concentrations where the Debye length was larger than the standard deviation of Brownian fluctuations of the particles in the traps, results were found to agree reasonably well with the predictions of DLVO theory. Experiments were also carried out where the salt concentration of the environment was changed in real-time while interactions were continuously measured. Specifically, single pairs of particles or emulsion droplets were held in a microfluidic channel in close proximity to an interface created between milliQ water and a 5 mM NaCl solution. Changes in the force–separation curves were measured as a function of time and used to monitor changes in the Debye length, and thus the local salt concentration, as ions diffused away from the interface. The results were shown to be consistent with expectations based on a relevant diffusion equation.

2) The advent of technologies that allow the interactions of individual microscopic particles to be probed “one-at-a-time” has paved the way for new experimental avenues of enquiry in colloidal systems. However, while, for example, investigating a particular pair of colloidal particles isolated from a macroscopic sample might adhere together when brought into close proximity is certainly possible, it is currently still an arduous task to perform the experiment hundreds or thousands of times in order to acquire datasets worthy of confident analysis. We have constructed an automated particle collider for measuring particle-particle interactions by combining elements of microfluidics, holographic optical tweezers and image analysis. We envisage that such robust approaches to the automation of “one-at-a-time” experiments will find applications in a large number of areas, enable previously un-thinkable experiments to be carried out in a timely fashion, and allow the focus to shift away from tedious experimental frustrations to more profound scientific questions. As an example we measure variations in the sticking probability of pairs of emulsion drops with zeta potential.

Biography



Bill Williams obtained an Honours degree in Physics with Astrophysics from Leeds University, UK and then undertook a PhD in NMR relaxation behaviour at the Open University. He went on to spend a number of years as a Postdoctoral Fellow in The Chemistry Department at York University, UK, working on various aspects of biological polymers. Subsequently he spent 4 years with Unilever Research, before returning to academia in March 2003, with a position in The Institute of Fundamental Sciences at Massey University, NZ, where he is working on biophysics and soft-matter.

Palmerston North – Oral Presentation Abstracts

WHEN LEGO BRICKS INSPIRE MICROSCOPIC MATERIALS: SUSTAINABLE PRODUCTION OF MULTIFUNCTIONAL PARTICLES

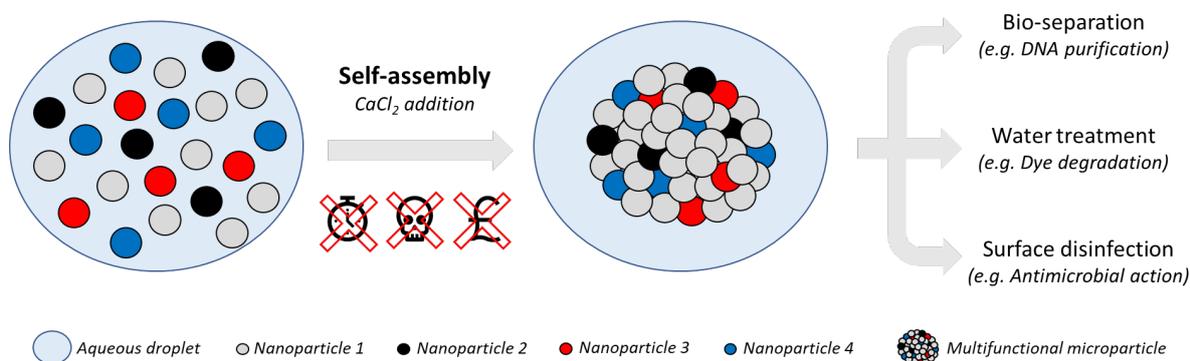
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Imagine reusable particles harvesting light to degrade organic pollutants from wastewater; magnetic particles able to extract and recover proteins of interest from solution or particles disinfecting surfaces before being recovered with a magnet. How many methods are needed to produce such systems? Based on current approaches, numerous, but what if the answer could be as simple as one?

