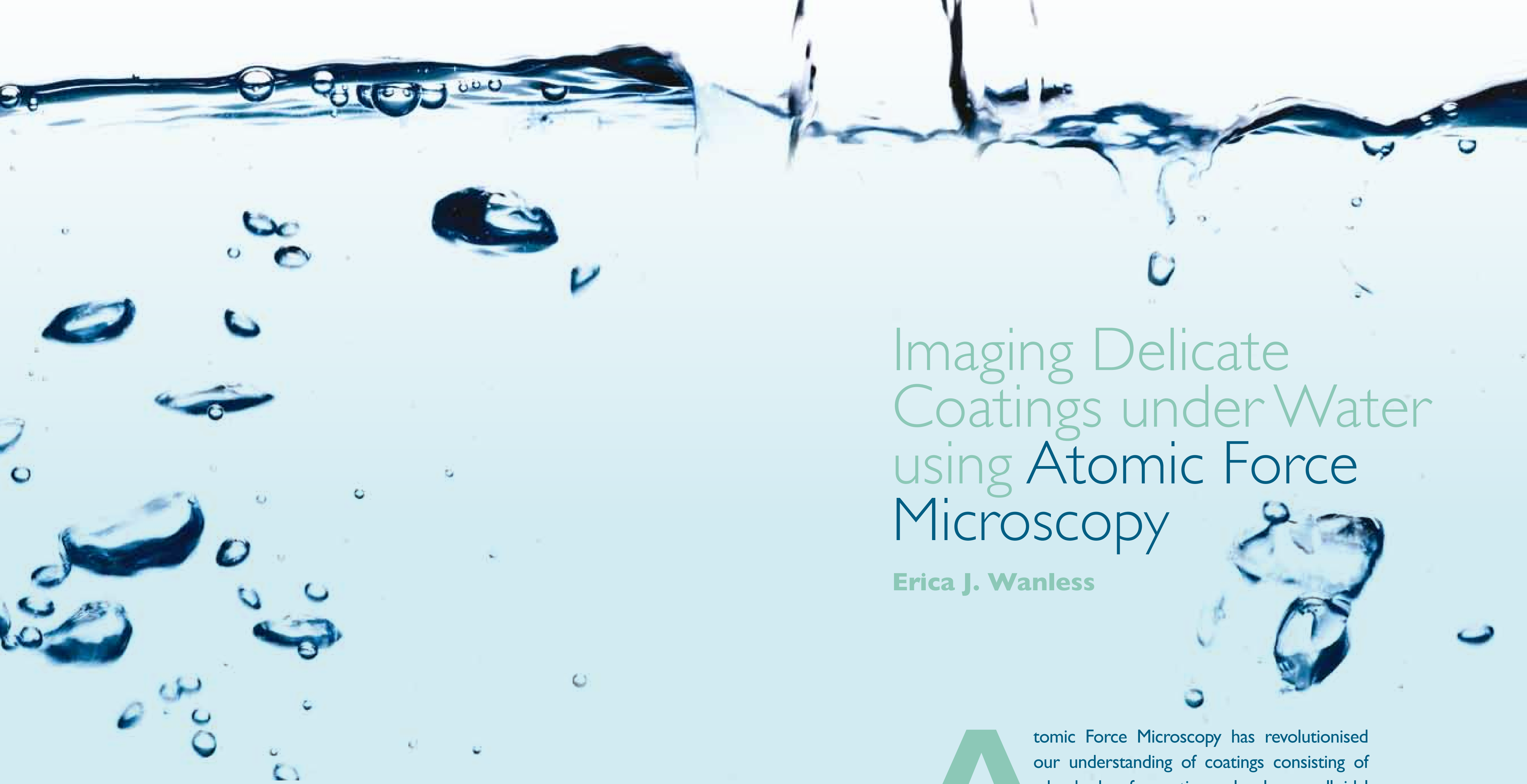

Imaging Delicate Coatings under Water using Atomic Force Microscopy

Erica J. Wanless

Atomic Force Microscopy has revolutionised our understanding of coatings consisting of adsorbed surface-active molecules or colloidal particles at the solid-liquid interface. These delicate structures may be present wherever the solution contacts a solid material.

