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Shedding Light on Solvated Surfaces and Interfaces

Durham Senior Fellowship Proposal

Submitted by:

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Summary

My application for a three-month fellowship is designed to foster interactions with three Durham University staff on topics related to the interaction of complex molecules with surfaces. Specific activities (and Durham staff) include: 1) improved computational methods for modelling mineral-fluid interactions (Dr. Chris Greenwell, host academic); 2) vibrational properties of adsorbed molecules (Dr. Colin Bain); and 3) the role of mineral surfaces on atmospheric methane levels (Dr. Richard Davies). Research activities are proposed at both the fundamental and applied levels and will benefit existing projects at Sandia National Laboratories and three Durham University institutes (Durham Energy Institute, Institute for Advanced Research Computing, and Biophysical Sciences Institute) as well as the Institute of Advanced Studies, to ensure a lasting relationship is established. Although this proposal is more closely aligned with a Senior Research Fellowship, the environmental policy implications suggest a possible fit with a Policy and Enterprise Fellowship.

Planned Activities

The interaction of complex molecules with solvated solid surfaces can now be described at the molecular level using both experimental and computational chemistry methods. Such studies are relevant to a wide range of scientific and technological fields, including catalysis, materials design, drug discovery, biomineralisation, the fate of contaminants in the environment, and the production and synthesis of fuels. This multidisciplinary approach to scientific inquiry is the focus of my existing research project, "Molecular Simulation and Spectroscopy of Dynamical Processes at Mineral-Aqueous Solution Interfaces," funded by the U.S. Department of Energy, Basic Energy Sciences. Additionally, the thermodynamic and spectroscopic behavior of biologically and geologically relevant molecules adsorbed onto surfaces closely aligns with the Durham Energy Institute and the Biophysical Sciences Institute. The purpose of my application for a Durham Senior Fellowship is to establish extended interactions with Durham University staff, leading to new and jointly beneficial collaborations in three key areas:

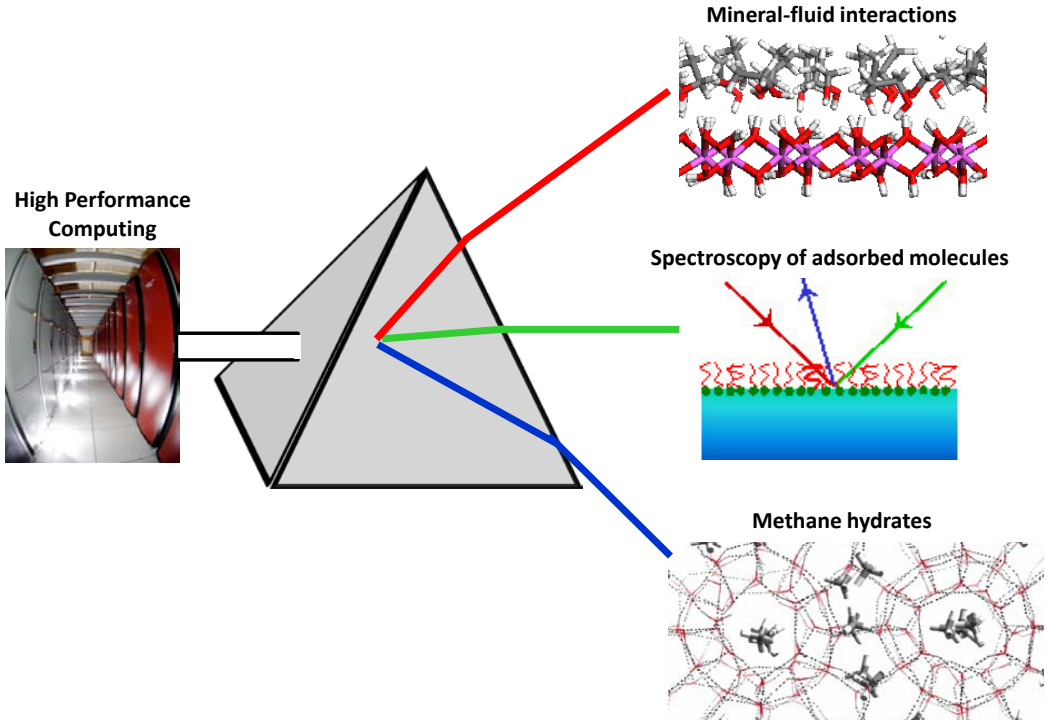
1. **Improved computational methods for modelling mineral-fluid interactions (Dr. Chris Greenwell).** Dr. Greenwell and I each use classical molecular simulations to study structural and dynamical properties of these complicated interfaces. The combination of atomic interaction potentials (force fields) specific to inorganic (mineral) and organic phases yields a qualitative description of these interfaces, but a unified force field based on electronic structure calculations of mixed inorganic-organic phases is needed to advance this field. Dr. Greenwell and I will design appropriate model systems and computational methods needed to create such a unified force field. These efforts will undoubtedly also involve interactions with Dr. Stewart Clark who, as a developer of the CASTEP DFT code, specialises in electronic structure calculations.
2. **Vibrational properties of adsorbed molecules (Dr. Colin Bain).** A key method to understand the mechanism of molecular adsorption involves changes in the vibrational properties of a molecule upon interacting with a surface. The evaluation of molecular vibration is possible using both computational and spectroscopic methods and forms the basis of this collaboration. I will apply computational methods that complement ongoing research in Dr. Bain's laboratory involving the spectroscopic investigation of surfactant adsorption on inorganic surfaces. This collaboration will extend my current interest in force field development to include the pH-dependent adsorption of molecules onto hydroxylated surfaces, also adding insight to a Leverhulme-funded project run by Dr. Greenwell on protein adsorption on layered minerals (working with a PDRA, Dr. Erastova).
3. **The role of mineral surfaces on atmospheric methane levels (Dr. Richard Davies).** Classical simulation methods have recently been used to understand the interface between ice-like gas hydrate phases and inorganic surfaces. An environmentally relevant application of these simulations involves methane hydrates, which form in offshore sediments and permafrost regions. Dr. Davies uses seismic imaging to better understand methane hydrates at geologic interfaces. Working from opposite ends of time and length scales, Dr. Davies and I will examine structural (sediment composition) and thermodynamic (temperature) properties that affect the geologic stability and seismic properties of methane hydrate deposits. This collaboration will also explore the relationship between atmospheric methane and climate change.

