Soft Matter in the MacDiarmid Institute

Kathryn M. McGrath

MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University, PO Box 600, Wellington (e-mail: Kate.McGrath@vuw.ac.nz)

The expression *where physics meets chemistry and where physics and chemistry meet biology* is a common catch phrase for soft matter. The study of soft matter is an interdisciplinary field of extreme breadth. It encompasses a wide range of materials bought together by their commonality of physicochemical characteristics and through possessing both solid and liquid-like properties, as opposed to accord in their chemical formulation or functionality. As such, another common descriptor often used is *think all things soft and squishy*–well at least from a chemical perspective–soft matter does not span the realm of soft furnishings but honey, chewing gum, LCDs, and proteins all fit the bill.

Soft materials characteristically exhibit hierarchical structures organized on multiple length scales that emerge from molecular and supramolecular self-assembly. Nature abounds with examples of soft materials that harness the unique physics and chemistry of the nano world, where *bottom-up* processing is performed with aplomb to generate smart, functional, viscoelastic matrices. Soft materials are aplenty in biology. They also find a home in industrial arenas as diverse as oil recovery, food technology, cosmetics and personal care products, electronics device miniaturisation, and also in biotechnologies such as microfluidics and targeted drug delivery. The study of how their macroscopic properties emerge as a consequence of the properties and interactions of their constituent molecules promises not only to illuminate Nature's design rules but also to inform us in the design of our own smart soft materials, *viz*. structure-function understanding par-excellence. The spatial and temporal richness of these hierarchical architectures necessitates the use of varied experimental techniques to address organisational phenomena and dynamics across many orders of magnitude. It is the complementary nature of the available experimental techniques through to theoretical capability, and the relevant expertise in the gamut of soft matter systems (that include emulsions, foams, lyotropic and thermotropic liquid crystals, colloidal suspensions, polymer and biopolymer solutions, gels and melts) that is the strength of this area of study.

Soft matter systems envelope small molecules through to large polymeric networks and gels, they encompass thermodynamic and kinetic stabilisation and, moreover, they are inherently dynamic systems. Biologically-based systems tend to be called complex soft matter, whereas synthetic models, or *simple complex systems* to coin an oxymoron, are so named only because of their limited number of constituents, as opposed to any necessary reduction in their complexity of behaviour. And indeed many simple complex systems are based on biological molecules.

Globally, under the guise of soft matter, all surfactant self-assembly can be characterised by a description of the phase behaviour of the system and similarly all linear flexible polymers conform in behaviour when placed in good, ideal or poor solvent. Differences can be imparted on the system through variations in the specific chemical functionality of the underlying molecules. Hence, not only is it essential to understand the physics of these systems, but also the chemistry. Together this knowledge opens up the possibility of fine tuning macroscopic responses via molecular level control.

Bill Williams (IFS, Massey University) is working to understand how the structures of biopolymers relate to their function, and how the small changes at a molecular level can modify their manifest properties.[1,2] In particular, he is interested in polysaccharides, a major class of structural biopolymers that are right at the heart of many biological structures from plant cell walls, to animal connective tissues. The structure and function of a particular polysaccharide is investigated by extracting it from living tissue, and characterising it chemically.[1-4] Then, the molecular structure of the polymer is manipulated slightly in a precisely known way, so as to examine how this affects the behaviour of the molecule, *e.g.* when it assembles into a gel as a useful model of how it would behave in a living system.[5]

One molecule that the team has worked extensively with is pectin, a polysaccharide present in the cell walls of all land plants.[2,3] Pectin is essentially a linear co-polymer of galacturonic acid (**1**) and its methyl-esterified counterpart, and it is arguably the most complex of the plant cell polysaccharides. This complexity, regulated by enzymes capable of modifying pectin fine structure in location and time, gives pectin its utility of function and ensures that the cell may optimally employ each macromolecule. In order to gain insight into structure/function relationships in pectin-based systems, methods for the robust characterization of pectin fine structure are crucial. In particular, it is not just the average degree of esterification but the inter- and intramolecular distributions that determine how the polymer interacts with Ca^{2+}, *e.g.* during the formation of ionotropic gels.

