Final Report on Leverhulme Trust Research Project Grant F/00 114/BI
Mapping molecular force fields and energy landscapes with picometre resolution

Philip Moriarty
*School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD**

Keywords: scanning probe microscopy; dynamic force microscopy; single molecule imaging; hydrogen bonding; force spectroscopy; submolecular resolution

I. THE GRANT: A BRIEF HISTORY

The research project funded by Grant F/00 114/BI ran from 01/02/2011 until 31/01/2014. The total budget was £145,790, of which the vast majority funded the salary costs of Dr. Adam Sweetman, the postdoctoral researcher who was responsible for the majority of the experimental work (and some of the theoretical calculations) associated with the project.

Project F/00 114/BI has been immensely important for Dr. Sweetman's career, enabling him to carry out, in collaboration with the co-workers listed below, a number of ground-breaking studies which have provided key insights into the extent to which dynamic force microscopy can indeed reliably map intra- and intermolecular force-fields (see Section V). The work funded by the grant led to a number of invited talks at prestigious institutions for Dr. Sweetman, played an important role in his securing two Japan Society for the Promotion of Science (JSPS) fellowships, and was a major factor in his award of a Leverhulme Trust Early Career Fellowship (which runs from 2014 - 2017). As has been discussed in the End-of-Year-1 and End-of-Year-2 reports for the project, the number of invited talks for Dr. Sweetman and the other investigators (see Section V below) led to a significant viring of funds from the consumables budget (which were covered by other grants held by the PI) to cover travel costs.

In addition to the funding of Dr. Sweetman directly from the project grant, a considerable number of other researchers, supported from a variety of sources, contributed to the success of the research programme. Unfortunately, one of the co-applicants on the original application submitted to the Trust, Prof. Natalio Krasnogor, left the University of Nottingham mid-way through the project. This led to some minor modification of the research activities (see Section III). Prof. Neil Champness, a co-applicant, provided samples and also made important contributions to the direction of the project, as did Prof. Peter Beton (another co-applicant). A significant proportion of the research was, however, carried out by Dr. Sweetman and Dr. Sam Jarvis, an EPSRC PhD+ fellow in the Nottingham Nanoscience group. Dr. Jarvis worked closely with Prof. Lev Kanotorovich (King's College London, and another co-applicant on the grant proposal) on density functional theory calculations which were essential in order to interpret the experimental data.

Dr. Sweetman also worked with Dr. Andrew Stannard (another Leverhulme Trust fellow) on the imaging and spectroscopy of surfaces and molecular assemblies. The density functional theory work was complemented by the Hückel molecular orbital (HMO) calculations carried out by Dr. Janette Dunn's group in Physics and Astronomy at Nottingham. A fourth postdoctoral researcher who made invaluable contributions to the project was Dr. Philipp Rahe (formerly at the University of Utah, and, since March 2014, a Marie Curie fellow at Nottingham). Dr. Rahe developed an atom-tracking facility[6] for the Omicron instrument used by the Nottingham group. This atom-tracking capability virtually eliminates thermal drift, allowing us to make measurements over the same molecule - indeed, the same bond - for periods of time of up to 40 hours.

A number of PhD students similarly made important contributions to the project: Ioannis Lekkas (funded from the ACRITAS Marie Curie Initial Training Network coordinated by the Principal Investigator, `www.acritas.eu`); Cristina Chiutu (supported by a combination of funds from the NANOCAGE Early Stage Training Marie Curie network (also coordinated by the PI) and an EPSRC Doctoral Training Account award)); and Andrew Lakin (funded by an EPSRC Doctoral Training Account grant), who played a particularly important role in the HMO calculations mentioned above.

II. OBJECTIVES

The original objectives of the proposal were exceptionally challenging and were as follows:

- Mapping forces and barriers via Qplus single molecule manipulation
- Molecule by molecule (de)construction of van der Waals assemblies.
- Measuring anisotropic force-fields for hydrogen-bonded templates.
- Charge density engineering: Substrate-mediated intermolecular interactions?

