

Preface

This book, like others in the *Advances in Atom and Single Molecule Machines* series, stems from a two-day workshop associated with the Atomic Scale and Single Molecule Logic Gate Technologies (AtMol) project funded by the European Commission's Future and Emerging Technologies programme. AtMol, a four-year project, was launched on 1 January 2011, involves eleven research teams, and has as its central objective the design and fabrication of the first ever encapsulated single-molecule chip.

Scanning probe microscopy is at the very heart of the AtMol project, enabling the imaging and manipulation of matter at the atomic, molecular, and sub-molecular scales. As such, the workshop from which the chapters in this volume arise was funded both by AtMol and the ACRITAS Initial Training Network (www.acritas.eu), a Marie Curie Training Project also funded by the European Commission and which is focussed on the development of new techniques and methods in atomic force microscopy.

The workshop in question, *Imaging and Manipulating of Adsorbates Using Dynamic Force Microscopy*, was held at the University of Nottingham during 16–17 April 2013. The contributions included in this volume represent a 'snapshot' of the state of the art in dynamic force microscopy (DFM, also called non-contact atomic force microscopy) at that time and cover a variety of fascinating topics including the accurate extraction of tip–sample forces from measured frequency shift curves; the imaging and manipulation of single atoms, molecules, clusters, and dangling bonds; the role of the Pauli exclusion principle in high-resolution DFM; and the combined mechanical and electrical properties of individual molecules.

At the time of writing, DFM is at an intriguing juncture in the evolution of the capabilities of the technique. There has been significant excitement about the possibility of imaging intramolecular, and, in particular, inter-molecular bonds, over the last 18 months or so. It has now become clear that the latter, i.e. the observation of contrast maxima *between* molecules in DFM images, has to be interpreted very carefully indeed. As with any scanning probe technique, the geometric and electronic structure of the apex of the tip (and its associated chemical functionality) is just as important in the imaging mechanism as the sample. This

convolution can be particularly severe in the so-called Pauli exclusion regime of imaging which was pioneered by IBM Zurich (Gross et al.) in 2009 (and which is increasingly becoming the norm for the acquisition of ultrahigh resolution DFM images).

As one of us (PM) and co-authors discuss in the chapter “[Pauli’s Principle in Probe Microscopy](#)” of this volume, the contribution of the dynamics and mechanics of the tip apex plays an exceptionally important role in generating image contrast. Seeing is not necessarily believing with any imaging technique, and this is especially true of scanning probe microscopy. On the other hand, there remains immense potential for the use of a range of different functional probes (including, but also moving beyond, CO, which is used extensively for intra molecular imaging at present) in DFM, enabling analysis of a variety of physicochemical phenomena. These include molecular magnetism, as also mentioned in the Foreword to this book. The exciting challenges and opportunities for ultrahigh resolution DFM will be discussed and debated in a workshop in Prague in February 2015 which has been organised by Pavel Jelinek, author of chapter “[Theoretical Challenges of Simultaneous Nc-AFM/STM Experiments](#)” of this volume (see below).

In the chapter “[Mechanical and Electrical Properties of Single Molecules](#)”, Thilo Glatzel provides a comprehensive overview of a number of the considerable advances of the Nanolino group at the University of Basel in imaging and characterising the mechanical and electrical properties of single molecules. For all of the reasons outlined by Christian Joachim in his Foreword, there are fundamental and technologically important motivations for the use of insulating, as opposed to metal or semiconductor, substrates as a ‘platform’ for molecular adsorption. Glatzel’s overview gives a good indication of the state of the art in the field and also highlights key differences between the properties of molecular adsorbates on metallic and insulating substrates.

Sugimoto and colleagues at Osaka University have been responsible for many of the key advances in atomic manipulation and single atom control using DFM. Prof. Sugimoto’s chapter reviews some of the work of the Osaka group (and their collaborators) in developing a number of fascinating and high-precision protocols for the controlled positioning of single atoms, with a particular focus on the lateral translation of silicon adatoms. Sugimoto discusses how the tip apex in a DFM manipulation experiment can be characterised through measurement of the short-range chemical force and, in particular, by using the maximum attractive force as a ‘metric’ or a diagnostic. In addition, however, he stresses how tip geometry—*asymmetry in particular*—plays a central role in determining the probability for manipulation events to occur.