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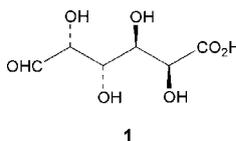
The methyl ester pattern along the backbone can be modified by the exploitation of different hydrolysis processes, *e.g.* chemically or enzymatically. The resulting distributions are measured used capillary electrophoresis (CE) in association with hydrolytic enzymes that fragment the chain in a methyl ester-dependent way. Once character-

ised, the functionality of these polymers is then examined by measuring the mechanical properties of the single chains with atomic force microscopy (AFM),[6] to studying the viscoelastic behaviour of ionotropic gels using microrheological methods (Fig. 1). These techniques measure the mean square displacement of embedded tracer beads, monitored with diffusing-wave spectroscopy and multiple particle tracking. They require minimal amounts of sample and give access to behaviour across a range of time and distance scales, including assessment of the heterogeneity of mechanical properties (Fig. 2).
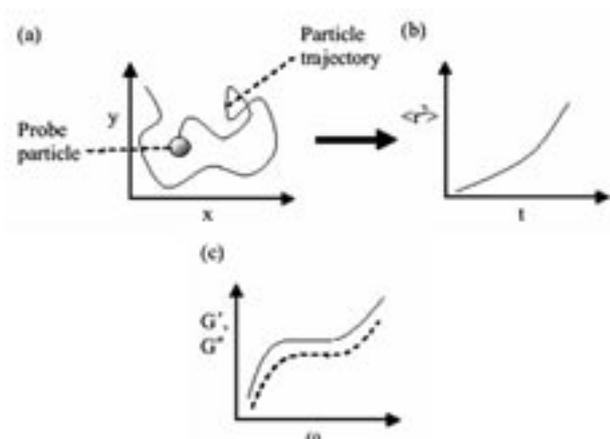

Fig. 1. Schematic of microrheology: (a) A probe particle associated with a polymer chain; (b) the mean squared displacement of the particle as a function of time; (c) the derived storage and loss moduli (G' and G") that indicate the solid and fluid characteristics of the sample, respectively.
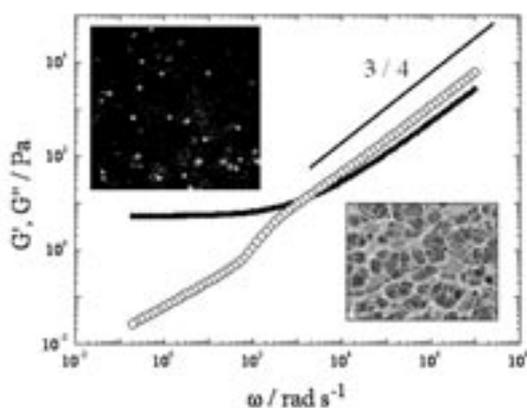

Fig. 2. Behaviour of a pectin gel measured microrheologically. Insets: (upper) optical image of the flour beads imbedded in the gel and (lower) scanning electron micrograph of the gel network.

This research has two aims. The first is simply to understand Nature so as to gain an appreciation of why biopolymers are used as they are, and they are manipulated to achieve structural changes. The second is to explore biomimetics, the possibility of making use of Nature's methodology to provide new soft materials for our own use. Naturally occurring materials tend to be very smart, *e.g.* they can change their mechanical properties in response to environmental signals, and we need to know about this in order to make equally smart synthetic soft materials.

Gerald Pereira (SCPS – VUW) focuses on understanding polymer self-assembly from a theoretical perspective. He does this by performing dynamic simulations using Monte Carlo and Brownian Dynamics models to investigate the movement towards phase equilibrium but increasingly numeric modelling is being incorporated. The particular interest of the group is with block co-polymers, *viz.* systems where two or more separate polymers are joined at their ends and arrange in block segments. The simplest are diblock copolymers[7] that are likely to find use in *e.g.* electronics. Device miniaturisation, ultimately leading to increased speed, capacity, and memory of digital media and equipment is important for the continued advancement of technology.[8] An important component of this advance is the development of photonic band-gap (PBG) materials. Such materials can be selectively and precisely tuned to accept only one wavelength of electromagnetic radiation and subsequently control its direction through internal reflection thereby allowing use as low loss waveguides for communication and efficient laser mirrors. Ultimately, 1-, 2- and 3-D patterned PBG materials, having characteristic lengths from 10-100 nm, ought to be fabricated.[9]