*URL: `www.nottingham.ac.uk/physics/research/nano`; Electronic address: philip.moriarty@nottingham.ac.uk

Although the core objective of the project, namely the mapping of force-fields for molecular assemblies (and single molecules), was achieved, the probe-induced molecular manipulation aspects proved to be difficult to implement for the reasons discussed in the following section. Moreover, although the issue of charge density engineering remains an open question, grant F/00 114/BI has allowed us to ascertain that cross-talk between the scanning tunnelling microscope (STM) and atomic force microscope (AFM) channels is a particularly pernicious problem on passivated semiconductor substrate such as the Ag:Si(111)-($\sqrt{3}$) surface extensively used in our work. This has an extremely important influence on our ability to monitor and probe charge density variations because STM is sensitive to an energy "window" of density of states whose width is determined by the tip-sample bias, whereas dynamic force microscopy is sensitive, in principle, to the total charge density.

III. RESEARCH ACTIVITY

The experimental technique at the core of our research activities is dynamic force microscopy. DFM measures the forces between atoms and molecules via shifts in the resonant frequency of a stiff quartz tuning fork sensor which has an atomically sharp tip attached at the end of a tine. As the sensor is scanned across the surface, the tuning fork frequency varies and this can be converted into an image which represents a map of constant force gradient (for small enough oscillation amplitudes). DFM can also be operated in the so-called spectroscopy mode where the tip is held at a point and the variation of the frequency shift as a function of probe-sample separation is recorded. This $\Delta f(z)$ curve can be mathematically inverted to a force-distance curve. (The video embedded in Section V below, *The Sound of Atoms Bonding*, gives a general, "popular science" introduction to the DFM technique).

The research programme comprised four distinct, but co-dependent, experimental and theoretical threads: (i) high resolution imaging of the "platform" used for molecular adsorption, the Ag:Si(111)-($\sqrt{3}$ x $\sqrt{3}$)R30°surface; (ii) characterisation and control of the tip state (a perennial issue in probe microscopy, see Fig. 1 for an example of the effectiveness of DFM for ascertaining the precise orientation of a C_{60} molecule at the apex of a DFM probe); (iii) development of methods to accurately measure intra- and intermolecular force fields; and (iv) mapping the force-field and potential energy landscape of a hydrogen bonded assembly.

Each of these aspects of the work were incorporated in the original proposal, but we skewed the description of work in the grant application rather too heavily, and much too optimistically, towards molecular manipulation. Although manipulation of single molecules played a central role in tip functionalisation during the work funded by grant F/00 114-BI (see Chiutu et al.[1], for example), vertical and lateral manipulation of hydrogen-bonded molecules (namely NTCDI) on the Ag:Si(111) and clean Si(111) surfaces proved to be difficult to reproduce in a systematic and "clean" fashion. We therefore focussed on using self-assembly to generate 2D molecular islands and overlayers and, as described in a recent paper[2], this proved to be a very successful strategy (see Fig. 2)[1].

