eMinerals: Science Outcomes enabled by new Grid Tools

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Abstract

In the eMinerals project we use computational modelling to research mineralogical processes at an atomistic level, providing information on transport and immobilisation processes of pollutants, including radioactive waste. Prior to the eMinerals project most calculations where undertaken on so-called model systems. With the new grid tools, available within the eMinerals project, we are instead approaching calculations on realistic systems. Initial science results; a few computational developments; and grid tools employed in the eMinerals project are presented in the paper.

1. Introduction

The aim of the eMinerals project (one of NERC's eScience testbed projects) is to use computational modelling to determine mineralogical processes at an atomic level. Such information is difficult to study experimentally, but provides key information for our understanding of the transport and immobilisation processes of contaminants, including both toxic elements such as As, Cd and Pb, and organic molecules *e.g.* persistent organic pollutants (POPs).

After running for nearly 3 years the eMinerals project is doing well in its way of combining computer and grid scientists with environmental scientists, chemists and physicists to model and handle realistic and complex environmental processes, which have not previously been possible to study. The groups are situated at Bath, Birkbeck, Cambridge, Daresbury, University College London (UCL), Reading and Royal Institution (RI). Here, we summarise how the new grid tools allow the scientists in the eMinerals project to achieve new scientific goals.

2. Grid Tools

2.1 Computer resources

The grid tools used in the eMinerals project are all described in more details in other papers (see for example *refs.* 1 and 2). Here we only give a brief summary.

Within the eMinerals project we have built the *eMinerals minigrid* consisting of: 3 Linux-based clusters situated at Bath, Cambridge and UCL. Each cluster has 16 nodes with 2GB of memory. The clusters are accessed via the Globus-tools in the same manner as the National Grid resources (NGS); 1 Linux-cluster at Cambridge with 8GB per node particularly designed for running demanding quantum-mechanical codes, which require large memory; and at Reading we have a 24-node IBM parallel machine.

We set up and maintain 3 *Condor-pools*: UCL (over 900 machines), Cambridge and Bath. The Condor-pools are especially suited for inter-atomic potential calculations.

In addition, we make use of the national facilities *e.g.* NGS, CSAR and HPCx when these machines are more favourable than the local resources. In using these resources

we link back to the data management capabilities of the *eMinerals* minigrid.

2.2 Data management

To simplify data management we use the *storage resource brokers* (SRB) at Bath, Cambridge (2), UCL, Reading and the central MCAT server at Daresbury. Effort has been put into developing some tools for Chemical Markup Language (*CML*) [3], which is a version of XML adapted to chemical applications. CML works as an important interface between different programs, and as an analysing tool of the results. For communication the *Personal Interface to the Access Grid* (PIG) is essential.

3 Science outcomes

3.1 Surfaces and Interfaces

To fully understand transport and immobilisation processes of contaminants we need an accurate description of the mineral/solvent interfaces. Classically the interfacial structure is described as an electrical double layer, where the mineral surface characterised by a positively or negatively charged layer attracts anions or cations, depending on the charge of the mineral surface, so that an oppositely charged layer is created in the solution [4]. However, the exact structure of aqueous solutions at the interface is not well understood because the distribution and local concentration of the various species is difficult to observe experimentally. Also computational studies of the mineral/solvent interface are limited by the fact that realistic ionic concentrations require the treatment of many water molecules (a factor of 50 at 1 mol/l). Developments in computer resources, such as in the eMinerals project, have rendered possible the simulation of a quantity of ions sufficient to produce statistically meaningful results.