Self-assembling block co-polymer melts offer one possibility for the fabrication of PBG materials. These polymers have natural tendencies to produce patterns that are physically the *free energy minimum states*. These are explored and the subsequent optical characteristics of the patterns investigated. Diblock copolymers in which the different chemical species do not mix homogeneously at low temperatures give rise to two blocks that try to exist in separate phases; the outcome is the formation of nano-periodical patterns (Fig. 3). Manipulation of the polymer characteristics varies the polymer self-assembly and the lengths achievable. The group has demonstrated important methods to achieve the requisite long-range order from diblock melts and grafted polymer solutions.[10]
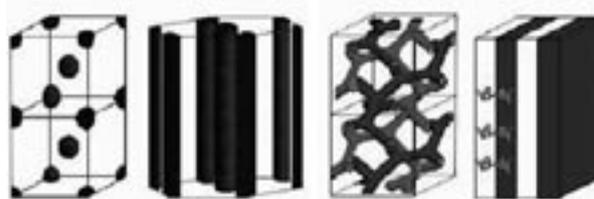

Fig. 3. Simulation outputs (L → R) for a discrete cubic, hexagonal, bicontinuous cubic, and lamellar phase formation in a diblock copolymer system.

While copolymers can be highly structurally regulated and confined, as described above, DNA is a biological copolymer in which the individual monomers are not required to exist as defined blocks. While one might assume that this would impart complete freedom on the polymer, DNA is semi-flexible with constraints on both its bending and rotational freedom.[11] Semi-flexibility is not restricted to the realm of biopolymers. It is also manifest in many important man made polymers, such as Teflon and polypropylene, and has widespread application in polymer science and engineering. Whereas fully flexible chains are modelled as Gaussian chains, semi-flexible ones have an additional bending energy that adds complexity to the modelling process.

One macroscopic manifestation of the differences inherent in the fully and semi-flexible chains is their behaviour in a poor solvent; fully-flexible polymers collapse into a dense ball whereas semi-flexible polymers form a toroid.[12] The latter enables the enormous condensation of polymer into a very small volume. Understanding how these immensely long molecules (of the order of metres in some cases) pack into extremely small volumes may help in mimicking for example, drug delivery.[13]

The systems outlined above are neutral molecules. However, most biological and commercial polymers from self-assembly comprise charged molecules that interact via long-ranged Coulomb forces and short-ranged van der Waals and steric interactions. While the theoretical understanding of neutral self-assembly is well advanced, the same cannot be said for charged systems primarily because of the large diversity in the inherent interaction length scales and associated thermal fluctuations present in all thermodynamic systems.[14]

One well known phenomenon caused by charge in polymer systems is *pearl-necklace instability*[15] where charged polymers (polyelectrolytes) balance the tendency to phase separate in poor solvents by minimizing surface-area structures. This balance causes the polyelectrolyte to undergo pearling. Gerald's group has recently predicted the shapes that the polyelectrolyte globules may take.[16]

Kathryn McGrath's group focuses on molecular self-assembly and pattern formation in both fluid and solid systems bought about through soft molecular interactions. Superposed on this is the determination of the role of equilibrium and non-equilibrium dynamics on the physical response of the materials to external and internal perturbations.

Nature presents a staggering multitude of patterning from sub-nanometre to centimetre and above lengths in solid and fluid systems, seemingly irrespective of chemical functionality. Lamellae, columnar, globular, cubic, and disordered-connected three-dimensional structures litter the natural world (see Fig. 3). From termite's nests, to marine sponges and liquid crystalline L_3 phases, a single 3-D structure is maintained despite changes in length by seven orders of magnitude; many other examples can be found. Moreover, the same pattern may be found in fluid and solid systems, and in thermodynamic and metastable systems. Couple these with the fact that Nature epitomises the use of out-of-equilibrium processes to go from one state to another such that a raft of phenomena that can be investigated in a variety of media. In particular, an understanding of the underlying physical phenomena that drive pattern formation and the inherent non-equilibrium conditions that dominate is sought.