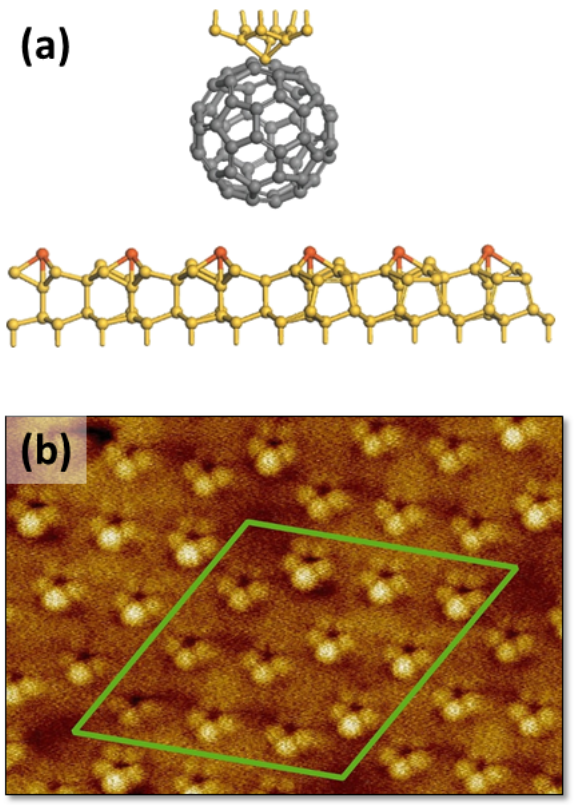

FIG. 1: Orienting a single molecule probe with atomic precision. (a) Schematic illustration of tip-sample geometry; (b) Constant frequency shift dynamic force microscope image of the adatoms of the Si(111)-(7x7) reconstruction using a C_{60}-terminated tip apex. Each adatom dangling bond acts as a "mini-tip" which maps out the atomic structure of the face of the fullerene cage which is closest to the Si(111) surface. (The green rhombus highlights the (7x7) unit cell). Ascertaining the precise geometric and chemical structure of the tip apex is exceptionally important in the interpretation of force-fields and potential energy landscapes derived from dynamic force microscopy measurements. Adapted from Chiutu et al.[1].

[1] In a parallel programme of research, not funded by F/00 114/BI and led by Dr. Jarvis, we are exploring the manipulation of large planar molecules (functionalised porphyrins) using DFM. This has led to two papers which will be submitted soon and which were the subject of Dr. Jarvis' prize acceptance lecture at the recent International Conference on the Structure of Surfaces (ICSOS-11) conference at the University of Warwick (July 21-25

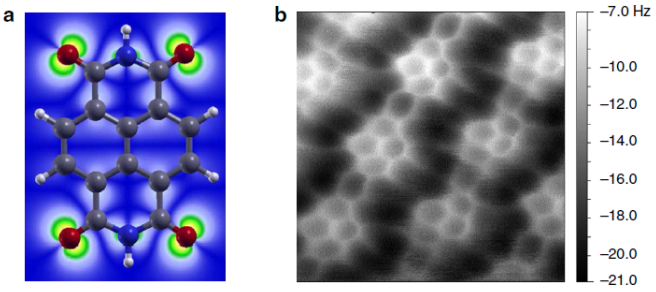

FIG. 2: Intra- and intermolecular contrast for a hydrogen-bonded molecular assembly. (a) Ball-and-stick model of naphthalene tetracarboxylic diimide (NTCDI) with a partial charge density isosurface superimposed (Colour coding: grey, carbon; white, hydrogen; red, oxygen; blue, nitrogen); (b) Constant height DFM image of a hydrogen-bonded NTCDI island on the Ag:Si(111)- ($\sqrt{3}$ x $\sqrt{3}$)R30°surface acquired at 77 K. Image size 2.1 nm by 2.0 nm. (Oscillation amplitude: 275 pm). From Sweetman et al.[2]

All of our experimental work was supported by detailed theoretical calculations which, in the case of density functional theory (DFT), involved substantial use of the University of Nottingham's High Performance Computing facility. The DFT calculations were complemented by Hückel molecular orbital theory restuls, which are much less computationally intensive and thus allowed for a rapid exploration and "screening" of the large parameter space associated with the orientation of a molecule at the apex of a scanning probe.

IV. CONCLUSIONS AND ACHIEVEMENTS

From the perspective of the scientists involved, F/00 114/BI has been a very successful project. Although we deviated to a certain extent from the original objectives of the grant (as discussed in the preceding section), a significant number of important results arose from what was a relatively small amount of investment. These include:

- Imaging the atomic structure of a single-molecule-terminated force microscope probe[1] and recovering the orientation of the probe molecule from convoluted orbitals[5];
- The first direct measurement of the pair potential for two C_{60} molecules[1];
- Mapping the force-field of a hydrogen-bonded molecular assembly[2];
- The demonstration that intramolecular structure can be attained in DFM on semiconducting (rather than metal) substrates and with an entirely new tip functionalisation strategy[3]
- Imaging and spectroscopy of covalent backbonds[4]

In addition to these and many other research achievements, the work funded by F/00 114/BI has, as described in the following section, played a major role in the award of two Japan Society for the Promotion of Science (JSPS) fellowships, a Leverhulme Trust Early Career Fellowship, and a Young Scientist award at a recent international conference. It has also substantially enhanced the international profile of the Nottingham Nanoscience group in the field of dynamic force microscopy.