Goethite/aqueous solution interface
Within the eMinerals projects we modelled the goethite (FeOOH)/water interface in the

presence of different concentrations of cations. The computational developments achieved within the project have allowed us to use many Molecular Dynamics (MD) simulations (classical potential) of aqueous solution/goethite interfaces at different ionic strength and surface charges. We have observed that the classical models of the electrical double layer do not accurately describe the distribution of ions near the surface and that such ionic distribution is present even when the surface is uncharged (see *Fig 1*). In fact they are correct in assuming that the ion distribution is controlled by the electrostatic potential but fail to reproduce the distribution at high salt concentration because the electrostatic contribution of the solvent is not taken into account (again reinforced by the fact that the effect of surface charges are limited).

We have shown that the explicit treatment of solvent molecules is crucial to capture all the effects of the mineral surface on the liquid phase and demonstrated that high-throughput atomistic simulations can be used to reconsider and extend phenomenological models in order to depict a more comprehensive picture of the solid-liquid interface.

Graphite
As a first effort to model organic interfaces we have explored the potential energy map for platinum atoms adsorbed on a graphite substrate within a highly accurate Density
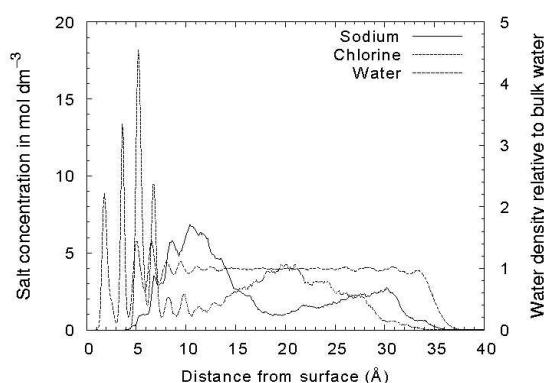

Fig. 1 The variation of salt concentration as a function of distance from the goethite surface in comparison to the water density.
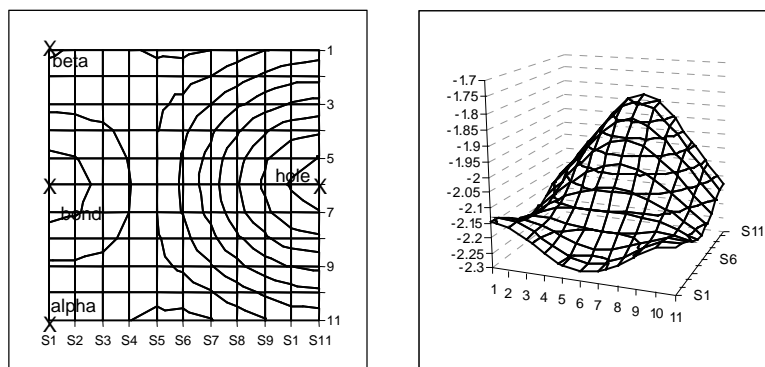
Fig. 2 Potential energy map of platinum on graphite; top view with sites indicated; the lowest contour line (next to the bond site) is at -2.25 eV, the energy difference between two lines is 0.05 eV.

Functional Theory (DFT) formalism. The graphite/metal interface is also researched for its application in polymer-electrolyte membrane fuel cells [5], representing an alternative (and renewable) energy resource to fossil fuels well known to produce greenhouse gases *e.g.* CO_2. With its ability to track phenomenon at the atomic scale, simulations can help, even if due to the size of the system, less reliable but efficient empirical potential (as opposed to first principles) models must be used. While the models describing the interaction within the adsorbates or the graphite substrate are as sophisticated and carefully investigated, the adsorbate/graphite interactions are still very ad-hoc and based on untested assumptions.

One aim of this research project is to derive high quality empirical potentials. Indeed it is costly to derive a good empirical potential, but Grid computing offers a solution, by enabling calculations of hundreds or more DFT simulations (in this case undertaken on the computer resources provided by the NGS) to explore the points in the phase space required to fit a transferable semi-empirical potential.