Three examples serve to illustrate these phenomena. The first is based on the fundamental biological process of exocytosis[17] where a cell expels content from the intracellular to extracellular medium. This allows the cell to regulate not only its interior chemical makeup but also to deliver self-made hormones to the exterior for use in subsequent processes. Exocytosis involves the transport of a vesicle

10-300 nm in diameter (in which the hormone was synthesized) to the cellular membrane, fusion of the vesicle to the cell wall, and then release of the vesicle contents. Superposed on this is the fact that the cellular membrane is a fluid that causes motion within the membrane region and of the membrane itself. The group has investigated exocytosis in gonadotroph cells that synthesize the hormone which triggers ovulation. Using electron and AF microscopy they have shown that the proposed *kiss and stay* mechanism,[18] involving vesicle-vesicle transportation that leads to pit and fusion pores (Fig. 4), occurs in pituitary cells but that it is a minor transport mechanism compared to the single fusion pore.[19]
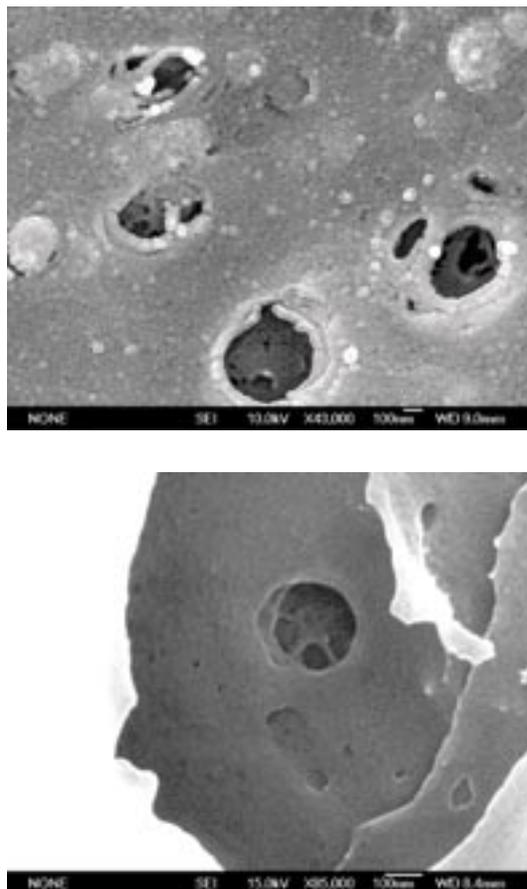

Fig. 4. SEM micrographs of pit and fusion pores on pituitary cell membranes showing the primary pore and secondary attachments expected for a *kiss and stay* exocytosis.

Inherently, emulsions are not in equilibrium but are stabilized by kinetic forces. They are mixtures of at least two immiscible liquids and they form the second example. The key to their behaviour is the interfacial domain between the immiscible liquids. As with cells, characteristic emulsion lengths range from the micron ($\equiv$ cell size) to the nanometre. The systems are fluxionally dynamic and evolve with time and, like cells, can be used as encapsulation media. Work has focused on understanding the intermolecular interactions between the oil and the emulsifier that defines interfacial integrity.[20-23] Emulsion microstructure is traditionally confined to a globular polydispersoid of one fluid in a continuum of the other. However, Kate's team has shown that a variety of different microstructures can be realized. These correlate to thermodynamically stable patterns formed at small lengths (liquid crystal and

microemulsion systems) and in large length kinetic systems such as foams (Fig. 5).[20] Moreover, these systems have proved to be far more complex than previously believed. Diffusion nuclear magnetic resonance (NMR) investigations have indicated that the continuous aqueous phase of many emulsions is a thermodynamically stable micro-emulsion and not just an aqueous solution of emulsifier.[22] Furthermore, motional averaging of the discrete liquid domains occurs indicating reversible coalescence.[20] This is counter to the classic DLVO theory used to describe colloidal stability.
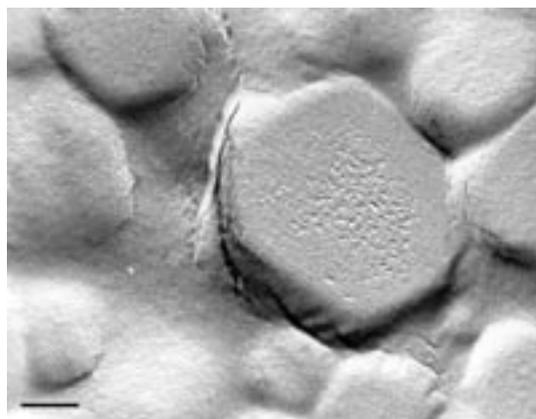

Fig. 5. TEM image (Scale Bar = 1 μm) of a concentrated emulsion in toluene/Triton X-100/water showing considerable flattening in the interfacial region akin to a foam.