Benefits to Durham University

The Fellowship will enable Durham to develop its internationalization strategy through key links with a renowned U.S. Department of Energy laboratory. These collaborations particularly strengthen the Durham Energy Institute's network and adds credence to its reputation on the international stage. The proposed research fits well with the emergence of the new Institute for Advanced Research Computing and interaction with Dr. Nick Holliman is envisaged to discuss visualisation of large data sets produced. Lasting collaboration may involve, for example, exchange of researchers with visits by Durham academics to Sandia. These collaborations represent but one facet of Sandia's focus on energy research, but they can open the door for wider engagement. I will also seek to utilise, if in place, the computational capacity within the Northern 8 (N8) University grouping, presently being installed at Leeds University, that Durham is a key partner in, as well as to build on emerging linkage between Durham and the high performance computing capacity developing at the Science & Technology Facility Council laboratories in Daresbury.

The IAS theme in 2013 is light, and light lies close to the heart of this proposed research. Changes in the infrared absorption spectra of molecules are used to experimentally validate simulation results. An understanding of the narrow bands in emission spectra were at the heart of the discovery of quantum mechanics, which allows the development of classical force fields. Additionally, the ultra-fast transmission of light in lightpaths for grid computing and high performance computing interconnects allows very large-scale simulations to be carried out.

In the schematic below, the light theme is used to illustrate the cross cutting nature of high performance computing as an underpinning tool to enable connection between the proposed molecular simulation methods and the relevant Institutes and Centres.



Anticipated Outputs

The extended discussions and collaborations expected during the fellowship period will provide each of us wider perspective on our research projects, resulting in a renewed focus on existing research and the creation of new ideas. Results from activities during the fellowship period and beyond will be submitted for publication in scientific journals. Due to the multidisciplinary nature of the proposed research, articles will be submitted to journals outside of those common to our individual efforts, including those aimed at energy-related, environmental science, or materials audiences. Additionally, the development of new ideas will result in collaborative research involving Durham University and Sandia National Laboratories, funded jointly or as separate projects (e.g., U.S. Department of Energy, EPSRC, NERC, STFC Leverhulme Foundation). Joint proposals for access to grid computing facilities will be submitted through U.S. (XSEDE) or U.K. (NES) programmes. Plans for follow-on meetings are already underway, including Greenwell's visit to Sandia (2014 or 2015) and the Euroclay 2015 meeting in Edinburgh. Finally, several outreach efforts are planned to share ideas with the Durham community and beyond, including:

- A workshop on molecular studies of interfaces to be held at Durham University.
- Technical presentations and discussions with colleagues at European universities.
- Submission of a review or perspectives paper highlighting these multidisciplinary research ideas.