As a proof of concept we started by exploring the potential energy map for platinum atoms adsorbed on the graphite substrate (see **Fig. 2**). The preferred adsorption sites are located midway above the bond between two carbon atoms with an activation barrier of ca. 0.5 eV. We also find that the interaction between a platinum atom and the graphite surface is much more energetic, has a stronger corrugation and a

very different adsorption sites geometry than the empirically devised form used in most current molecular dynamics cluster simulations. We have also tested different realistic alternatives to these simplistic forms, starting from a Steele (2D fourrier) expansion of the DFT PES to a new Bond-Order parameterisation.

Perovskite

In all mineral processes we are dealing with impurities, which change not only the crystal structures, but also modify the
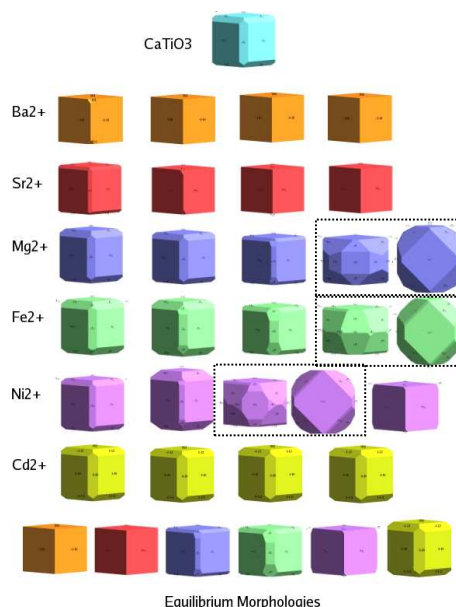

Fig. 3 Calculated crystal morphologies of $CaTiO_3$ as a function of dopant type and concentration; both uniform concentration of dopants on each surface, and equilibrium conditions are presented. Morphologies grouped with dashed squares correspond to the same dopant concentration, viewed along perpendicular directions.

surface structures and reactivity. With the Condor-pools we have excellent tools to study such compositional effects. To understand how the crystal shapes are modified in the presence of impurities we have defined an alternative method to obtain surface energies as a function of their segregation energy, and employed this technique to the mineral perovskite ($CaTiO_3$), which is present in silica poor rocks such as feldspathoids. However, $CaTiO_3$ also represents the perovskite group of minerals (ABO_3), where we find for example $CdTiO_3$. Many calculations on different impurities, including alkali ions (Mg^{2+}, Sr^{2+} and Ba^{2+}) and transition metals ions (Ni^{2+}, Fe^{2+} and Cd^{2+}) as well as various concentrations of guest ions in the mineral perovskite ($CaTiO_3$) have been performed, suggesting that the dopants modify the reactivity not only because of the presence of impurities but also due to changes in the crystal shapes.

3.2 Crystal structures and Phase transitions
Mineralogical properties are highly determined by the crystalline structure of the mineral, which can change in different re-crystallisation or precipitation processes. Such phase transitions can be triggered by compositional variations, or changes in temperatures and pressures.

Layered silicates
Layered silicates, *i.e.* phyllosilicates, include the group of clay minerals known to readily adsorb and store heavy metals. Here we studied layered alkali silicates $M_2Si_2O_5$ known to change their physical properties nonlinearly depending on the chemical composition. We have for the first time
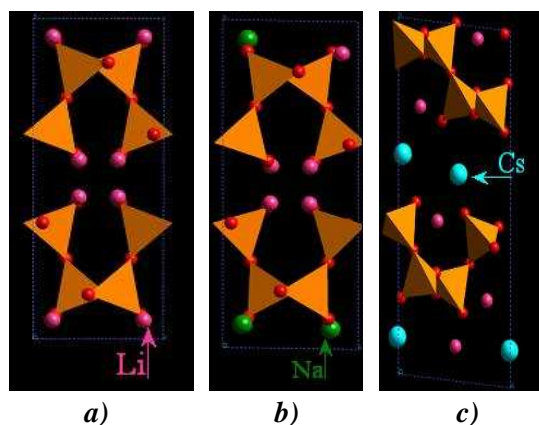

a)   *b)*   *c)*

Fig. 4 Lithium silicates: the pure structure, showing views of (a) the *a-b* plane of the framework; (b) 37.5% Na^+; and (c) 37.5% Cs^+ (Li = pink, Na = green ball, Cs = blue ball, O = red ball, SiO_4 shown as tetrahedral, and alkali ions have been omitted for clarity).

undertaken a comprehensive study on a wide range of solid solutions of these layered silicates, containing up to three alkali components. All mono-valent cations chosen for this work are naturally present in the environment.

