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Advances in computer modelling of mineral properties

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The following six papers were presented at a meeting, held in September 1994, which reviewed some of the recent advances in the application of computational methods to mineralogy. Talks covered the developing and challenging field of *ab initio* quantum mechanical computations as well as new applications and insights afforded by the use and refinement of the more established methods of empirical simulation and modelling. The former attempt to solve Schrödinger's equation for the material in question, and in doing so determine the energy surface and electronic structure. The latter use parameterized interatomic potentials to describe the energy of interaction between pairs or groups of atoms, the parameters typically derived either by fitting to the results of quantum mechanical calculations of small clusters, or empirically determined from fitting to the known physical properties of crystals (e.g. to the elastic constants, structural parameters or dielectric constants). A certain rivalry and antipathy occasionally surfaces between computational theorists from either camp. The quantum mechanical modellers might claim that the potentials used by the empirical modellers are unphysical and, hence, cannot answer questions about the underlying fundamentals of structure and properties, whereas they attempt to model the crystalline state with as few *a priori* assumptions as they can get away with. The empirical modellers, on the other hand, point to the fact that their potentials are transferable between structures, predictive, and can solve some of the 'real' problems of complex minerals that are, as yet, well beyond the scope of quantum mechanical computation. In reality, of course, both approaches have significant roles to

play and insights to offer, as was apparent from the meeting itself. Furthermore, it was clear from the healthy attendance at the meeting that the application of computational modelling to mineralogy is burgeoning. As well as the plethora of computer programs that have been developed over the last ten to fifteen years and are generally freely available to academics, the modelling tools incorporated in commercially-available packages such as Cerius and Biosym will undoubtedly further widen the use of the technique. These packages already offer empirical and quantum mechanical code in an accessible 'black box' form which has, for example, proven useful for determining diffusion paths through zeolites and the interaction between organic molecules and inorganic crystalline surfaces. Today's advances in computer modelling promise to find wider application throughout mineralogy tomorrow, especially if the trend for computational resources to become cheaper and more powerful continues at its present rate.

A number of good reviews of the subject of computer simulation in mineralogy now exist and I should, perhaps, point the interested newcomer towards these. Most recently, Tossel (1995) gives a very readable introduction to the application of quantum mechanical methods to minerals, in particular to mineral surfaces, in which he outlines the strengths and weaknesses of both the Hartree Fock (HF) and local density functional (LDF) methods (the two approaches to solving the Schrödinger equation by approximating the many-electron reality of a crystal to the product of independent electron contributions). A further survey of quantum chemical calculations of the

electronic structure of minerals has been provided by Dolin and Sherman (1994).

Price and Urusov (1994) give the briefest of introductions to the principles of empirical simulation (for those without much time to read extensively!). The subject of lattice dynamical simulation of minerals is dealt with in more detail by Price and Parker (1988), and that of molecular dynamics is reviewed by Dove (1988). The strength of static lattice energy minimisation procedures and lattice dynamic calculation using empirical potentials is well illustrated by Winkler *et al.* (1991), who show that such potentials work across a diverse range of aluminosilicate mineral structures. These techniques have been used extensively to predict mineral properties at conditions which are experimentally inaccessible, as well as to predict totally new crystal polymorphs.

So much for looking back, what progress and developments were reported at the meeting at which the following papers were presented? Read on to discover for yourself, here I shall outline some of the main points, as well as report on two additional papers which were presented but do not appear in this volume.

The first (Winkler *et al.*, this volume) outlined progress that has been made using *ab initio* calculations reliant on the local density approximation (LDA). The authors' program, 'CASTEP', has been applied to a number of silicate minerals, and shows that the method now succeeds in modelling complex mineral structures to a high degree of reliability. The increased use of parallel computers should open the way to applying this approach to increasingly complex mineralogical problems, but as it is the current power of workstations allows relatively large-celled aluminosilicates such as cordierite to be modelled in a matter of only a few days. At the meeting, Refson carried the discussion of the application of the LDA to the surface chemistry of periclase, showing that hydroxylation to brucite occurs topotactically, and that quantum mechanical methods can be used to look at dirty surfaces so long as the dirt is well characterised! Sherman then took the theme from surfaces to deep Earth, presenting the results of *ab initio* calculations of the electronic properties of FeO under core conditions. He showed how such calculations can be used to discount ideas that a high-*P* phase of FeO might be metallic, with the consequence that Fe-FeO solid solutions are unlikely to occur in the core, while Fe-FeS solid solution is possible. The discussion of *ab initio* calculations was concluded with a paper on quantum mechanical molecular dynamics calculations (Vocadlo *et al.*, this volume). Solving the Schrödinger equation for a large ensemble over a large number of time steps is clearly a huge challenge for computing resources, and is likely to be applied to a very limited

number of problems. So far such calculations have only been made for liquid Li, and it seems unlikely that true high-temperature simulations will be carried out for silicates in the near future, although it is pointed out that MD simulation has an important role as a geometry optimizer for 0 K calculations.

The theme next shifted to empirical modelling. The success of empirical modelling in solving complex mineralogical problems was apparent, the technique having reached a useful level of maturity and applicability. The study of mineral morphology is itself one of the oldest branches of mineralogy. Rohl and Gay (this volume) showed how code which uses both ionic and molecular mechanics force fields as well as 3- and 4-body potentials can be used to enhance our fundamental understanding of the growth morphology of crystals. Their calculations show up the discrepancy between equilibrium morphology and observed morphology; demonstrating that, in particular, higher-index faces are stabilised by relaxation. The poor agreement between calculation and observed behaviour that they find highlights the potential importance of detailed growth mechanisms in controlling real crystal morphology. Following this, Jackson *et al.* (this volume) outlined the progress made in empirical modelling of phosphates and perchlorates, and highlighted some of the difficulties in fitting potentials of molecular anions and cations. It is clear, however, that the routine use of transferable potentials is now well established, and finding increasing application.

The final two papers deal with aspects of computer simulations that have shed new light on processes associated with phase transitions in minerals. Tsatsikis and Salje (this volume) demonstrate how simple potential models can be usefully applied to complex problems. Their paper details how an elastic model for cation ordering has been successfully applied to model kinetically controlled microstructures in K-feldspars. Such modelling, involving a Monte Carlo simulation with relaxation of 10^6 interatomic bonds using a parallel processor, replicates and explains the observed development of preferentially oriented tweed microstructures during Al/Si ordering in K-feldspars. Dove *et al.* (this volume) wrap up the discussion by explaining how, by modelling the rigid-unit mode spectrum of a mineral, it is possible to unambiguously determine the driving mechanisms of structural phase transitions and other high-*T* and *P* processes. Once more, their work demonstrates the strengths of very simple models of interatomic interactions in modelling complex processes.

The meeting, therefore, spanned the spectrum of computational mineralogy, moving from the use of complicated interactions to model simple structures

to the use of simple interactions to model complex minerals and processes. It is clear that computational mineralogy is addressing increasingly complex and taxing problems, and has the potential to make a significant impact in Earth sciences generally. The computer modelling of mineral properties is clearly advancing to meet new applications as rapidly as computing technology, human resourcefulness and theoretical developments will allow.

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