V. PUBLICATIONS AND DISSEMINATION

The results of the work have been disseminated both through traditional channels such as journal publications[2], book chapters, and seminars/conference talks, and via social media. In addition, a number of the results have been used in undergraduate teaching.

Journal Papers

1. *Precise orientation of a single C_{60} molecule on the tip of a scanning probe microscope*, C. Chiutu, A. Sweetman, et al., Phys. Rev. Lett. **108**, 268302 (2012)
2. *Mapping the force field of a hydrogen-bonded assembly*, A. Sweetman, *et al.*, Nature Comms., **5**, 3931 (2014)
3. *Intramolecular bonds resolved on a semiconductor surface*, A. Sweetman *et al.*, submitted (2014)
4. *Unique determination of "subatomic" contrast by imaging covalent backbonding*, A. Sweetman, P. Rahe, and P. Moriarty, Nano Lett. **14**, 2265 (2014)
5. *Recovering molecular orientation from convoluted orbitals*, A. J. Lakin, C. Chiutu, A. M. Sweetman, P. Moriarty, and J. L. Dunn, Phys. Rev. B **88**, 035447 (2013)
6. *Uncertainties in forces extracted from non-contact atomic force microscopy measurements by fitting of long-range background forces*, A. Sweetman and A. Stannard, Beilstein J. Nanotechnol. **5**, 386 (2014)
7. *Simultaneous non-contact AFM and STM of Ag:Si(111)-($\sqrt{3}$ x $\sqrt{3}$)R30°*, A. Sweetman, *et al.*, Phys. Rev. B **87**, 075310 (2013)

2014). Dr. Jarvis was awarded the ICSOS Young Scientist prize.

[2] Adam Sweetman, the postdoc funded by F/00 114/BI, has also contributed to two other papers, not listed in Section V, during the course of the project. The results of these papers are not directly related to the theme of F/00 114/BI but we include them here for completeness.

1. *Critical assessment of the evidence for striped nanoparticles*, J. Stirling et al., submitted to PLOS ONE; also available at the condensed matter arXiv: `http://arxiv.org/abs/1312.6812v1` See also PubPeer pre-publication peer review: `https://pubpeer.com/publications/B02C5ED24DB280ABD0FCC59B872D04`

2. *Point-contact probe microscopy of nanoparticle supracrystals*, A. Sweetman *et al.*(to be submitted)

8. *Can dynamic force microscopy measure the orientational dependence of intermolecular dispersion forces?*, A. Sweetman et al., in preparation (2014)

Book chapters

1. *Atom-technology and Beyond: Manipulating Matter using Scanning Probes*, P.Moriarty, in "Nanoscience Volume 1: Nanostructures through Chemistry", edt. P OBrien, Royal Society of Chemistry (2012)
2. *Submolecular Resolution Imaging of C_{60}: From Orbital Density to Bond Order*, P. Moriarty, in "Imaging and Manipulating Molecular Orbitals", edt. C. Joachim and L. Grill, Springer (2013). `http://www.springer.com/physics/condensed+matter+physics/book/978-3-642-38808-8`
3. *Pauli's Principle in Probe Microscopy*, S. Jarvis, A. Sweetman, L. Kantorovich, E. McGlynn, and P. Moriarty, in "Imaging and Manipulation of Adsorbates using Dynamic Force Microscopy", edt. P. Moriarty and S. Gauthier. Springer-Verlag. To be published late 2014.