Initially, we have investigated how the crystal structure of $Li_2Si_2O_5$ changes when Li are replaced by different mono-valent cations (Na, K, Rb and Cs). The structure of lithium phyllosilicate is built up of a framework of six-membered rings of silica tetrahedra in the *a-c* plane, featuring a symmetric "chair" structure in the *a-b* plane (shown in *Fig 4a*). Our study has revealed that the replacement of sodium for lithium ions does not alter significantly the original features of the lithium compound structure, such as the symmetric 'chair' conformation of the silicate chains (*Fig 4b*). However, for the bigger guest cations, the substitution

Table 1 Exchange reactions of sodium cations in aqueous environment with host potassium cations in solid solutions as well as associated enthalpies.

Process	Enthalpy (kJ/mol)
$K_4Li_4Si_8O_{20} \rightarrow M_4Li_4Si_8O_{20}$	
(1) $K_4Li_4Si_8O_{20} + Na^+(aq) \rightarrow K_3NaLi_4Si_8O_{20} + K^+(aq)$	-30.9
(2) $K_3NaLi_4Si_8O_{20} + Na^+(aq) \rightarrow K_2Na_2Li_4Si_8O_{20} + K^+(aq)$	-26.2
(3) $K_2Na_2Li_4Si_8O_{20} + Na^+(aq) \rightarrow KNa_3Li_4Si_8O_{20} + K^+(aq)$	-37.9
(4) $KNa_3Li_4Si_8O_{20} + Na^+(aq) \rightarrow Na_4Li_4Si_8O_{20} + K^+(aq)$	-40.9

does cause distortion of the structure where the extent of the distortion varies with the size of the guest cations (*e.g.* **Fig. 4c** for Cs impurities). The calculated solid solution energies indicates that the replacement of the first lithium ion by a guest ion is energetically unfavourable for all guest cations, but once the lattice has accommodated the first guest ion, further incorporation is facilitated.

In the ternary alkali solid solutions based on the $KLiSi_2O_5$ structure our calculations show that the original structure is always retained, with six-membered rings of silica tetrahedral linked by the alkali ions to form continuous pseudo-channels throughout the structure. The ternary cation mixtures formed from replacing potassium ions by guest ions in the potassium-lithium compound are energetically much more stable than those obtained from the substitution of lithium. In fact, the replacement of lithium ions by bigger alkali ions leads to buckling of the silica sheets, where the extent of buckling is dependent on the size of the cation. On the other hand, there is no clear trend in the buckling of the SiO_4 sheets with increasing size of the cations for mixtures with varying compositions.

Although solid solutions of all guest ions in silicates are often thermodynamically feasible, cation exchange from solution is generally an endothermic process and only K-Na exchange can be expected to occur to a significant degree (see **Table 1** for the exchange energies of these reactions).

To eliminate unnecessary duplication of calculations, a program based on symmetry arguments is employed to identify equivalent configurations. Even so, a large number of calculations needed to sample the complete set of non-equivalent configurations for a wide range of solid solutions. This has been possible making use of the eMinerals minigrid, Condor-clusters and the SRB.

