Institution: Loughborough University

Unit of Assessment: B10 Mathematical Sciences

Title of case study: Quantum and classical atomistic methods to enable improved processing and performance of materials

1. Summary of the impact (indicative maximum 100 words)

This study describes two atomistic methods that have been used to explain better the behaviour and improve performance of materials. The research at Loughborough University from 2006-2013 has led to improved awareness and understanding in the areas of thin film growth and in irradiated structural materials for nuclear power. It has also led to changes in the operational models that Atomic Weapons Establishment (AWE) use. One of the algorithms developed has been incorporated into standard quantum chemistry packages, due to its increased accuracy and efficiency. The outcomes of the research have also contributed to changing UK government policy with regards to working with India in the area of nuclear research.

2. Underpinning research (indicative maximum 500 words)

Multi-timescale algorithm

This computational method involves an extension of the molecular dynamics (MD) method to long timescales **[3.1, 3.2]**. A major problem with MD is the limited timescales that can be modelled. This is at most of the order of microseconds, because the numerical integration time step cannot exceed ~ 10^{-15}s. However, a typical deposition rate for thin film growth is 1 monolayer per second so even to model the growth of a few layers would be computationally excessive using MD alone. To extend the time scales, a new method has been devised in which the fast processes are calculated by MD and then the slower transitions are calculated adaptively using a parallelised saddle point finding algorithm. This method has been applied to the growth of thin films, giving guidance to industrialists as to the optimum conditions for growth **[3.1, 3.2]**. Extended time scale methods have also been applied to the modelling of radiation effects with applications to the nuclear industry **[3.3, 3.4]**. This work was carried out at Loughborough University from 2006-2013.

Bader Charge Algorithm

Bader charge analysis is a way of dividing molecules up into atoms when solving Schrödinger's equation. The methodology solves two outstanding problems relating classical and quantum descriptions of a solid.

The first application of the Bader method relates to the way in which charge is allocated to individual atoms in a quantum mechanical system. In the classical description of the electron the charge is well-defined, but in a quantum mechanical description of a solid what is calculated is a charge density. The way to allocate charge density to atoms was developed by Richard Bader [*Atoms in Molecules* OUP, 1994] but to do this in an accurate and numerically efficient way, processing the output of quantum chemistry packages, has in the past been highly inefficient and inaccurate. **3.5** and **3.6** describe the numerical method that not only does this accurately but also scales linearly with the number of interatomic surfaces in the system, so now it is feasible on a small computer. This improved method is currently used in conjunction with quantum chemistry packages such as VASP and GAUSSIAN. The outline algorithm was initially devised by Henkelman but corrected and improved at Loughborough University.

The second application of the Bader method allows potential energy in a quantum system to be allocated to an atom. In a quantum description of a solid, the concept of a potential energy per atom is not defined. The paper **[3.5]** uses the Bader charge allocation to define a potential energy per atom in a quantum system in a unique way, which can then be used accurately to parameterise classical potential functions, thus allowing computation of large systems of atoms beyond the scope of numerical quantum calculations.

This work was carried out at Loughborough University from 2006-2009.

Key Researchers:

Smith, R. (Lecturer and Professor of Mathematical Engineering: 1971 -), Kenny, S.D. (Senior Lecturer and Reader: 2000 -), Sanville, E. (PDRA: 2006-2009), Scott, C. (PDRA: 2011-2013).

Research Students:

Vernon, L. (PhD: 2006-10) Funded by EPSRC grant on modelling functional coatings.

Robinson, M. (PhD: 2006-10) Partially funded by the Atomic Weapons Establishment (AWE) on long time radiation effects in plutonium.

Scott, C. (PhD: 2008-11) Partially funded by Los Alamos National Laboratory.

Kittiratanawasin, L. (PhD: 2007-11) Partially funded by Los Alamos National Laboratory.

Bacorisen, D. (PhD: 2003-2007) Partially funded by Los Alamos National Laboratory.

Blackwell S. (PhD: 2009-2012) Partially funded by CREST (Renewable Energy Centre) at Loughborough

The work was also funded by the EPSRC Materials Modelling Grant EP/C524322/1 for a consortium of five universities, led by Loughborough. Project partners were Applied Multilayers and Pilkington.