We have designed a sustainable approach for producing multifunctional microparticles via salt-driven assembly of commercial nanoparticles dispersed in a water-in-oil emulsion.^{1,2} In this method, the aqueous droplets act as a geometrical template controlling both the shape and size of the final particles. The use of nanoparticles as building blocks enables facile production of materials combining multiple properties, for instance magnetic, catalytic and adsorption. Using those two features, complex microstructures can be produced without the use of toxic chemicals, high temperatures, or bespoke lab equipment. The potential of this approach for real-life challenges is vast. Magnetic silica particles ($\text{Fe}_3\text{O}_4/\text{SiO}_2$) have recently been prepared for use in a low-cost biological separation technique for developing countries. Magnetic photocatalysts ($\text{TiO}_2/\text{Fe}_3\text{O}_4/\text{SiO}_2$) have been produced as an easily recoverable system for adsorption and light-induced degradation of synthetic dyes from wastewater.² Antibacterial magnetic particles ($\text{ZnO}/\text{CuO}/\text{Fe}_3\text{O}_4/\text{SiO}_2$) are currently being investigated as an inexpensive approach for disinfecting surfaces. All of these confirm our hypothesis that multifunctional microparticles can simply be *built up* in the same way as Lego.



1. D.F.F Brossault et al. Salt-driven assembly of magnetic silica microbeads with tunable porosity. *J. Colloid Interface Sci.* **562** (2020) 381–390.
2. D.F.F Brossault et al. Self-assembly of $\text{TiO}_2/\text{Fe}_3\text{O}_4/\text{SiO}_2$ microbeads: A green approach to produce magnetic photocatalysts. *J. Colloid Interface Sci.* (DOI: 10.1016/j.jcis.2020.10.001) (2020)

Cytotoxicity of peptide self-assemblies of different structure, phase and reversibility towards neuronal and glial cells

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Functional amyloids have been found in a wide range of organisms, including humans, invertebrates and microorganisms. A decade ago, over 30 human peptide/protein hormones were shown to form functional amyloid aggregates inside the secretory granules of neurosecretory cells and exocrine cells¹. Although interactions of disease-associated amyloids with biomolecules and cell membranes/model lipid membranes have been widely explored, limited literature is available on that of functional amyloids. In this context, we investigated the cytotoxicity profile of different types of molecular species formed during the neuropeptide self-assembly process, including soluble species and mature nanofibrils or nanotubes, either precipitates or as mesophases, towards two types of model brain cells, neuronal cells and glial cells. Three self-assembling human neuropeptides which were previously characterised by our group were used in this study^{2,3,4}. Using a set of cell viability assays and biophysical techniques, we show concentration- and structure-dependent cytotoxicity of the neuropeptide self-assemblies. Peptide soluble species and liquid crystalline arrays of neuropeptide nanostructures are non-toxic. However, amorphous aggregates/precipitates formed at high neuropeptide concentration in cell culture media were correlated to cytotoxicity towards neuroblastoma cells and microglia. In contrast, amorphous aggregates formed by amyloidogenic peptides exhibited moderate cytotoxicity towards neuronal brain cell lines at all the concentrations studied. Our discovery will enhance the current understanding of functional amyloid toxicity and alarm the use of multicomponent solvent systems such as cell culture media to prepare the nanostructures for both fundamental and application research.

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High Voltage Supercapacitors using microemulsion electrolytes

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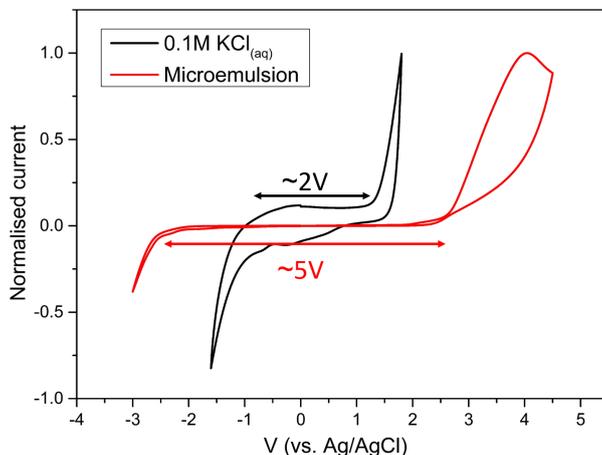
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In the diverse energy storage landscape, supercapacitors offer the advantage of fast charge and discharge making them ideal for high power applications such as accelerating vehicles or voltage stabilisation. The current standard electrolyte used in supercapacitors consists of an organic solvent (such as acetonitrile or propylene carbonate) and a quaternary ammonium salt. This combination has good electrochemical stability but is costly as well as potentially hazardous.