Pyrite

Iron-bearing sulphide minerals play an important role in the control of acid mine drainage and transport of heavy metals like arsenic. In the specific case of FeS_2 pyrite, which is the most abundant mineral of all metal sulphides, the control of the As transport is twofold: first the As mobility is largely governed by the adsorption on pyrite surfaces and second, the As level in solution depends on pyrite dissolution since large As concentrations occur in this phase (up to ca. 10.0 wt.%, [6]). It is therefore important to understand the incorporation mechanisms and bonding properties of As in the pyrite bulk structure.

As a preliminary study we investigated the electronic structure and bonding properties of the pure FeS_2 pyrite by calculating its vibrational properties. This work represents the first detailed investigation of the phonon frequencies and their pressure dependence in pyrite by plane wave DFT calculations. The structural and electronic properties were obtained using the computational facilities provided by the eMinerals minigrid, while the phonon properties were computed within the linear response theory on the HPCx. Results show a good agreement with the experimentally determined pressure-dependence of the Raman frequencies [7] and we predict the evolution with pressure of the infrared-active modes for which no high-pressure spectroscopic data have been reported so far. Over the wide pressure range investigated here (0-150 GPa), all vibrational frequencies depend nonlinearly on pressure; their pressure dependence has been explained with respect to the atomic vibrations and quantified by determining the mode Grüneisen parameters. The phonon spectra can also be used to predict phase transitions in the mineral. This study has been facilitated by the use of the SRB for transferring and storing the generated files.

Oxides

Traditional DFT techniques often fail in reproducing Iron-bearing minerals, for which we seek alternative methods. For this purpose we have successfully employed so called hybrid-functional DFT and quantum Monte-Carlo (QMC) calculations to scan the phase space of the minerals wüstite (FeO) and periclase (MgO). Such an

investigation with the hybrid-functionals requires many independent calculations that are ideal to perform on the Condor-pools. With the SRB tool we can easily store and access the data for later analysis. For the QMC calculations we instead require many parallel processors with large memory available at the HPCx, where we used up to 1024 processors. For the first time we have successfully determined bulk properties and phase transitions in oxides with the QMC technique.

3.3 Radioactive waste

One of the main problems of environmental relevance studied in the eMinerals project is nuclear waste disposal, and in particular its possible encapsulation in ceramic materials devised for the purpose. The ultimate goal of this project is identification of the best waste forms to be used to immobilize surplus Pu and high-radiation waste (hrw). An important element of the proposed research is fundamental understanding of what defines resistance to amorphisation by radiation damage, which will enable a targeted search for resistant waste forms.