Research Facilities

No special facilities required beyond those that already exist at Durham University. Use will be made of the Hamilton high performance computing facility.

Curriculum Vita of Jeffery A. Greathouse

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Research Summary

Atomistic simulation with applications to geosciences and materials science. Characterization of complex multi-layered, nanoporous, natural and engineered materials, as well as the interfaces between these materials and interacting fluids.

Education

Ph.D. Physical Chemistry, University of California, Davis, 1996. (Dissertation: "Ion adsorption effects in electrical double layer calculations; Advisor: Donald McQuarrie)

B.S. Chemistry and Mathematics, Southwestern University, 1992. *magna cum laude*

Experience

2012 – present	Principal Member of Technical Staff, Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico
2004 – 2012	Senior Member of Technical Staff, Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico
1999 – 2004	Assistant Professor, Chemistry Department, St. Lawrence University, Canton, New York
1997 – 1999	Assistant Professor, University of the Incarnate Word, San Antonio, Texas
1996 – 1997	Visiting Assistant Professor, Allegheny College, Meadville, Pennsylvania
1996	Postdoctoral Associate, Univ. California Berkeley and Lawrence Berkeley National Laboratory, Berkeley, California (Advisor: Garrison Sposito)

Professional Activities

Session chair at scientific conferences: American Chemical Society, Clay Minerals Society, Goldschmidt Conference, International Clay Conference

Professional Society Leadership

Advisor, American Chemical Society, Central New Mexico Section, 2012 - present
Content Editor, Clay Minerals Society News in *Elements*, 2010 – present
Chair, Clay Minerals Society Program Development Committee, 2008 – 2010

Invited lectures

CECAM (Centre Européen de Calcul Atomique et Moléculaire), 2006
3rd European Workshop on Clay Geosciences, sponsored by Actinet, 2006
Clay Minerals Society short course, 2005
Numerous invited conference presentations and department seminars

Research supervision: 13 undergraduate students, 2 graduate students, 4 postdocs

Manuscript and proposal reviews (approximately 12 per year, 1999 – present)

Current Funding (U.S. Department of Energy)

1. Geochemistry of Interfaces: From Surfaces to Interlayers to Clusters. (co-PI)
2. Evaluation of Generic Engineered Barrier System Design Concepts and Process Models. (molecular modeling lead)
3. Novel Metal-organic Frameworks for Efficient Stationary Energy Sources via Oxyfuel Combustion. (molecular modeling lead)
4. Iodine Capture and Storage Studies. (molecular modeling lead)
5. Methane Hydrate Formation on Clay Mineral Surfaces: Thermodynamic Stability and Heterogeneous Nucleation Mechanisms. (team member)

Publications

39 journal articles (h-index 15)
3 book chapters
7 technical reports (Sandia National Laboratories)
2 conference proceedings

Key publications (geosciences, gas hydrates)