Invited Talks/Seminars

We list here only *invited* talks/seminars for which work funded by Grant F/00 114-BI was presented and discussed. In addition to the invited talks below, research funded by F/00 114-BI was presented in eight contributed conference talks during the course of the grant.

1. *Mapping the force-field of a hydrogen-bonded assembly*, P. Moriarty, "Atomic structure of nanosystems from first-principles simulations and microscopy experiments". Helsinki-Stockholm. June 3 - 5 2014.
2. *2*014 Gordon Research Conference on Crystal Engineering. Neil Champness. Keynote Lecture. (New Hampshire, 06/2014)
3. BCA Spring Meeting, *Crystallography@100: Learning from the past, looking to the future.* (Loughborough 04/2014). Neil Champness.
4. *Mapping the force-field of a hydrogen-bonded assembly*, P. Moriarty, APS March Meeting, Denver March 2014. `http://meetings.aps.org/Meeting/MAR14/Session/M38`
5. 247th ACS meeting, Inorganic Supramolecular Chemistry symposium (Dallas, 03/2014). Neil Champness. Keynote Lecture.
6. *Mapping intermolecular force-fields with sub-Angstrom reslution*, P. Moriarty. MANA International symposium, Tsukuba, Japan. March 2014.
7. McBain Medal Symposium, Colloid and Interface Science groups of the RSC and the SCI (Cambridge, 12/13). Neil Champness.
8. *Mechanical Atom Manipulation (and the Trouble with Tips)*, P. Moriarty. Keynote lecture. Trends in Nanotechnology, Seville, Sept. 9 13 2013
9. *Mechanical Atom Manipulation (and The Trouble with Tips)*, P. Moriarty. Plenary Lecture. Annual Conference - Institute of Physics in Singapore. Singapore. March 5 2013
10. *Measuring intermolecular forces using qPlus NC-AFM*, Adam Sweetman, OIST, Japan, Apr. 2012
11. *Measuring intermolecular forces using qPlus NC-AFM*, Adam Sweetman, NIMS, Tsukuba, Japan May 2012
12. *Mechanical Atom Manipulation (and The Trouble with Tips)*, P. Moriarty, Foresight Conference, San Francisco, January 2013
13. *NC-AFM Manipulation of Single Atoms and Molecules*, P. Moriarty, Les Houches Winter School, France, Jan 27 30 2013
14. *Mechanical Atom Manipulation (and The Trouble with Tips)*, P. Moriarty, RSC Symposium on Nanotechnology, University of Birmingham, 14 Dec. 2012
15. *Combining orbital imaging with atomic resolution for tip-adsorbed molecules*, P. Moriarty, Imaging and Manipulating Molecular Orbitals, Berlin Sept. 24 2012
16. *Mapping and Manipulating the Atomic World*, P. Moriarty Images and Visualisation - ESF Research Conference, Sept. 17 2012, Norrkoping, Sweden
17. *Atom manipulation and sub-molecular imaging using qPlus NC-AFM*, A. Sweetman, Osaka University, Japan. Nov. 2011
18. *Atom manipulation and sub-molecular imaging using qPlus NC-AFM*, A. Sweetman, Institute of Physics of Czech Academy, Prague, Czech Republic Oct. 2011
19. *Probing the limits of atomic scale control by NC-AFM*, A. Sweetman, 2011 Nano S and T conference, Dalian, China. Oct. 2011

YouTube

The School of Physics and Astronomy at the University of Nottingham collaborates with Brady Haran (`www.bradyharan.com`) on a successful YouTube channel called Sixty Symbols (`www.sixtysymbols.com`). One of the key motivations for the Sixty Symbols project, as described in a recent Physics World article[7] written by the PI, is to open up scientific research, including the trials and tribulations of the day-to-day work, to a wider audience. The Nottingham Nanoscience group has contributed to a number of Sixty Symbols videos which have focussed on research within the group. The most successful of these to date had as its focus the research theme at the heart of project F/00 114/BI – ultrahigh resolution imaging and force spectroscopy of hydrogen-bonded assemblies. The video in question, `https://www.youtube.com/watch?v=Ehw8PTA4QkE`, is embedded below and has at the time of writing (July 2014) accrued over 160,000 views.