Introduction to Atomic Force Microscopy

The atomic force microscope (AFM) was invented by Binnig, Quate & Gerber (1986) following closely after the invention by Binnig & Rohrer of the scanning tunnelling microscope (STM) in 1981. Both techniques were developed at the Zurich IBM laboratories and were made possible by new piezoelectric ceramic materials which exhibited very linear expansion and contraction on a subnanometre scale under an applied voltage. These materials formed the basis of the high resolution raster scanning of the sample inherent in these new scanning probe microscopes. A great increase in resolution was suddenly possible with 0.1 nm lateral and 0.01 nm in the vertical direction, now typical. In both microscopes, a sharp tip is traced across the sample surface like a record player (for those who remember what that was!). The image is then constructed from either the tunnelling current between the tip and sample (in STM), or the tip deflection (in AFM). While STM is perfect for conducting or semiconducting surfaces, AFM can readily be used to image the surface of insulating materials and most importantly for this review, it can readily be operated on samples immersed in water.

> *The basis of AFM imaging is the deflection of a weak spring or cantilever with a sharp tip at the end.*

The basis of AFM imaging is the deflection of a weak spring or cantilever with a sharp tip at the end. As the tip is scanned across a sample, the cantilever deflects in response to topographical changes but also in response to changes in interaction force (e.g. van der Waals, electrostatic, hydrophobic) between the tip and sample. This cantilever deflection is translated via Hooke's Law into a force. The sample image can then be constructed based upon either topography or as a force map. Importantly in the latter case, an atomically flat but heterogeneous surface can still yield a useful and interesting image. It is this inherent force measurement which can be translated into an image that has made AFM such a valuable tool for surface and colloid science, with its fundamental basis in understanding the intermolecular forces between materials.

Imaging Adsorbed Surfactant Micelles

One of the most fascinating classes of molecules from a surface chemistry point of view is surfactants. You may know of these molecules under a different name based upon their application; perhaps as detergents, emulsifiers or collectors? In all cases, the role of the surfactant is to lower the energy of a phase boundary through adsorption at that interface. Another behaviour exhibited by surfactants in solution is that they spontaneously assemble into aggregates of various shapes including spherical or cylindrical micelles, vesicles or bilayers. For example, lipids (biological surfactants) self-assemble into cellular membranes. The driving force behind this assembly is also to lower the system free energy by minimising the contact between the hydrophobic hydrocarbon section of the molecule and the solvent, which in this case is water. The result is a compartmentalisation of the solution into aqueous zones and hydrophobic zones. This coexistence of regions of very different polarity can be readily harnessed to, for example, solubilise a hydrophobic drug, dye or fragrance. Small self-assembled aggregates such as spherical micelles can thus be used to solubilise and then transport hydrophobic molecules through aqueous media in all manner of applications from medicine to materials science and engineering.

AFM has proven invaluable for clarifying the morphology of surfactant aggregates adsorbed at the solid-aqueous solution interface. The traditional view of monolayers and bilayers has been replaced with a richer family of periodic nanostructures since

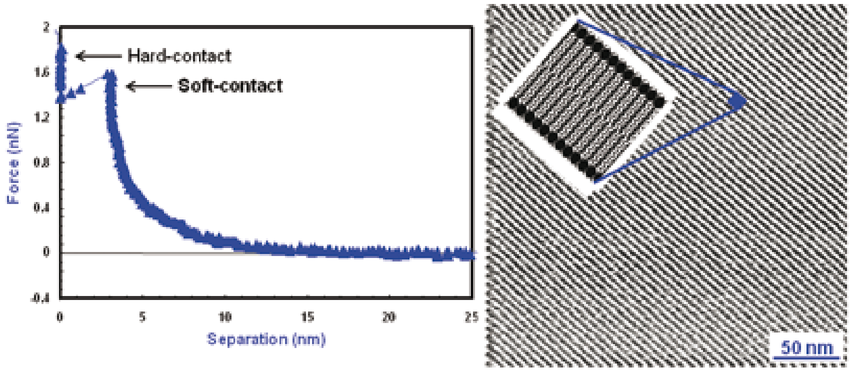

Fig. 1. *The soft-contact AFM imaging method illustrated for adsorbed sodium dodecylsulfate hemimicelles on graphite. The force curve between the tip and sample shows the soft-contact and hard-contact imaging regions. The deflection image shows the hemicylindrical surfactant aggregates and their alignment with the substrate crystal symmetry.*