Using a water-based electrolyte is an attractive option, however, above a potential of 1.23V it is thermodynamically favourable for water to split into oxygen and hydrogen gasses. This means that under most circumstances aqueous supercapacitors are limited to around 1V at maximum. Traditional supercapacitors achieve voltages of between 2.7-3V, above which it is the electrode material (activated carbon) that begins to degrade rather than the electrolyte. This means that aqueous devices inherently have a lower energy density than organic devices.

I will present the first use of a microemulsion electrolyte, with water as the major component, in a supercapacitor with which we can achieve the standard voltage of 2.7 V. By breaking the 1.23 V barrier while remaining cheap and sustainable, we anticipate this electrolyte to have significant impact on aqueous electrochemical energy storage technologies. Commercialisation efforts are being actively undertaken and I will include aspects of this journey in my presentation.



Slip-Induced Dynamics of Janus Spheres: Experiments

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In recent years, clusters of Janus particles have emerged as a new division of colloidal structures. Janus spheres have two distinct hemispheres¹ (Figure a), an asymmetry contributing towards interesting emergent structures when they aggregate. Our interest in the emergent properties of Janus spheres is driven by two factors. Firstly, there are untested simulation results suggesting that Janus particle clusters can form interesting phases.² Secondly, the asymmetry of Janus spheres suggests that the aggregation process could be controlled. One potential mechanism for controlling self-assembly involves the self-orientation of Janus spheres in flow. This is the subject of our current research relating to the dynamics of colloids with slip boundary conditions.¹ In preliminary experiments, free diffusion studies have been conducted to measure the diffusion coefficients of 600 nm and 800 nm diameter silica spheres. Control silica spheres were compared with hydrophobic (silane coated) silica spheres (see Figure b). Initial results indicate no detectable difference between the diffusivity of these beads, and further experimental studies are ongoing. The overall goal is to develop and study assemblies of asymmetric Janus spheres which have novel and/or interesting emergent properties, that is, macroscopic physical properties.

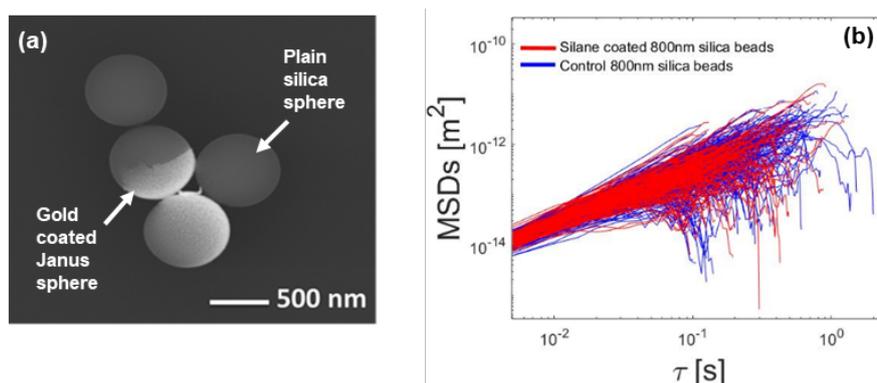


Figure: (a) SEM image of 800 nm gold coated silica Janus particles, and (b) mean square displacements (MSDs) as a function of time for diffusing 800 nm control and silane coated silica spheres.

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Branching out: Dynamic interactions of surface decorated nanoparticles at the nano-bio interface

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Effective delivery of therapeutic compounds remains limited by our understanding of interactions between drug carriers at the nano-bio interface. Cationic cell penetrating peptides (CPPs) are reported to enhance the cellular absorption of therapeutic compounds. We anticipate CPP architecture to play a crucial role, but it has not been explored systematically in this context.

We designed CPPs with three distinct architectures to study the influence of CPP structure on cell interactions. Poly(lactic-co-glycolic) acid (PLGA) nanoparticles functionalized with CPPs were produced using microfluidics (Fig. 1A). Using single particle tracking we followed the dynamic behaviour of individual CPP-tagged nanoparticles and observed localisation of the nanoparticles in close proximity to the cell membrane (Fig. 1B). After 1 h, branched TAT displayed mobility behaviour distinct from the other peptides with a higher degree of membrane interaction. CPP architecture influenced nanoparticle-cell interactions and provides insights into the drivers that govern cell uptake of nanomedicines.

