Application for a TSM-DTC funded PhD studentship

Please complete this form electronically
and submit to Lilian Wanjohi (l.wanjohi@imperial.ac.uk)
by Friday January 8, 2010

1st supervisor
Name: Prof. M. W. Finnis
CID (IC only): 461974
Institution, Department, Address: Department of Materials and Department of Physics, Imperial College London, Exhibition Road, London SW7 2AZ
Email: m.finnis@imperial.ac.uk
Phone: +44 (0) 207 59 46812

2nd supervisor
Name: Prof. G. Jackson
CID (IC only): 170163
Institution, Department, Address: Department of Chemical Engineering, Imperial College London, Exhibition Road, London SW7 2AZ
Email: g.jackson@imperial.ac.uk
Phone: +44 (0) 207 59 45640

3rd supervisor (optional)
Name: Dr. Amparo Galindo
CID (IC only):
Institution, Department, Address: Department of Chemical Engineering, Imperial College London, Exhibition Road, London SW7 2AZ
Email: a.galindo@imperial.ac.uk
Phone: +44 (0) 207 59 45606

Please complete the following:

1. Project title: The thermodynamics of charged defects in ionic crystals

2. Project abstract (≤ 200 words please and please add 1 or 2 key references)

An underlying statistical mechanical problem in the defect chemistry of ionic crystals relevant to a wide range of materials science topics is addressed. The interpretation of impedance spectroscopy, the ionic conductivity of cathode materials in solid-oxide fuel cells, the electrical conductivity of oxides, all depend on the concentration of charged point defects. One can now calculate the formation energy of charged point defects *in the dilute limit* with electronic structure codes such as CASTEP and VASP, eg Hine et al[1]. However, in materials of interest such as titania, yttrium stabilized zirconia, or perovskites like strontium titanate, it is standard for experimentalists and theorists to use such single defect energies within an *ideal (dilute) solution* treatment to calculate defect concentrations, even when these exceed 1%. Yet it is well known in the fluids community that such *regular* solution models are inadequate for concentrations >0.1%! As a step forward we combine some tools

of ionic liquid theory, including classical density functional theory (DFT) and the Widom insertion method, with lattice Monte Carlo simulations of point charges in a dielectric medium. We aim to construct a classical free-energy functional that will also describe inhomogeneous charge distributions, to treat screening of charged grain boundaries.

3. What is the multi-scale nature of the project? (≤ 100 words please)
The energy of isolated charged defects, whether at boundaries or in bulk crystals, is a matter for electronic structure calculations. However, space charges that screen charged interfaces may extend over many tens of nanometers, and must be temperature dependent. By analogy to electronic structure theory, to predict an inhomogeneous distribution of charged defects we require the correlation (free) energy, which could then be used in a local density approximation. To evaluate this part of the free energy we must apply the tools of statistical mechanics. The student would develop insights at both atomic structure and statistical thermodynamic levels.

4. How do the expertises of the supervisors complement each other? (≤ 100 words please)

The nature of the project is to combine the ideas of liquid state theory in the treatment of materials. Finnis has experience of point defects and interfaces, and has supervised student projects on very simple classical DFT and solving the Poisson-Boltzmann equation.
Jackson has expertise of statistical mechanical approaches and variational techniques.
Galindo is an expert in statistical thermodynamics of electrolyte solutions.
The involvement of Dr. Andrew Haslam (a senior Research Fellow), who has experience both in the statistical thermodynamics of fluids and in the simulation of the dynamics of defects in metals, will be invaluable.

5. Is there a self-contained 12-week MSc project that would usefully initiate this PhD project? (If the answer is no the project will not be offered as an MSc project)
Yes (the calculation of the free energy of a single charged species on a lattice with compensating uniform background).

1. Hine, N. D. M.; Frensch, K.; Foulkes, W. M. C.; Finnis, M. W., Supercell size scaling of density functional theory formation energies of charged defects. *Physical Review B* **2009,** *79*, 024112 -1-13.