Manne *et al.* (1994) reported the first AFM images of adsorbed surfactant aggregates in equilibrium with an aqueous surfactant solution. In order to understand how this imaging breakthrough was made, we need to turn to slightly earlier in 1994 when Senden *et al.* reported on "*AFM imaging with electrical double layer interactions*". In this seminal work, they showed that the AFM image was distinctly different if imaged in hard contact (in the high force Born repulsion regime) compared to when it was imaged in soft contact (on the lower force electrical double layer between tip and sample). This is precisely the methodology used by Manne *et al.* (1994) to visualise hemimicelles of the surfactant hexadecyltrimethylammonium bromide adsorbed on graphite. In soft-contact mode the image of force variation (known as a deflection image) across the sample resolved long hemicylindrical surface micelles of diameter 4.2±0.4 nm rigidly aligned to the underlying crystalline graphite. The measured period equates to twice the length of the surfactant molecule. Manne's method is illustrated in Figure 1 for surface aggregates of a similar surfactant. The force necessary to image the adsorbed surfactant is marked by the soft-contact region which arises due to an electrostatic repulsion between the anionic surfactant and the imaging tip. If more force had been applied, the substrate would have been imaged in the hard-contact region and no features would be visible on this scale. Thus careful control of the imaging force is required to resolve these delicate structures which are in equilibrium and molecular exchange with the adjacent solution.

In this deflection image, the parallel lines are the surfactant hemimicelles. Another example is shown in Figure 2 in which the parallel lines can be seen at two orientations at 60° to one another. Grain boundaries can be seen where hemicylinders of two different orientations meet. The very straight parallel nature of the aggregates is evidence of the

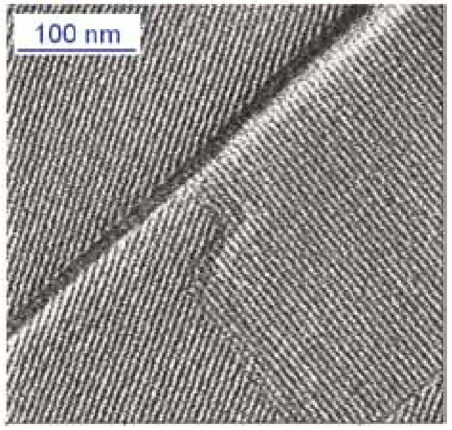

Fig. 2. *The cationic surfactant hexadecylpyridinium chloride adsorbed on graphite. The heavy diagonal line is a step on the graphite substate. Also evident are grain boundaries between surfactant aggregates templated on different substrate crystal axes.*

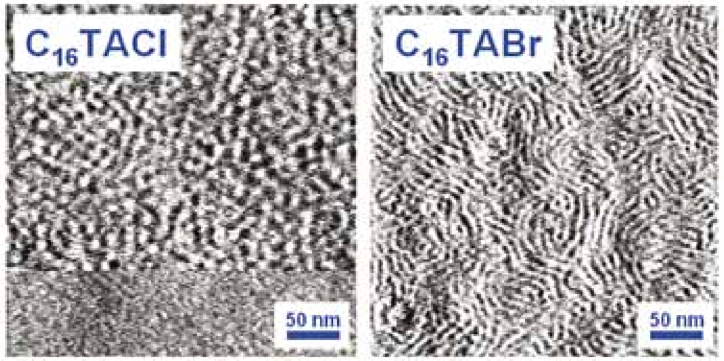

Fig. 3. *Surface micelles of two cationic surfactants on silica. The only difference between the surfactants is their counterion: chloride on the left, bromide on the right. The lefthand image also shows the difference between soft-contact and hard-contact imaging at this scale. The lower quarter of the image shows the substrate 5 nm beneath the surfactant aggregates.*