Extrapolation of the above to solid systems leads to an understanding of the non-equilibrium processes of crystal nucleation and growth in biological systems that produce biominerals.[24] These solid or solid-like materials are hierarchical, with patterning spanning the subnanometre to centimetre length scales. The group focuses on understanding the role of the soft interactions between organic and biological molecules, and the constituents of the inorganic material that control pattern formation.[25] Templation and self-assembly are incorporated into the systems by choosing appropriate organic molecules and/or model cellular membranes as nucleation substrates. In biomineralisation in sea urchins, the group has shown that the glycan functionality of the acidic glycoproteins is more important than the protein itself in defining the crystal morphology of calcium carbonate. Since glycan modification of the protein is not genetically encoded, the finding further muddies the waters with respect to elucidating a biomineralisation mechanism.

Paul Callaghan (Director of the Institute) develops new NMR methodologies and hardware to the study of molecular dynamics and molecular organisation in soft matter and porous materials. His main focus is on the flow characteristics of these systems, utilising traditional rheology, Rheo-NMR, diffusion NMR and most recently Rheo-optic techniques that combine diffusing wave spectroscopy and ellipsometry with rheology.

NMR methods are ideally suited to studying mesophase properties in soft materials. While neutron, X-ray and light scattering are excellent methods for investigating long-range order, NMR is good at investigating local properties. Dipolar and quadrupole interaction can be measured

from 0.1 – 10 nm, NMR imaging for the 1 nm to 100 μm range, and diffusion measurements for the 0.1 – 10 μm range. The combination of these techniques is ideal for investigating soft materials. As an example consider Rheo-NMR.[26] This technique combines the controlled deformation of a rheology experiment with the ability to monitor sample response to the deformation via NMR techniques such as velocimetry and diffusion measurements. It allows for experimental probing of questions central to generic soft materials, *e.g.* molecular organization and fluctuation in flow in say a capillary under a defined deformation (Fig. 6).[27] Links to established methods ensure the acceptance of the many new experimental techniques developed.
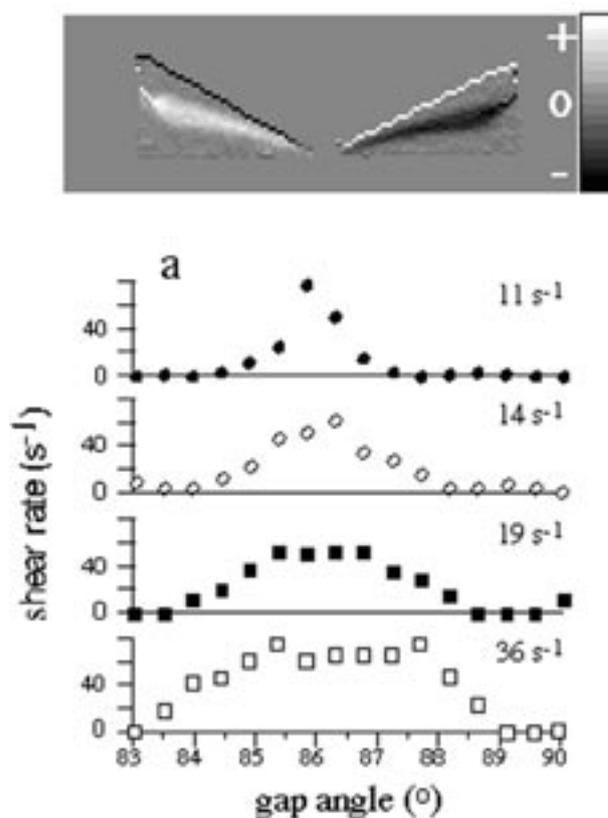

Fig. 6. (Upper) NMR image of shear rate (rate of change of velocity) in the gap of a cone and plate cell - a wormlike micelle solution showing *shear-banding*; (lower) shear rate profiles across the gap indicate how the growth in size as the cone rotation rate is increased (adapted with permission from *Reports of Progress in Physics*, IOP Publishing - see ref. 26).

One area where Rheo-NMR has been used effectively is with aging and rejuvenation. While aging is a common phenomenon, rejuvenation can be equally important, *e.g.* in complex glassy fluids both are common. Glassy complex fluids encompass a wide range of physically distinct materials that include foams, emulsions, and suspensions. Many of these materials exhibit similar rheological behaviour and this has lead some to argue for the generic presence of slow glassy dynamics. The aging behaviour is seen in both linear and non-linear rheology and indicates a fundamental response of the material. Rheo-NMR methods follow the changing response of the material to constant shear both temporally and spatially.[28] The age and temperature dependent evolution of the velocimetry

data shed light on the internal dynamics of the system and allude to the importance of interactivity between the elements.