In the UK, the current pressing problem is the handling of surplus Pu, primarily from reprocessed fuel, with projected amounts of several tens of tons. In the current stock, some Pu decayed into Am, a
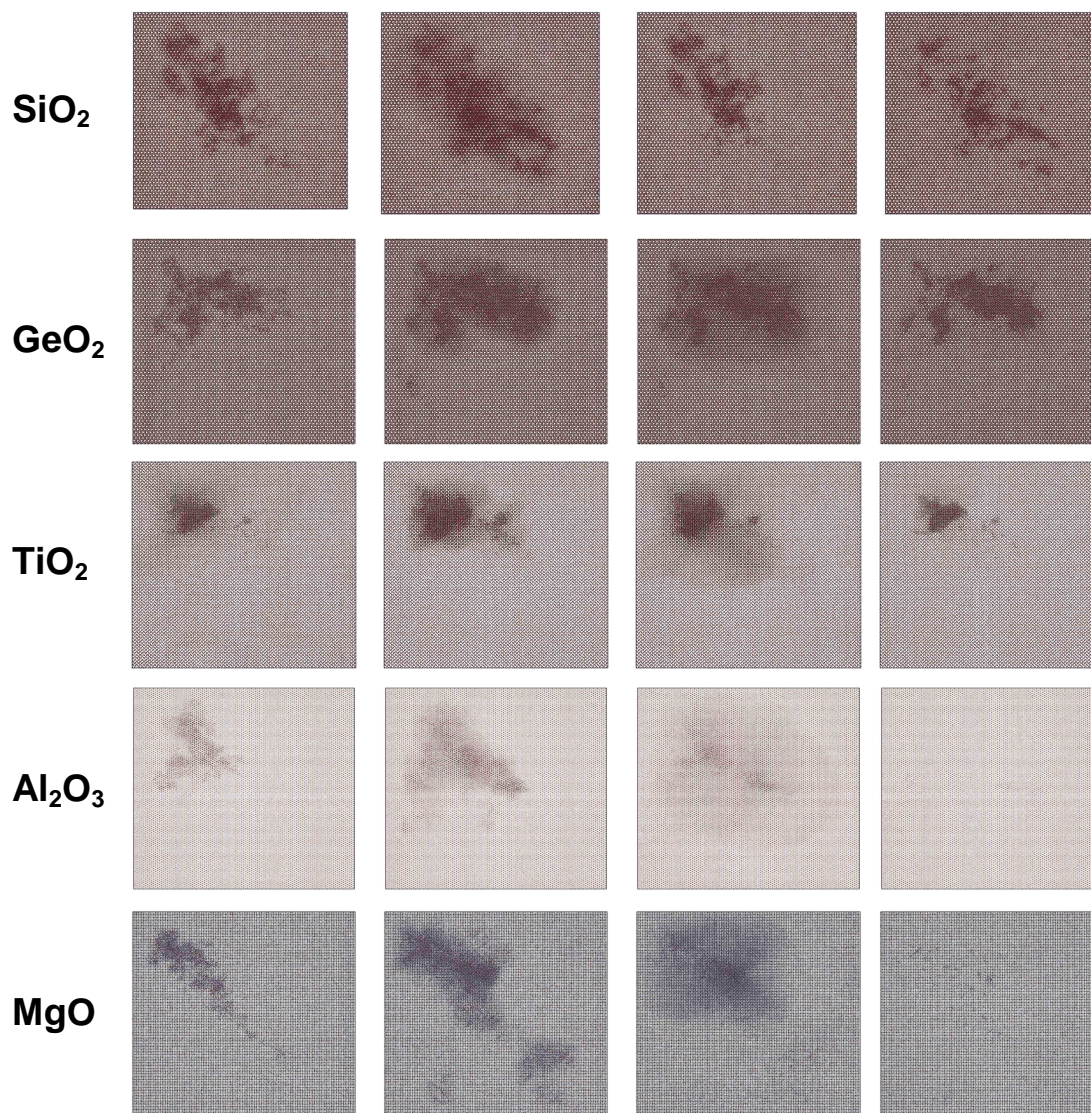

Fig. 5 Snapshots of MD-generated damaged structures, caused by 40 keV U recoil in different binary oxides. Recoil moves from upper left to lower right part of the figure. Progressive damage healing is seen in materials from left to right.

neutron poison, which makes it unusable in reactors as mixed oxide fuel and is now recognised as waste (the remaining surplus Pu can be reprocessed into a mixed fuel oxide to be burned in nuclear reactors, but the high cost of this process and the risk of Pu proliferation are often put forward as reasons against reprocessing and in favour of encapsulation). According to the recent report by a stakeholder dialogue group and representatives of Nuclear Sciences and Technology Services, some of the current Pu stocks will be immobilised, as determined by the Nuclear Decommissioning Authority. The report states that "ceramics, rather than glass, waste forms, are the preferred route for Pu immobilisation" [8] because they offer much better durability and stability over long time periods than the borosilicate glasses.

However, most of the currently considered waste forms are inevitably damaged (amorphised) by irradiation from hrw, with most structural damage coming from recoils in alpha-decay, each producing several thousands of atomic displacements. A damaged ceramic waste form may show the increase of diffusion, which, if too high, may result in the "loss" of radioactive materials into the environment. Experimentally, the increased diffusion is still considerably lower than in glasses, however its effect needs to be accounted for in projecting a stability of a waste form over very long times, because actinides are long-lived isotopes. At the same time, a small number of waste forms have been found that are very "resistant" to amorphisation by radiation damage and do not show any loss of crystallinity even at high radiation doses. These materials would be free from the negative effect of diffusion increase, however some of them do not chemically "accept" certain radioactive isotopes. Hence there is a need for optimisation, with the essential condition that a waste form should remain a safe immobilisation barrier over the time period of the order of 1 million years.