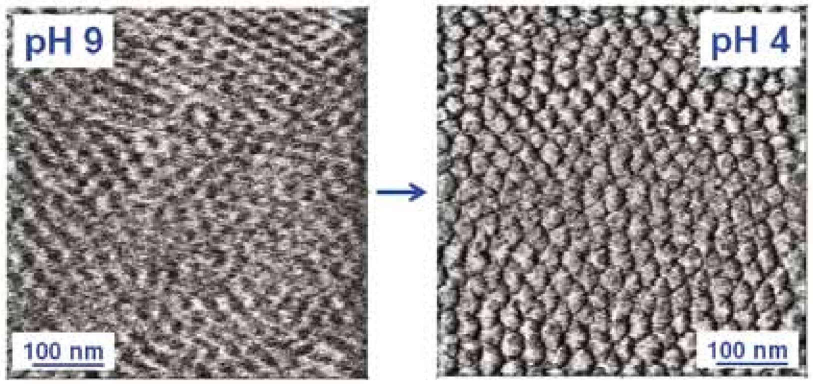

Fig. 4. *The diblock copolymer PDMA-b-PDEA adsorbed to mica from a solution of spherical micelles above the polymer pKa. Upon reduction in the overlying solution pH, the surface micelles swell with solvent and form a close-packed micellar coating.*

templating influence of the hexagonally-symmetric substrate (as shown in the schematic in Figure 1).

Traditionally these adsorbed layers on hydrophobic substrates were viewed as monolayers (Zettlemoyer, 1968) yet here is evidence of a periodic structure that could not be resolved using any other technique. This finding opened the door to a flurry of investigations to catalogue and characterise interfacial surfactant aggregates, and thus understand their relationship to substrate character. Much of this early research has been reviewed by Warr (2000). On hydrophobic substrates, the surfactant hydrocarbon tails are in contact with the substrate as illustrated in Figure 1 and hemimicelles predominate. On hydrophilic substrates, surfactant headgroups face both the substrate and the solution, so full micellar aggregates are generally formed. Occasional systems do form traditional monolayers or bilayers.

Much effort has also gone into understanding the relationship between interfacial aggregates and the geometry of self-assembly of surfactants in solution as exemplified by the critical packing parameter of Israelachvili *et al.* (1976). Wanless & Ducker (1996) lead the way by demonstrating that the addition of salt reduced the interheadgroup repulsion and thus the periodicity of hemimicellar aggregates on graphite. Crystalline graphite proved to very strongly template the adsorbed layer and override expected differences on the basis of solution micelle geometry. Thus, the research effort then shifted to hydrophilic substrates such as mica and silica. In 1999, Patrick *et al.* demonstrated on a mica substrate that, just as occurs in solution, lengthening the surfactant tail leads to a lower curvature surface micelle (e.g. cylindrical compared to spherical) and that increasing the surfactant headgoup size leads to a higher curvature surface micelle (spherical compared to cylindrical). Likewise the more strongly bound bromide counterion promotes the sphere-to-cylinder transition when compared to a chloride counterion, as demonstrated by Patrick *et al.* (1999) on mica and Velegol *et al.* (2000) on silica. This effect is shown in Figure 3 which visualises spherical hexadecyltrimethylammonium chloride micelles and cylindrical hexadecyltrimethylammonium bromide micelles adsorbed on silica. Note that both adsorbed micelles are in equilibrium with spherical solution micelles. The elongation of the interfacial micelles with the bromide counterion at a concentration below that at which the transition is observed in solution is attributed to the substrate acting as a plane of additional counterions.

> *Interfacial aggregates represent a balance between surfactant molecular geometry and substrate influences such as crystallinity and polarity.*

When it comes to surfactants such as those illustrated in this review so far, researchers now have a good understanding of the relationship between surfactant self-assembly in bulk solution and at the solid-liquid interface. Interfacial aggregates represent a balance between surfactant molecular geometry and substrate influences such as crystallinity and polarity. This advance in understanding has only been possible through *in situ* AFM soft-contact imaging. There are several reasons for this. Firstly, only AFM has the vertical resolution to distinguish the subtle change in force as the tip is scanned gently across the top of the adsorbed layer. In addition, the molecules within the adsorbed layer structure are readily exchangeable with solution micelles, so the adsorbed layer is not preserved if the overlying solution is diluted nor if the substrate is taken through the air-water interface for analysis by some alternative technique.