Soft matter systems also include the class known as *porous media*. The subject of flow, dispersion, and diffusion in porous media has major interdisciplinary significance underpinning, *e.g.* chromatographic separation technology, biological perfusion, oil recovery, and wood treatment technologies. Mass transport in porous media is particularly important as it applies to oil and water in rock, contaminants in groundwater, separation and mixing in micro- and nano-fluidic devices, and reagents in packed-bed chemical reactors. Dispersion is the phenomenon whereby particles on the same streamline separate during flow; it is governed by stochastic processes that arise from interplay between advective velocity gradients, molecular diffusion, and boundary layer effects. Paul's group has shown that diffusion NMR gives information about velocity correlations in porous media,[29] and this has led to the measurement of dispersion as a function of displacement, ultimately yielding information on non-local dispersion.

NMR also provides information on wetting, important in pore-to-pore exchange in porous media. The wettability of a material is its preference to be in contact with one fluid rather than another. In porous media, characterization of how the wettability affects fluid movement between pores is important in technological applications. The group has developed a NMR technique based on transverse relaxation times (T2) that allows separate observation of the exchange of water and oil between pores in a porous system;[30] T2 time distribution in a sample reflects the distribution of its pore sizes. Using model glass microspheres of differing wettability saturated with both oil and water, the group recorded a change in exchange rates of the two components that depended on the wettability (Fig. 7). Importantly, they note that water, although the faster diffusing component, has its movement constrained by association with the surface, while the slower diffusing oil is unconstrained and is freer to move.

Pablo Etchegoin specializes in Surface Enhanced Raman Scattering (SERS) and plasmon resonance enhancement of fluorescence. His laboratory at Victoria University boasts a confocal Raman microscope that provides ultra-sensitive spectroscopy, *viz.* the detection of minute numbers of molecules that, nowadays, is the detection of just one! By controlling all of the conditions under which SERS is performed, it becomes the ultimate analytical tool and a wealth of applications ranging from the tracing of tagged biomolecules to forensic investigations is envisioned; SERS is at the stage of development that NMR was in the 1970s. The *strength* of the effect is measured by a quantity called the *cross section* that turns out to be extremely difficult to measure. One method, termed *vibrational pumping*, involves creating vibrations in the molecule through interaction with the laser and, while described 10 years ago, the available experimental evidence has been in dispute. Pablo's group has now resolved the issue with an alternative demonstration of vibrational pumping.[30] They also developed what is believed to be the most conclusive proof so far of single molecule sensitivity in SERS

(Fig. 8).[31,32] Spectrum B shows signals originated from a large number of molecules as this is a statistically mix of BZT and R6G. However, spectra A and C are each of one dye only and are observed in many points; these originate from one or, at most, a few molecules.
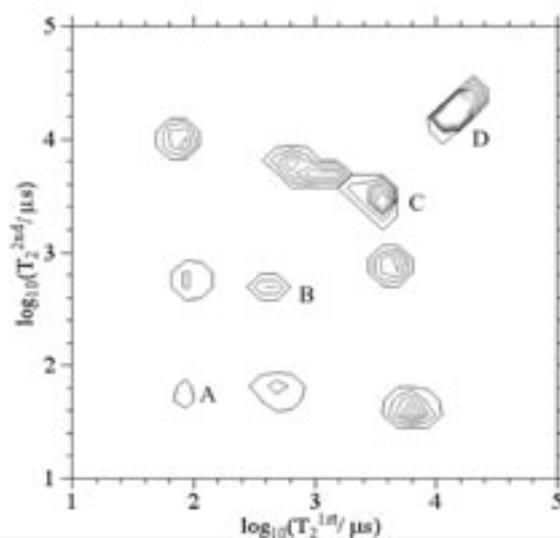