The Sound of Atoms Bonding.

Undergraduate Teaching

The PI has a keen interest in incorporating new research results in undergraduate physics courses. He is one of three members of staff at Nottingham who delivers the first year undergraduate *Frontiers in Physics* module. A number of the results stemming from grant F/00 114/BI have been discussed in the *Frontiers* course material, including the direct measurement of an intermolecular pair potential described by Chiutu et al.[1], which was used in the 2012-2013 exam paper for the module. An ebook for the *Frontiers* module (which contains the links to results acquired in the course of F/00 114/BI) is available at `http://www.nottingham.ac.uk/~ppzpjm/Frontiers-Nano-Ver1-1-May2014.pdf`

VI. FUTURE RESEARCH PLANS

The research made possible by grant F/00 114/BI has played a central role in establishing the Nottingham Nanoscience group as a strong international presence in the dynamic force microscopy field. Nottingham also remains the only group in the UK which is active in the exciting, and highly competitive, area of qPlus dynamic force microscopy. Since the start of the Research Project grant in January 2011, the Nanoscience group has successfully applied for funding of an 11-partner (and 13 associate partner) Marie Curie Initial Training Network, ACRITAS, which involves many of the world-leading groups in atomic force microscopy (`www.acritas.eu`). In addition, Dr. Sweetman has recently been awarded a three year Early Career Fellowship by the Trust.

We are therefore extremely well-placed to build on the successes of F/00 114/BI. Two grant applications are currently being prepared for submission. The first of these, entitled "Molecular Linkage by Brute Force: Catalytic Mechanochemistry at the Single Bond Limit", will shortly be submitted to the Leverhulme Trust as an outline proposal. This application will extend recent experiments and theoretical work on the manipulation of functionalised porphryin molecules to incorporate a number of the experimental protocols developed in the course of F/00 114/BI in order to explore the possibility of carrying out chemomechanically driven catalysis with single bond precision via DFM. Careful mapping of molecular force-fields will play a particularly important role in this work.

A second proposal, based on atomic manipulation and again using chemomechanical force applied by the probe of a dynamic force microscope, will complement research currently carried out as part of the ACRITAS network on developing probe-based methods of constructing 3D structures, atom by atom, on silicon surfaces. The focus of the new research proposal will be to extend these methods to III-V semiconductors, where the contribution of the ionic character of the bond will make a significant difference to the interatomic forcefields which are sensed and exploited by the probe.

[1] *Precise orientation of a single C_{60} molecule on the tip of a scanning probe microscope*, C. Chiutu, A. Sweetman, AJ Lakin, A. Stannard, S. Jarvis et al., Phys. Rev. Lett. **108**, 268302 (2012)

[2] *Mapping the force field of a hydrogen-bonded assembly*, A. Sweetman, *et al.*, Nature Comms., **5**, 3931 (2014)

[3] *Intramolecular bonds resolved on a semiconductor surface*, A. Sweetman *et al.*, submitted (2014)

[4] *Unique determination of "subatomic" contrast by imaging covalent backbonding*, A. Sweetman, P. Rahe, and P. Moriarty, Nano Lett. **14**, 2265 (2014)

[5] *Recovering molecular orientation from convoluted orbitals*, A. J. Lakin, C. Chiutu, A. M. Sweetman, P. Moriarty, and J. L. Dunn, Phys. Rev. B **88**, 035447 (2013)

[6] *Flexible drift-compensation system for precise 3D force mapping in severe drift environments*, P. Rahe, J. Schtte, W. Schniederberend, M.Reichling, M. Abe, Y. Sugimoto, and A. Kühnle, Rev. Sci. Instrum. **82** 063704 (2011)

[7] *The Power of YouTube*, P. Moriarty, Physics World **27**(**3**) 31 (2014); `http://www.nottingham.ac.uk/~ppzstm/pdfs/Moriarty_youtube.pdf`