1. J.A. Greathouse, D.B. Hart, and M.E. Ochs. "Alcohol and Thiol Adsorption on (Oxy)hydroxide and Carbon Surfaces: Molecular Dynamics Simulation and Desorption Experiments", *Journal of Physical Chemistry C* **2013**, in press. http://dx.doi.org/10.1021/jp305275q
2. J.A. Greathouse and R.T. Cygan. "Molecular Simulations of Clay Minerals", in *Handbook of Clay Science*, F. Bergaya and B.K.G. Theng, Eds., Elsevier, **2012**, in press.
3. N.W. Ockwig, J.A. Greathouse, J.S. Durkin, R.T. Cygan, L.L. Daemen, and T.M. Nenoff, "Nanoconfined Water in Magnesium-Rich 2:1 Phyllosilicates", *Journal of the American Chemical Society* **2009**, *131*, 8155-8162.
4. R.T. Cygan, J.A. Greathouse, H. Heinz, A.G. Kalinichev, "Molecular Models and Simulations of Layered Materials", *Journal of Materials Chemistry* **2009**, *19*, 2470-2481. (**COVER ARTICLE**)
5. J.A. Greathouse, R.T. Cygan, R.A. Bradshaw, E.H. Majzoub, and B.A. Simmons, "Computational and Spectroscopic Studies of Dichlorofluroethane Hydrate Structure and Stability", *Journal of Physical Chemistry C* **2007**, *111 (45)*, 16787-16795.
6. J.P. Larentzos, J.A. Greathouse, and R.T. Cygan, "An ab Initio and Classical Molecular Dynamics Investigation of the Structural and Vibrational Properties of Talc and Pyrophyllite", *Journal of Physical Chemistry C* **2007**, *111*, 12752-12759.
7. J.A. Greathouse, R.T. Cygan, and B.A. Simmons, "Vibrational Spectra of Methane Clathrate Hydrates from Molecular Dynamics Simulation", *Journal of Physical Chemistry B* **2006**, *110*, 6428-6431.
8. J.A. Greathouse and R.T. Cygan, "Water Structure and Aqueous Uranyl (VI) Adsorption Equilibria onto External Surfaces of Beidellite, Montmorillonite, and Pyrophyllite: Results from Molecular Simulations", *Environmental Science & Technology* **2006**, *40 (12)*, 3865-3871.
9. J.A. Greathouse and G. Sposito, "Electrical Double Layer at Particles", in *Encyclopedia of Surface and Colloid Science*, A. T. Hubbard, Ed., Marcel Dekker, **2002**, 1642.
10. J.A. Greathouse, K. Refson and G. Sposito, "Molecular Dynamics Simulation of Water Mobility in Magnesium-Smectite Hydrates", *Journal of the American Chemical Society* **2000**, *122*, 11459.
11. G. Sposito, N.T. Skipper, R. Sutton, S.-H. Park, A.K. Soper and J. Greathouse, "Surface Geochemistry of the Clay Minerals", *Proceedings of the National Academy of Sciences USA* **1999**, *96*, 3358.

Key publications (materials science/metal-organic frameworks)

1. T.R. Zeitler, M.D. Allendorf, J.A. Greathouse. "Grand Canonical Monte Carlo Simulation of Low-pressure Methane Adsorption in Nanoporous Framework Materials for Sensing Applications", *Journal of Physical Chemistry C* **2012**, *116*, 3492-3502.
2. S.T. Meek, J.A. Greathouse, and M.D. Allendorf, "Metal-Organic Frameworks: A Rapidly Growing Class of Versatile Nanoporous Materials", *Advanced Materials* **2011**, *23*, 249-267. (**COVER ARTICLE**)
3. D.F. Sava, M.A. Rodriguez, K.W. Chapman, P.J. Chupas, J.A. Greathouse, P.S. Crozier, and T.M. Nenoff, "Capture of Volatile Iodine, a Gaseous Fission Product, by Zeolitic Imidazolate Framework-8", *Journal of the American Chemical Society* **2011**, *133*, 12398-12401.
4. J.A. Greathouse, N.W. Ockwig, L.J. Criscenti, T.R. Guilinger, P. Pohl, and M.D. Allendorf, "Computational Screening of Metal-Organic Frameworks for Large-Molecule Chemical Sensing", *Physical Chemistry Chemical Physics* **2010**, *12*, 12621-12629.
5. R.K. Bhakta, J.L. Herberg, B. Jacobs, A. Highley, R. Behrens, N.W. Ockwig, J.A. Greathouse, and M.D. Allendorf, "Metal-Organic Frameworks as Templates for Nanoscale $NaAlH_4$", *Journal of the American Chemical Society* **2009**, *131(37)*, 13198-13199.
6. J.A. Greathouse and M.D. Allendorf, "Force Field Validation for Molecular Dynamics Simulations of IRMOF-1 and Other Isoreticular Zinc Carboxylate Coordination Polymers", *Journal of Physical Chemistry C* **2008**, *112*(*15*), 5795-5802.
7. J.A. Greathouse and M.D. Allendorf, "The Interaction of Water with MOF-5 Simulated by Molecular Dynamics", *Journal of the American Chemical Society* **2006**, *128*, 10678-10679.