Imaging Adsorbed Polymeric Micelles

Diblock copolymer micelles may also be adsorbed at the solid-solution interface and characterised using AFM imaging. High glass transition temperature copolymer micelles with their glassy cores have long-lifetimes and can be robust to post-drying imaging (e.g. Potemkin *et al.* 1999). However, adsorbed low-glass transition temperature copolymer micelles are best characterised at equilibrium in solution using direct soft-contact imaging methods as used for the small molecule surfactants discussed above. One family of such polymers that we have studied in detail are tertiary amine based methacrylates such as poly(2-(dimethylamino)ethyl methacrylate)-b-poly(2-(diethylamino)ethyl methacrylate), PDMA-b-PDEA. This polymer forms micelles in aqueous solution above pH 8 owing to poor solubility of the PDEA block which forms the micelle core. The PDMA block is slightly less hydrophobic and forms the micelle corona. The polymeric micelles adsorb on substrates like mica and silica and form a self-organised adsorbed layer of micelles not dissimilar to the surfactant surface micelles shown in Figure 3. Figure 4 shows one polymer from this family adsorbed onto mica and imaged using soft-contact mode AFM (Webber *et al.* (2002)). What is most remarkable about this image is that we now know that the adsorbed layer is predominantly water (>

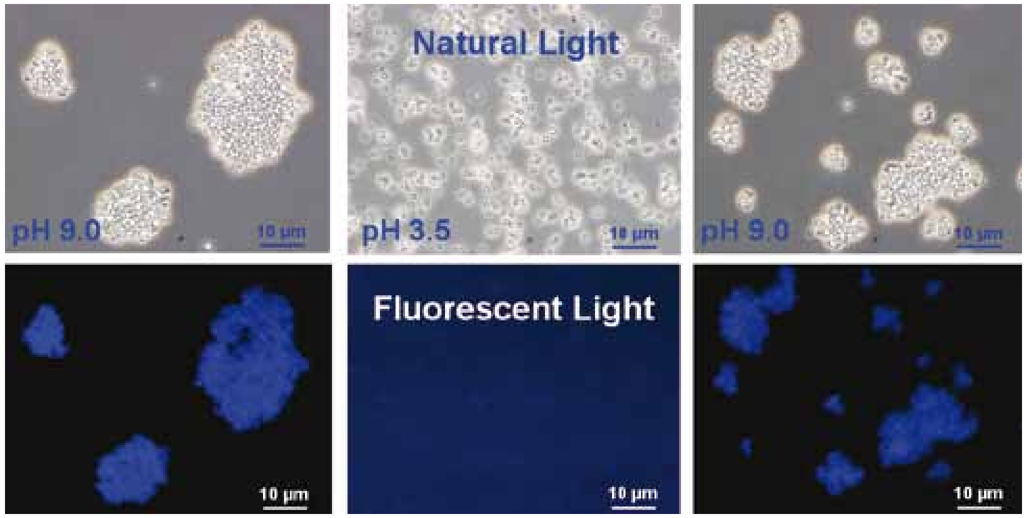

Fig. 5. *Conventional (top) and fluorescent (bottom) light micrographs of PDMA-b-PDEA copolymer coated silica particles in the presence of a saturated aqueous pyrene solution. The micrographs show both the pyrene encapsulation and the colloid stability when the pH was successively adjusted at 9.0 (surface micelles, pyrene capture), 3.5 (polymer brush, pyrene release), and again 9.0 (surface micelles, pyrene capture).*

80% as determined by quartz crystal microbalance) with the remainder consisting of the polymer (Sakai *et al.* (2006)). Thus, once more the unique capability of soft-contact AFM imaging is proven.

Now this copolymer has a characteristic response to pH variation that consists of the micelles reversibly forming above the pKa ~ pH 8 and disintegrating below this pH owing to protonation and hence greater solubility. We were thus interested as to what would happen to surface micelles exposed to pH variation. The result is shown in the right hand image of Figure 4. The surface micelles have swollen to be completely space-filling in the plane of the surface and this is attributed to their protonation and solvent uptake (as is also evident in the AFM force curves). This is in marked contrast to what would happen to analogous surfactant micelles which would simply wash off the surface. So the copolymer micelle coating is far more robust than the surfactant micelle coatings discussed earlier.