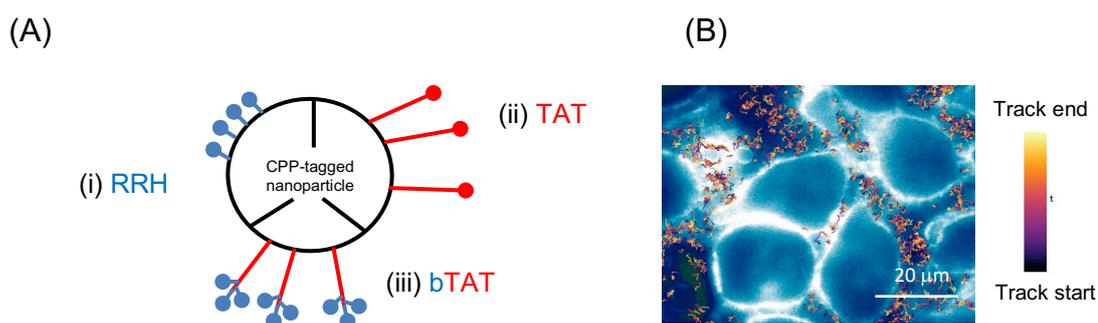


Fig. 1 (A) Schematic diagram of CPP-tagged PLGA nanoparticles. CPPs of different architecture (i) short arginine-arginine-histidine (RRH) (ii) long linear trans-activating transcriptional activator (TAT) (iii) Branched TAT, TAT with three terminal RRH groups (B) Single particle tracking of fluorescently-labelled PLGA nanoparticles during incubation with HeLa cells.

Formation of fibrous aggregates of DNA and amphiphilic molecules at the air/water interface

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Although the interactions of nucleic acids with oppositely charged molecules have been studied for more than forty years, this subject still attracts great interest mainly due to the application of DNA/surfactant and DNA/polyelectrolyte complexes to the gene transfection into target cells. Although it is known that the layers of amphiphilic molecules at a liquid surface can be considered as physical models of biological membranes, and the information on DNA/surfactant interactions in the surface layer can facilitate the determination of the formation mechanism of the aggregates in biological systems, most of the authors considered the interactions of nucleic acids with surfactants and polyelectrolytes in bulk phases.

This work is devoted to the investigation of static and dynamic surface properties of mixed solutions of DNA with surfactants or hydrophobically modified polyelectrolytes, and to the estimation of the adsorption layer structure. Measurements of the kinetic dependencies of surface properties of the mixed solutions discovered a noticeable synergistic effect when the deviations from the results for solutions of individual components indicated the formation of a rigid network at the interface. The atomic force microscopy allowed estimation of the morphology of the adsorption layer as a function of the molar ratio of the two components.

Acknowledgements

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Molecular Dynamics Study of Janus Dimer Instability in Shear Flows

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Janus nanoparticles have received considerable interest recently due to the way that they interact with each other to self-assemble into complex nanostructures.¹ Theoretical studies suggest that these nanoparticles experience a torque in fluid flows due to their slip-asymmetric boundary conditions.² The torque on individual Janus nanoparticles promotes break-up of the aggregates into isolated spheres (see figure).³ In this work, we investigate the effect of the hydrophobicity on the thermal- and shear break-up of amphiphilic Janus dimers. We will present our latest results on the possible break-up mechanisms and propose a descriptive equation for calculation of the break-up rate.