Fig. 7. Distribution of T_2 for 160 ms mixing. Diagonal peaks A-D represent pores where the molecules have remained in residence; off-diagonals correspond to molecules changing pores [Reproduced with permission from from ref. 30. Copyright (2006) American Physical Society].
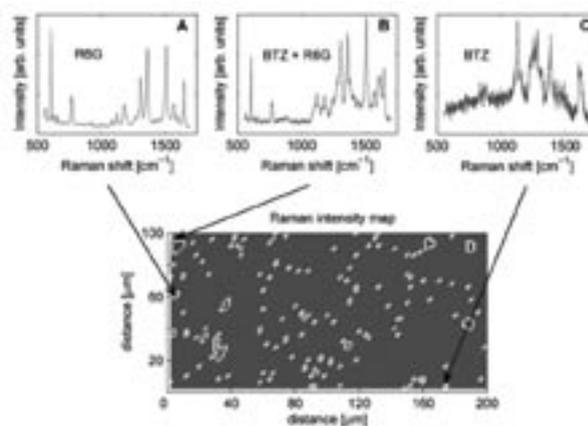

Fig. 8. Bi-analyte SERS on a mixture of the two dyes BTZ and R6G. 2D Raman intensity map (lower), spectrum B from a statistically mix of BZT and R6G; and spectra A and C each of one dye only at representative points on the surface. Reprinted with permission from ref. 31. Copyright (2006) American Chemical Society.

References

1. Hunt, J.J; Cameron, R.; Williams, M.A.K. *Biochim. Biophys. Acta* **2006**, *1760*, 1696–1703. Goubet, F.; Ström, A.; Quemener, B.; Stephens, E.; *et al. Glycobiol.* **2006**, *16*, 29-35.

2. Ström, A.; Ralet, M-C.; Thibault, J-F.; Williams, M.A.K. *Carbohydr. Polym.* **2005**, *60*, 467-473.

3. Goubet, F.; Ström, A.; Dupree, P.; Williams, M.A.K. *Carbohyr. Res.* **2005**, *340*, 1193-1199. Ström, A.; Williams, M.A.K. *Carbohyr. Res.* **2004**, *339*, 1711-1716. Williams, M.A.K.; Foster, T.J.; Schols, H.A. *J. Agr. Food Chem.* **2003**, *51*, 1777-1782.

4. Williams, M.A.K.; Benen, J.A.E. *Biochem. J.* **2002**, *367*, 511-515, 2002. Williams, M.A.K.; Buffet, G.M.C.; Foster, T.J. *Anal. Biochem.* **2002**, *301*, 117-122.

5. Ström, A.; Williams, M.A.K. *J. Phys. Chem.* **2003**, *107*, 10995-10999.

6. Haverkamp, R.G.; Williams, M.A.K.; Scott, J.E. *Biomacromol.* **2005**, *6*, 1816-1818.

7. Bates, F.S.; Fredrickson, G.H. *Phys. Today* **1998**, *52*, 32-38.

8. Park, C.; Yoon, J.; Thomas, E.L. *Polymer* **2003**, *44*, 6725-6760.

9. Joannopoulos, J.D.; Meade, R.; Winn, J.N. *Photonic crystals: Moulding the flow of light* Princeton University Press: Princeton NJ, 1995. Fink, Y.; Winn, J.N.; Fan, S.; Chen, C.; Michel, J.; Joannopoulos, J.D.; Thomas, E.L. *Science* **1998**, *282*, 1679-1682.

10. Pereira, G.G.; Williams, D.R.M. *Macromol.* **1999**, *32*, 8115- 8120. Pereira, G.G. *Phys. Rev. E* **2001**, *63*, 061809-061814, *Eur. Phys. J. E* **2002**, *7*, 273-289. Pattanayek, S.K.; Pereira, G.G. *Macromol. Th. Simul.* **2005**, *14*, 347-357. Pattanayek, S.K.; Pham, T.T.; Pereira, G.G. *Curr. Appl. Phys.* **2006**, *6*, 571-574.

11. Hud, N.V.; Vilfan, I.D. *Ann. Rev. Biomol. Struct.* **2005**, *35*, 295-318.

12. Manning, G.S. *Biopolymers* **1980**, *19*, 37-59.

13. Pereira, G.G.; Williams, D.R.M. *ANZIAM J.* **2004**, *45*, C163-C173. Miller, I.C.B.; Keentok, M.; Pereira, G.G.; Williams, D.R.M. *Phys. Rev. E* **2005**, *71*, 31802-31809.

14. Holm, C.; Kekicheff, P.; Podgornik, R. (Eds), *NATO Science Series* Kluwer Academic Publishers: Dordrecht, 2001.

15. Kantor, Y.; Kardar, M. *Phys. Rev. E* **1994**, *51*, 1299-1311. Dobrynin, A.V.; Rubinstein, M.; Obukhov, S.P. *Macromol.* **1996**, *29*, 2974-2979.