In a second contribution from the Nottingham group,¹ Andrew Stannard and Adam Sweetman explore the difficulties and subtleties associated with extracting accurate quantitative force measurements from dynamic force microscopy measurements of frequency shift versus tip–sample separation. Although DFM is an

¹Disclaimer: one of the editors (PM) is a member of this group.

exceptionally powerful tool for the measurement of tip–sample force fields and potential energy landscapes, it is far from trivial to extract accurate and reliable quantitative force values from the primary experimental observable, i.e. the frequency shift (Δf). Subtraction of the contribution of the long-range van der Waals interaction, in which the short-range chemical force curve is ‘buried’, is a perennial, and particularly thorny, issue. Stannard and Sweetman describe protocols for the systematic treatment of $\Delta f(z)$ curves (where z represents the tip–sample separation) so as to minimise the uncertainties in converting the experimental data to a plot of $F_{\text{SR}}(z)$, i.e. the short-range force curve associated with the interaction of just the atom/molecule terminating the tip apex with the underlying sample surface atom(s).

The chapter “[Theoretical Challenges of Simultaneous Nc-AFM/STM Experiments](#)”, authored by Pavel Jelinek of the Academy of Sciences of the Czech Republic, is an authoritative and fascinating review of the current state of the art in theoretical descriptions of ‘hybrid’ scanning tunnelling microscopy (STM)—DFM measurements. Jelinek’s group has carried out pioneering and influential work on this topic, and he provides an accessible and readable introduction—perhaps written with experimentalists in mind—of the latest developments in the use of density functional theory, coupled with a Green’s function² approach, to simulate not only the geometric and chemical interactions occurring at the tip–sample junction, but to accurately predict the (far from equilibrium) tunnel current driven through the system by the application of a bias voltage. The question of just how the distance dependence of the tunnel current compares to that of the short-range chemical force has been a long-standing issue in scanning probe microscopy, and Jelinek discusses the key theoretical advances that have elucidated the underlying physics. He also highlights the fascinating, and ‘far beyond perturbative’, influence of the formation of a covalent bond on the tunnelling barrier experienced by electrons flowing from tip to sample (or vice versa).

The next chapter, written by Clemens Barth (CNRS, Aix-Marseille University), explores the use of DFM to manipulate objects rather larger than the single atom/molecule adsorbates discussed thus far: nanoscale clusters. As discussed in the Foreword, nanoscale clusters and nanoparticles have a key role to play in enabling the development of next-generation atomic circuitry, particularly with regard to interfacing single atom and sub-molecular functionality to the microscopic, and ultimately macroscopic, world. Barth describes the challenges underpinning controlled translation of clusters and discusses how his group has developed techniques to control the positioning and dynamics of Au nanoparticles on NaCl substrates. The importance of the wide electronic band gap of insulating surfaces and substrates was also stressed repeatedly by Joachim in the Foreword, and it is encouraging that Barth shows that not only is nanoparticle manipulation on wide bandgap substrates achievable, but that the presence of surface defects does not

²Given the venue for the workshop from which this volume stemmed, it would be remiss of me not to highlight that George Green, of Green’s function fame, did his mathematics while working as a miller in Nottingham in the nineteenth century.

preclude controlled positioning. Indeed, the chapter “[Manipulation of Metal Nanoparticles on Insulating Surfaces](#)” provides compelling evidence that defects are an integral part of the manipulation process, first stabilizing, and then acting in concert with the nanocluster as it is moved across the surface by the DFM tip.

In the chapter “[Imaging of Defects on Ge\(001\):H by Non-contact Atomic Force Microscopy](#)”, we remain with the theme of defect-mediated interactions but return to the imaging and quantitative analysis of semiconductor, rather than insulator, surfaces. Bartosz Such (Jagiellonian University, Kraków) focuses on a prototypical passivated, i.e. low free energy, semiconductor surface—hydrogen-terminated Ge (100)—and describes the significant differences between force curves acquired over passivated surface regions as compared to those measured above single dangling bond defects (i.e. regions of the surface where a Ge atom is not hydrogen ‘capped’). As has also been observed for the H:Si(100) surface, the chemically inert hydrogen-passivated regions are associated with a negligible attractive interaction with the DFM tip. As such, atomic resolution imaging is achieved within the range of the tip–sample interaction potential where the repulsive component of the total force plays a significant role (as discussed in the chapter “[Pauli’s Principle in Probe Microscopy](#)” in relation to the Pauli exclusion principle). Above a dangling bond defect, however, there is a much stronger attractive force due to the short-range tip–sample interaction arising from the formation of a chemical (presumably covalent) bond. Such discusses how the force of this single dangling bond can be measured.