A slightly different polymer from the same family with a shorter PDMA block was subsequently shown by Webber *et al.* (2004) to form a similar adsorbed layer at pH 9, but a laterally featureless adsorbed layer at pH 4 quite unlike the fish-scale morphology of Figure 4. This anchored polymer brush layer is uninteresting in terms of the AFM image which is therefore not shown, however, the structure is confirmed by the force curve and other physical measurements. Importantly, this structure was able to be switched back into surface micelles like those shown in the lefthand side of Figure 4 simply by raising the pH again. This reversible switch in adsorbed layer structure was then harnessed to reversibly capture the fluorescent hydrophobic molecule pyrene into the surface micelle cores and then release it back into solution as shown in Figure 5 for the adsorbed layer on silica particles. A particulate substrate was used in this case to illustrate the potential use of these active coatings for capture and release of small target molecules.

Building on our success of characterising adsorbed layers of the diblock copolymer micelles, we recently demonstrated that by taking great care it is even possible to image each layer of an electrostatically assembled micelle-micelle multilayer of these low glass transition temperature diblock copolymers (Smith *et al.* (2007)). Others had previously imaged micellar multilayers with rigid cores (Cho *et al.* 2006) but, as shown in Figure 6, we were able to do this with the highly hydrated low glass transition temperature soft core micelles of PDMA-b-PDEA as the cationic layer and a related anionic copolymer. The figure shows the successful construction of a four layer micelle stack, with micelles confirmed to be present in each layer. This is despite the fact that simply mixing the two polymers in solution would result in overall complexation and precipitation. By imaging the fourth layer at slightly greater force we were even able to scrape away the top layer and show micelles present in the bottom of the 12 nm deep hole created, providing solid proof of the integrity of the multilayer. Such complex coatings are increasingly being touted for controlled release applications.

Imaging Adsorbed Polymeric Microgel Latexes

The final example that illustrates what careful AFM imaging can yield, consists of objects an order of magnitude larger than the copolymer micelles. These lightly cross-linked polymer latex particles or microgels swell in good solvents and return to their latex form in poor solvents. They can be thought of as permanent micelles for the purpose of this discussion: adsorbing for the same reason (electrostatic attraction). We have demonstrated that the swollen and deswollen states can be imaged directly with AFM as shown in Figure 7 (FitzGerald, 007)). Note that the polymer used in this case is poly(2-vinylpyridine) which has a glass transition temperature far in excess of room temperature.

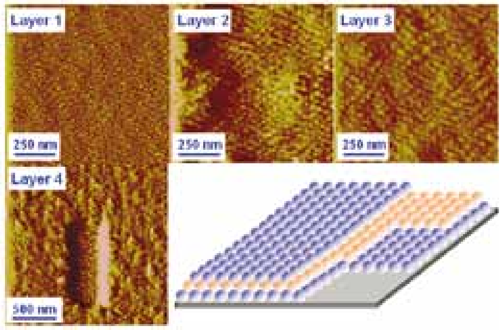

Fig. 6. *Images recorded during the construction of a low glass transition temperature diblock copolymer micelle multilayer adsorbed onto silica. The odd numbered layers are cationic micelles whereas the even numbered layers are anionic micelles. The image of layer four contains a central hole dug by imaging at slightly higher force and shows that micelles are still present in the underlying layer. The schematic shows the idealised adsorbed layer structure.*

The most obvious manifestation of this is that the adsorbed latex particles in (a) appear to flatten very little upon adsorption. In solution when the solvent is made more acidic than the polymer pKa, each monomer is protonated and the solvent swells the particle volume by a factor of 39. It is clear from (b) that when present at the interface, the latex-to-microgel transition is hindered. However, the particles clearly swell within the constraints of their nearest neighbours and in fact displace about 75% of the initially adsorbed particles. Subsequently the particles can be deswollen (c) and remain fixed in position. The number of adsorbed particles remains constant with further changes to the overlying solution pH.