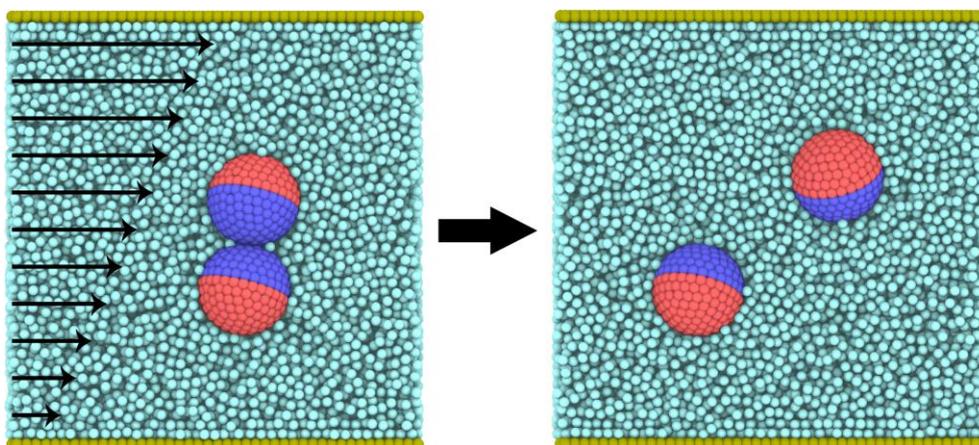


Figure: When an amphiphilic Janus dimer is in a shear flow, individual particles of the dimer encounter torque in opposite directions. This promotes break-up of the dimer into isolated spheres.

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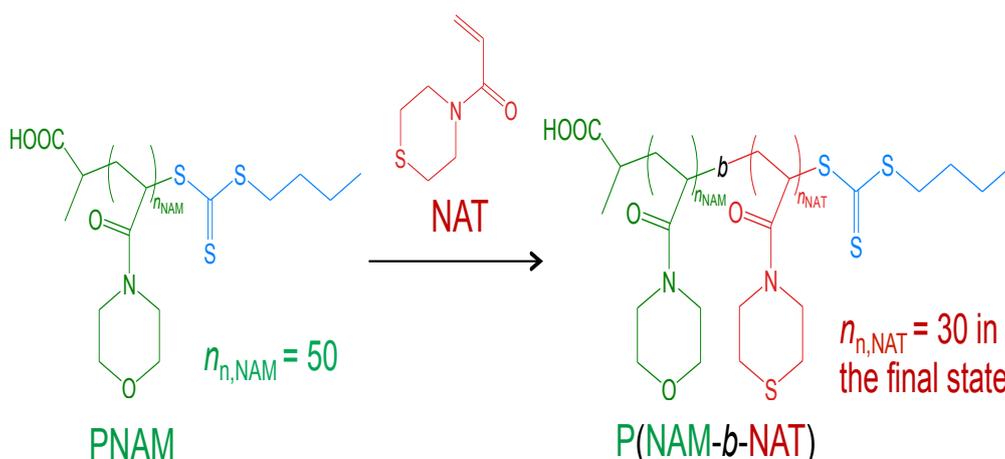
A Kinetical Analysis of RAFT-Polymerization Induced Self-Assembly by Decoupling the Chain propagation and the Micelle Formation

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Upon extending a hydrophobic polymer chain from end of a preceding hydrophilic chain in aqueous solutions, the resultant block copolymers may eventually undergo self-assembly. Further chain propagation continues in the newly formed hydrophobic polymer rich domain. This process is often referred to as polymerization-induced self-assembly (PISA). Its kinetics are determined by the polymerization and the micelle formation/growth, which may influence each other. In this study, we examined PISA in aqueous solution on the reversible addition fragmentation chain transfer (RAFT) dispersion polymerization of poly(N-acryloylmorpholine)-b-poly(N-acryloylthiomorpholine). Using in situ small-angle X-ray scattering (SAXS) and nuclear magnetic resonance spectroscopy (NMR), the polymerization and micelle formation were observed. In the analysis, because the time scale of the micelle formation/growth is much shorter than that of the polymerization, the polymerization and micelle formation/growth can be decoupled. Thus, these were separately analysed in depth, and a combination of the kinetics of RAFT polymerization and the simple scaling theory of the micellar structures can quantitatively describe the overall micellar structural development during PISA.



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Protein adsorption at the oil-water interface: role of protein self-association

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Many food emulsions are stabilised against drop flocculation and coalescence by thick films of adsorbed milk proteins at the drop surfaces.¹ The major protein in milk serum is β -lactoglobulin, a small globular protein. Depending on the pH, temperature, and salt concentration, β -lactoglobulin exists in aqueous solutions as monomers, dimers, or higher oligomers.² β -lactoglobulin diffuses rapidly from the aqueous phase to the oil-water interface. There it unfolds irreversibly to form a viscoelastic layer.³ The surface charge of β -lactoglobulin and the hydrophobicity of the oil phase are known to affect the adsorption process.⁴⁻⁶ In this talk, I will present results from a study done under conditions designed to tease out the differences in interfacial activity between the monomer and dimer species of β -lactoglobulin. We used drop profile tensiometry and interfacial shear rheology to probe the dynamics of the protein adsorption at the oil-water interface from aqueous salt solutions. We explored the influence of the salt concentration and the type of salt present on the elasticity of the protein network. Our key finding is that the formation of the viscoelastic layer is directly linked to the proportion of dimer present in solution. These results suggest simple routes for tailoring the properties of β -lactoglobulin networks at immiscible interfaces.