We subsequently return to a discussion of insulating surfaces in the chapter “[Adsorption Structures of Amino Acids on Calcite\(104\)](#)” but here the focus is on calcite rather than the alkali halides exploited by Barth et al. for the nanocluster manipulation described in the chapter “[Manipulation of Metal Nanoparticles on Insulating Surfaces](#)”. As Felix Kling, Markus Kittelmann and Angelika Kühnle discuss, calcite is a fascinating and exceptionally important substrate in the context of the study of biomineralisation. They exploit the cleavage plane of calcite, i.e. calcite(104), as a platform and template for the self-assembly of five different amino acids. Although the larger molecules of those they studied, namely tryptophan, tyrosine, and aspartic acid, exhibit strikingly similar behaviour on the calcite surface with regard to the superstructures they adopt, the smaller amino acids (glycine and alanine) behave in a very different manner. A rather elegant aspect of Kling and co-worker’s study is that they unambiguously define molecular chirality from a careful analysis of the relationship of the alignment of adsorbed superstructure with the crystallographic directions of the underlying substrate.

The final chapter of this volume, by Antoine Hinaut and colleagues, continues with the topic of molecular adsorption on an insulating surface but has a specific focus on the electrostatic properties of the adsorbed molecules (which, like the amino acids studied by Kling et al., form highly ordered superstructures on the substrate). Hinaut et al. have carried out a combined DFM and Kelvin probe force microscopy (KPFM) study of a triphenylene derivative, 2,3,6,7,10,11-hexacyano-propyl-oxytriphenylene, on a KBr surface. A systematic, comparative, and detailed study of the KPFM data acquired above the bare KBr surface and on the molecular islands showed that the Kelvin probe signal, which provides a measure of the local

work function of the sample, could be interpreted in terms of the conformation-dependent polarisation of the molecular overlayer. Classical electrostatic calculations of the KPFM signal, based on a spherical tip apex, were found to provide good agreement with the experimental data. Given that there has been considerable discussion and debate regarding the origin and physicochemical underpinnings of KPFM measurements, Hinaut et al.'s work provides key insights into the extent to which intuition and models from classical physics can be used to interpret Kelvin probe data.

Taken together, the nine chapters in this volume capture the state of the art in dynamic force microscopy at an intriguing and exciting time in the evolution of the field. Five years on from the pioneering work of Leo Gross and colleagues at IBM Zurich, who showed that the 'architecture' of adsorbed molecules could be resolved in exquisite detail, there remain a variety of exciting questions to be addressed about the ultimate limits of DFM. Christian Joachim has touched on some of these open questions in his Foreword, and we echo his comments regarding the possibility of measuring local spin density and pushing the magnetic measurement capabilities of the instrument, as explored by Schwarz, Wiesendanger and colleagues at Hamburg, to wider, more challenging, horizons. The recent availability of commercial instruments capable of carrying out DFM in relatively high magnetic fields will of course provide an impetus for this direction of research.

Developments in instrumentation will clearly proceed apace—Franz Giessibl, whose farsighted introduction of the qPlus sensor (followed by the commercialisation of this technology by companies such as Omicron Nanotechnology (now part of Oxford Instruments) and Createc) has driven the wide adoption of DFM in labs across the world, continues to innovate with regard to both sensor design and the application of the qPlus technique to exciting scientific problems. As we write this in early 2015, DFM remains a very slow technique—the effective image generation bandwidth is sub-Hz rather than kHz or MHz. There thus remains particularly exciting scope for the development of DFM instruments capable of providing much greater temporal resolution, to complement the impressively high level of spatial resolution that is now possible with DFM.

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Philip Moriarty
Sebasti n Gauthier

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