16. Pattanayek, S.K.; Pereira, G.G., *Phys. Rev. E* submitted. Pereira, G.G.; Pattanayek, S.K. *J. Non-Newt. Fluid Mech.* submitted.

17. Fernandez-Peruchena, C.; Navas, S.; Montes, M.A.; Alvarez de Toledo, G. *Brain Res. Rev.* **2005**, *49*, 406-415.

18. Nemoto, T.; Kimura, R.; Ito, K.; Tachikawa, A.; *et al. Nature Cell Biol.* **2001**, *3*, 253-258. Leung, Y.M.; Sheu, L.; Kwan, E.; Wang, G.; *et al. Biochem. Biophys. Res. Comm.* **2002**, *292*, 980-986. Allersma, M.W.; Wang, L.; Axelrod, D.; Holz, R.W. *Mol. Bio. Cell.* **2004**, *15*, 4658-4668. Thorn, P.; Fogarty, K.E.; Parker, I. *Proc. Nat. Acad. Sci.* **2004**, *101*, 6774-6779.

19. Savigny, P.; Evans, J.J.; McGrath, K.M. *Endocrinology* submitted.

20. Liu, E.-H.; Callaghan, P.T.; McGrath, K.M. *Langmuir* **2003**, *19*, 7249-7258.

21. Liu, E.-H.; McGrath, K.M. *Colloids & Surfaces A* **2005**, *262*, 101-112. Liu, E.-H.; Egger, H.; McGrath, K.M. *J. Phys. Chem. B* **2005**, *109*, 13332-13341.

22. Egger, H.; McGrath, K.M. *J. Colloid Interface Sci.* **2006**, *299*, 890-899.

23. Egger, H.; McGrath, K.M. *Colloids Surfaces A* **2006**, *275*, 107-113.

24. MacKenzie, C.R.; Wilbanks, S.M.; McGrath, K.M. *J. Mater. Chem.* **2004**, *14*, 1238-1244.

25. McGrath, K.M.; Dabbs, D.; Yao, N.; *et al. Science* **1997**, *277*, 552-556. Putnam, R.L.; Nakagawa, N.; McGrath, K.M.; Yao, N.; *et al. Chem. Mater.* **1997**, *9*, 2690-2693. McGrath, K.M.; Dabbs, D.; Yao, N.; Edler, K.J.; *et al. Langmuir* **2000**, *16*, 98-406. McGrath, K.M. *Adv. Mater.* **2001**, *13*, 989-992. Dickinson, S.R.; Henderson, G.E.; McGrath, K.M. *J. Cryst. Growth* **2002**, *244*, 369-378. Dickinson, S.R.; McGrath, K.M. *J. Mater. Chem.* **2003**, *13*, 928-933; *Cryst. Growth Design* **2004**, *4*, 1411-1418. Henderson, G.E.; Murray, B.J.; McGrath, K.M. *Cryst. Growth Design* submitted.

26. Callaghan, P.T. *Rep. Prog. Phys.* **1999**, *62*, 599-670. Fischer, E.; Callaghan, P.T. *Phys. Rev. E* **2001**, *64*, 11501/1-11501/15.

27. Britton, M.M; Callaghan, P.T. *Phys. Rev. Lett.* **1997**, *78*, 4930-4933. Cormier, R.J.; Kilfoil, M.L.; Callaghan, P.T. *Phys. Rev. E* **2001**, *64*, 51809/1-51809/11.

28. Wassenius, H.; Callaghan, P.T. *Eur. Phys. J.* **2005**, *18*, 69-84.

29. Khrapitchev, A.A.; Callaghan, P.T. *Phys. Fluids* **2003**, *15*, 2649-2660.

30. Washburn, K.E.; Callaghan, P.T. *Phys. Rev. Lett.* **2006**, *97*, 175502/1-175502/4.

31. Maher, R.C.; Etchegoin, P.G.; Le Ru, E.C.; Cohen, L. F. *J. Phys. Chem. B* **2006**, *110*, 11757-11760.

32. Le Ru, E.C.; Meyer, M.; Etchegoin, P.G. *J. Phys. Chem. B* **2006**, *110*, 1944-1948; see also: Analytical Chemistry News, *Anal. Chem.* **2006**, *78*, 2083.

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