3. References to the research (indicative maximum of six references)

Journal Publications

3.1. Blackwell, S., Kenny, S.D., Smith, R. and Walls J.M., (2012), Modeling evaporation, ion-beam assist, and magnetron sputtering of thin metal films over realistic time scales, *Physical Review B*, **86,** 035416, DOI: 10.1103/PhysRevB.86.035416

3.2. **Scott, C., Blackwell, S., Vernon, L., Kenny, S.D., Walls, J. M., and Smith, R., (2011), Atomistic surface erosion and thin film growth modelled over realistic time scales, *The Journal of Chemical Physics*, 135, 174706, DOI: 10.1063/1.3657436**

3.3. Robinson, M., Kenny, S.D., Smith, R. and Storr, M.T., (2012), Point defect formation and migration in Ga stabilised δ-Pu, *Journal of Nuclear Materials,* **423,** 16-21, DOI: 10.1016/j.jnucmat.2011.11.046

3.4. **Uberuaga, B.P., Bacorisen, D., Smith, R., Ball, R.J.A., Grimes, R.W., Voter, A.F. and Sickafus, K.E., (2007), Defect kinetics in spinels: Long-time simulations of $MgAl_2O_4$, $MgGa_2O_4$, and $MgIn_2O_4$, *Physical Review B*, 75, 104116, DOI: 10.1103/PhysRevB.75.104116**

3.5. **Sanville, E., Kenny, S.D., Smith, R., and Henkelman, G., (2007), Improved Grid-based algorithm for Bader charge allocation, *Journal of Computational Chemistry*, 28, 899-908, DOI: 10.1002/jcc.20575**

3.6. Tang, W., Sanville, E. and Henkelman, G., (2009), A grid-based Bader analysis algorithm without lattice bias, *Journal of Physics: Condensed Matter,* 21, 084204, DOI: 10.1088/0953-8984/21/8/084204

Grants

EP/C524322/1 A Multiscale Modelling Approach to Engineering Functional Coatings, 10/2005 – 09/2009, £413,532, R. Smith and S.D. Kenny.

EU project PERFORM60, 1/2010-9/2013 £50,000.

EP/I003150/1 Performance and Reliability of Metallic Materials for Nuclear Fission Power Generation, 12/2010-11/2014, £106,955, R. Smith and S.D. Kenny.

AWE Modelling Radiation Damage and He Bubble Formation in Plutonium and the Effect of H Solubility and Diffusivity, 1/2012-12/2012, £95,735.

AWE Modelling Radiation Damage and He Bubble Formation in Plutonium and the Effect of H Solubility and Diffusivity, 1/2013-6/2014, £147,456.

The quality of this work is evidenced by the fact that [3.5] has over 400 citations and that work using the methodologies in [3.1] was the subject of an invited publication due to a presentation at the Materials Research Society meeting. Work in this area has also received grants totalling over £800k.

4. Details of the impact (indicative maximum 750 words)

The underpinning research detailed in section 2 and as evidenced by the publications and funding detailed in section 3 has had impact in a number of areas. In the commentary below we detail the impact that this research has made in five different areas.

The research **[3.1, 3.2]** has changed awareness and understanding within Pilkington and Applied Multilayers (subsequently Power Vision) **[5.1]** of the optimized production conditions for depositing optical thin film coatings with the best crystallinity and in the development of new transparent conducting oxide materials. This has led to cost savings as it is difficult to vary growth conditions and assess film quality experimentally, but through computer simulation it is possible to predict the type of growth that will occur for many different choices of parameter values, and thus optimise the growth process. The research is further supported by funding from Asahi Glass.

The work has also been taken up by the nuclear industry following investigation of long time evolution of irradiated materials and dose effects in radiation damage studies **[3.3]**. The impact in the civil nuclear programme has been through an improved prediction of ageing effects in irrradiated structural materials used in nuclear reactors and the behaviour of nuclear fuels. This has also led to funding to optimise the safe disposal of nuclear waste.

The Bader charge algorithm developed within this research **[3.5]** has been incorporated into standard quantum chemistry packages such as VASP and GAUSSIAN **[5.2]**; these packages are used by thousands of research scientists internationally. The algorithm developed has completely replaced the techniques that were previously used for this analysis.

Prof. Smith was invited by EPSRC to attend two meetings (one in London and one in Oxford) with politicians and representatives of India's Department of Atomic Energy. These meetings resulted in a change of UK government policy towards nuclear collaboration with India with funding being made available for joint projects **[5.3]**.

The research has also changed the operational models that are used by AWE to understanding ageing in the nuclear weapons stockpile as evidenced by the supporting letter **[5.4]**. The measure of AWE's interest in this work is recognised through their continuing funding of research at Loughborough for the last 7 years.

5. Sources to corroborate the impact (indicative maximum of 10 references)

The following sources of corroboration can be made available at request:

5.1. Letter from Power Vision Ltd, Herald Park, Crewe, Cheshire, CW1 6EA

5.2. Software downloadable from VASP Tools: Bader Charge Analysis http://theory.cm.utexas.edu/vtsttools/bader/

5.3. Letter from Chief Scientific Advisor to the Foreign and Commonwealth Office

5.4. Letter from Modelling Team, AWE, Aldermaston UK