For imaging the microgel latexes, we found that soft-contact was not the optimal AFM imaging mode as even these gentle forces were sufficient to

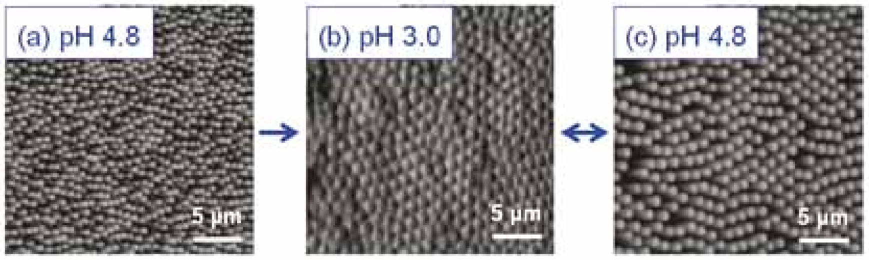

Fig. 7. *Tapping mode images of poly(2-vinylpyridine) microgel particles on a silica surface: (a) initial latex at pH 4.8 (b) swollen microgel particles at pH 3.0 and (c) deswollen particles upon returning to pH 4.8. The sample pH was cycled several times between (b) pH 3.0 and (c) pH 4.8, and the morphology was fully reversible (as noted by the arrows).*

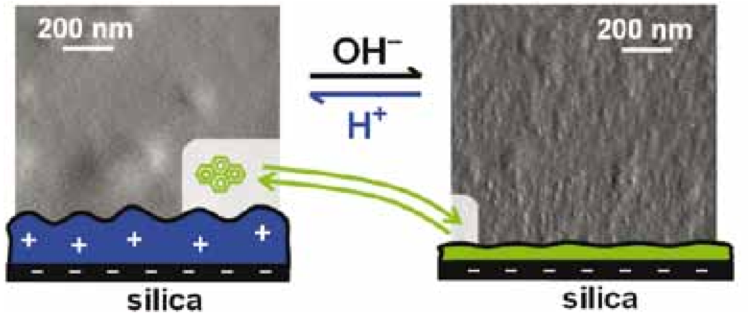

Fig. 8. *Film of coalesced PDEA latex particles adsorbed onto silica from aqueous solution at pH 8.5 and then swollen in acid. The collapsed film is also shown. The film swelling is reversible as is the uptake and release of the fluorophore, pyrene which prefers the hydrophobic environment of the collapsed film over the aqueous solution.*

move the relatively large particles laterally on the substrate. Instead we used tapping mode, a dynamic mode in which the cantilever is oscillated near its resonant frequency and the lateral force on the adsorbed layer is thus reduced since the tip comes out of contact between each pixel of the image.

When we tried a similar imaging experiment with a soft PDEA microgel latex, a very different adsorbed layer resulted and a genuine film was formed (FitzGerald *et al.* (2008)). This process is illustrated in Figure 8 and is attributed to the glass transition temperature being well below the room temperature of the experiment. Importantly, in solution these 455 nm diameter latexes also exhibit a significant increase in volume (by a factor of 20) when the pH is below the polymer pKa. It is more difficult to tell from the images whether any swelling occurs in the adsorbed film. However, using ellipsometry we measured the dry film thickness to be only 9 nm, but the AFM force curve normal to the lefthand image suggests that the layer is now 200 nm thick. That is the swelling ability of the microgel coating is significant. This was once again proven by uptake and release experiments with pyrene as per Figure 5. This film-forming microgel is an excellent example of the formation of a tunable surface coating from colloidal particles that can be readily synthesised by emulsion polymerisation.

Conclusion

Through the examples presented, soft-contact imaging is illustrated to be a valuable AFM imaging mode that is not widely used. For certain delicate samples requiring *in situ* imaging it offers the best possible resolution relying as it does on understanding and controlling the surface forces in the system. In this way, soft-contact imaging has resulted in new models for the adsorption of surface active molecules based upon discrete surface micelles that had previously only been dreamed about. Importantly these surface micelles can be exchanging molecules with solution micelles during imaging. While the focus of this review has been on AFM imaging, the conclusions relating to many of the examples draw upon other complementary physical measurements leading to system understanding that is greater than microscopy alone could provide.

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The underlying theme of Erica's research is the understanding of solid-liquid interfacial structure on the nanoscale. This theme commenced at Otago where her pioneering work used AFM to reveal detail of the lateral structure of adsorbed surfactant layers on the molecular scale. At Newcastle she has applied these methods and others to the detailed investigation of the adsorption of water-soluble pH-responsive diblock copolymers. This research has been a very fruitful collaboration with Steven Armes at the University of Sheffield.

In 2009, Erica Wanless was elected a Fellow of the Royal Australian Chemical Institute for which she currently serves as the Vice-Chair of the Colloid and Surface Science Division.