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Ferrofluid Drop Impacts

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When placed in a magnetic field, drops of ferrofluid form spiky Rosensweig instabilities, so that their shape is often likened to that of a hedgehog. These fluids are suspensions of magnetic particles in a solvent, and instabilities arise from competition between surface tension and the tendency of the particles to line up along magnetic field lines.¹ The dynamics of these drops are not well-studied, and this presentation will discuss high-speed photography of vertical ferrofluid drop impacts on to a glass slide. A non-uniform magnetic field is present due to a bar magnet placed under the slide.

The form of the drop is of interest both before and after impact. Prior to reaching the surface, elongation of the drop (Figure, left) depends on the release height and the positioning of the magnet. Following impact, instabilities emerge on the spreading lamella and rim at various positions and times. When the magnet is close enough to the slide, the ferrofluid can be drawn radially outwards into a rim at the edge of the magnet (Figure, right).

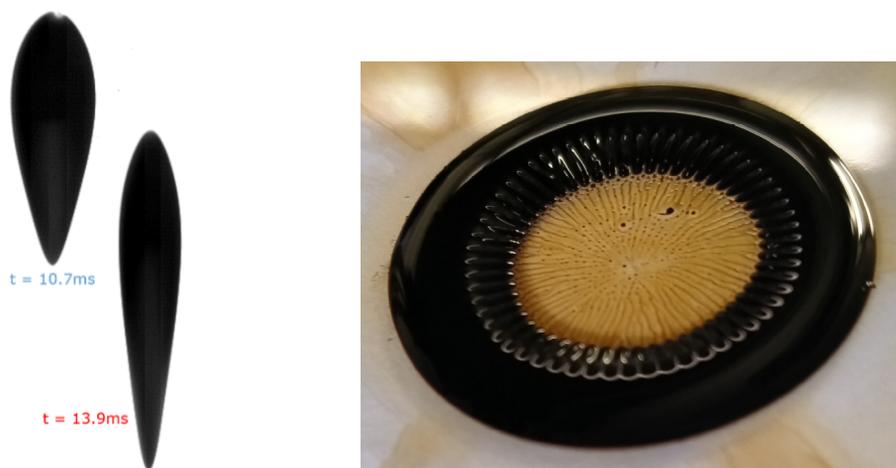


Figure: Left, ferrofluid drop profiles prior to drop impact on a glass slide placed above a bar magnet, labelled with relative time elapsed, and (right) a drop following impact.

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Palmerston North – Poster Abstracts

Diagnostic platform using Exhaled Breath Condensate

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Extracellular vesicles (EV) are tiny particles released by all mammalian cells and are found in bodily fluids, such as blood, plasma, serum and breast milk. The biogenesis of EVs leads to unique compositions that can be related to the parent cell (cell of origin) and can therefore be used in disease diagnosis. Various studies have shown that transmembrane and adhesion proteins present on EV membrane have the potential to serve as disease biomarkers. Our research group recently reported the isolation and characterisation of breath-derived extracellular vesicles for the first time.¹ This project builds on the previous findings to explore EVs as a non-invasive alternative for detection of lung-related problems. Breath-derived extracellular vesicles will be captured onto a gold substrate modified with a self-assembled monolayer and an aptamer to target specific ligands on the extracellular vesicle surface. Preliminary results show that electrical impedance is a reliable technique for measurement. Choice of thioic acid, period of immobilisation and surface preparation play vital roles influencing the electrode performance. Successful adaptation could provide a cheap, rapid and non-invasive diagnostic platform for lung-related problems.