The ultimate goal of this project is identification of the best waste forms to be used to immobilise surplus Pu and hrw. An important element of the proposed research is fundamental understanding of what defines resistance to amorphisation by radiation damage, which will enable a targeted search for resistant waste forms. The origin of resistance to amorphisation by radiation damage is not understood at present and is of general scientific interest.

With the support of the eMinerals project, we have recently developed the DL_POLY3 MD program to simulate high-energy radiation damage events in very large systems: over 5 million atoms, and we used 512 HPCx processors to perform the simulation. To the best of our knowledge, this represents the largest system with electrostatic interactions, simulated so far in the MD simulations, setting the current record for the size of atomistic simulations. This has provided us with important insights as to what defines resistance to amorphisation by radiation damage. In *Fig. 5* we show the initial damage caused by amorphisation (seen as dark areas) and the 'healing process' of the materials. We find that the resistance to amorphisation is highest for MgO and Al_2O_3, while SiO_2 and GeO_2 show the largest damages.

One aspect that has not been considered so far is assessing the importance of local electronic heating in that damage. A recoiling nucleus diplays velocities of between 0.1 and 0.2 atomic units, quite capable of efficient electronic excitation. Electronic stopping power of ions in materials has been studied for more than twenty years, even if mainly focussing on metals. The knowledge for ceramics is much more limited, but there are measurements in systems like Al_2O_3, SiO_2, and LiF, which display similar electronic band gaps and chemical character to some of the host materials being considered.

For the mentioned velocities, the measured stopping power in those materials is of the order of 1 eV/Ång, i.e., 1 eV given by the ion to the electrons per Ång. along the path. However, in order to ascertain the electronic effects in radiation damage more precise values would be needed for the different host candidate materials. Given the difficulty of these measurements, we have devised a way to calculate electronic

stopping power from first principles. It is based on time-dependent DFT, and works by following the evolution of the expectation value of the electronic energy of the solid in the presence of the moving ion. The computation demands (1) automatic managing of many independent time-evolution runs (one per value of the velocity and per host material) in the grid and (2) output monitoring of the different (long) runs."

Results have been obtained for LiF, which display good agreement with experiments, and will be sought for candidate host materials. The latter calculations were done on the eMinerals minigrid computers using the SRB.

4. Summary and Future

Prior the eMinerals project the data presented here would take several years, involving many projects. Many of the calculations on realistic systems were also out of reach, such as the modelling of the electrical double layer at the solvent/mineral interface and the radiation damage in different oxides, using more than 5 millions ions in the simulation.

During the 3 years the eMinerals project has been up and running we scientist have learnt that we need new routines when we plan our calculations, relaying on automatic workflows designed for our specific calculations. We are also in need of data storage provided by the SRB, and automatic tools to monitor the calculations and analyse the large amount of data. The latter being one of the most challenging issues that needs to be resolved in the near future, but work is in progress by the computer scientists. One solution is a "Web portal" [9], where the data can be accessed, analysed and modified. We have also adapted the computer codes in the eMinerals project so that they run on all available platforms. In addition, CML has been implemented to all codes used in the project, which assists when creating automatic workflow. The calculations are submitted via Condor-G or Globus. In theory this means that we can submit jobs to all machines available within the eMinerals minigrid from our own workstation.

We have learnt that we need close collaborations between scientists working in different fields, *i.e.* computer, grid, environmental and mineral physics scientists. This is possible via the PIG, MAST and WIKI.

Acknowledgements

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