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Investigation into the application of light-manipulated Marangoni Flow in fluids

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Fluid motion typically is driven by a pump, mixer or other physical methods whereas biological systems often utilize the natural surplus of energy at interfaces to achieve flow. Recent developments in material science have shown the ability to achieve autonomous flow of fluid for almost no cost using the natural almost infinite surplus of energy at surfaces and interfaces, termed Marangoni flow.

This project investigated how to utilise this energy to drive droplet flow using phototaxis as already seen in literature, and the potential applications of such a system. Phototaxis of a droplet is achieved through the droplet containing a photoactive species and will be illustrated figure 1. Upon illumination of the droplet, the side illuminated will begin converting the photoactive species to a compound with different surface activity, causing a local surface tension gradient on the droplet. This gradient will cause a flow at the droplet interface which will transfer momentum to both the dispersed and continuous phase to drive droplet motion.

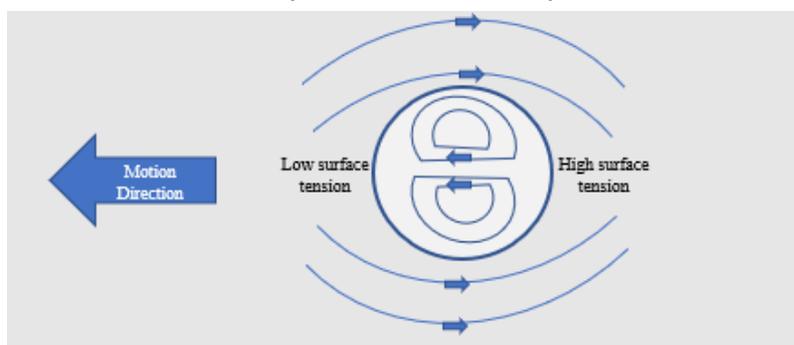


Figure 1: Schematic of droplet moving from Marangoni flow (based on schematic by Xiao et al. (2018))

The system investigated droplet motion and subsequent merge and polymerisation of two droplets, for potential additive manufacturing application. It was found that photo-induced polymerisation of two separate droplets was successful, but droplet motion did not occur with the given materials. These results showed the light wavelength (405nm)/photoactive compound (BAPO) combination could not provide enough energy to drive droplet motion and stresses the fact that such a system requires a strong combination to drive motion. This warrants further investigation into the system, including the use of a different photo-active compound and the use of a photosensitiser.

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Hydrogen Sulfide Donor Particles

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In ischemic tissue, reperfusion leads to increase in reactive oxygen species (ROS) that can lead to further damage. Hydrogen sulfide (H₂S) has been shown to help mitigate this damage¹, therefore supplementation via polymeric particles could help reduce long term consequences of ischemic events². Enhanced ROS levels can be used to trigger the generation of H₂S from the polymeric particles allowing tissue specific release. The H₂S was generated from the polymer itself; during degradation releasing a precursor that is enzymatically converted to H₂S, bypassing low particle encapsulation of small molecules.

ARGET ATRP was used for polymer synthesis with a target MW of 11 kDa using a mPEG initiator and ascorbic acid as the reducing agent in a heterogenous solvent system. Hydrogen peroxide responsiveness was introduced via boronic ester pinacol groups on the monomers. Polymers were self-assembled using nanoprecipitation. Generation of hydrogen sulfide was measured via turn on fluorescence of 7-azido-4-methylcoumarin from polymeric particles when triggered via H₂O₂. Nanoreactors were formulated via loading of the particles with enzyme and removal of unencapsulated via centrifuge filters.

A series of polymers were synthesised that could generate H₂S upon triggering with H₂O₂ in the presence of enzyme. These polymers formed a heterogenous population of particles comprising of compound vesicles, vesicles and spongesomes, that upon exposure to H₂O₂ cross-linked and formed stable particles. Exposure to H₂O₂ also led to generation of H₂S as detected via turn on of fluorescent probe. The presence of enzyme encapsulated within the particle allowed self-conversion of precursors to H₂S. Enzyme did not escape from triggered particles yet small hydrophilic compounds did, suggesting the cross-linking allowed free exchange across the bilayer.

Polymers were synthesised that were able to generate H₂S in environments of high oxidative stress, in response to H₂O₂. The cross linking of the particles allows encapsulation and retention of enzymes for self-conversion of the precursor to H₂S. This opens for the potential use in ischemia reperfusion injury prevention.

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