AB INITIO APPROACHES TO THE PHYSICAL PROPERTIES OF PLANETARY ICES. A. D. Fortes[1] J. P. Brodholt,[1] and L. Vočadlo[1], [1]Centre for Planetary Sciences, Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, United Kingdom (andrew.fortes@ucl.ac.uk).

Introduction: Planetary bodies are essentially crystalline aggregates. The structure and evolution of all such bodies are thus fundamentally due to the microscopic behaviour of the component crystals - equilibrium structures, elasticity, and transport properties for example. Determining the magnitudes of these properties for the different 'ices' and for the highly hydrated phases thought to exist in the interiors of outer solar-system moons requires a coordinated multidisciplinary approach involving a combination of experimental and computational techniques. All of the substances of interest exhibit complex polymorphism over the range of pressures and temperatures found in the largest icy moons; however, apart from the case of water ice, little is known about the existence, stability fields, and physical properties of these numerous polymorphs. The objective of this contribution is to describe the applicability of quantum mechanical first-principles techniques to addressing a range of problems, with a particular emphasis on diffusion creep.

Computational method: Material properties can be calculated with high precision from quantum mechanical first principles. These so-called '*ab initio*' methods use only the fundamental physical constants (e.g., the Planck Constant and the mass of the electron), the nuclear mass and the atomic coordinates as inputs. There are no empirical parameters in the ideal solution and so the problem of transferability does not arise, as it does with fitted potentials. The most efficient (i.e., least computationally expensive) technique is the electron density-based approach embodied in Kohn-Sham Density Functional Theory (DFT) [1]; the approximations necessary to solve the Schrödinger equation (in particular those relating to the electron exchange and correlation energy) have been shown to give good results with hydrogen-bonded crystals [e.g., 2]. Any property we wish to determine may be found from derivatives of the total energy of the crystal as it is perturbed from its equilibrium state. For example, the incompressibility is determined from the change in internal energy due to changes in the molar volume (at absolute zero temperature); elastic constants are found by calculating the change in internal energy when a crystal structure is strained; and vibrational frequencies are found from the change in internal energy as individual atoms are shifted fractionally from their equilibrium positions. We can sample the total energy hypersurface any way we desire. Although many planetary ices and hydrates have complex crystal structures (low symmetry and large unit-cells), *ab initio* calculations are tractable, as demonstrated in the contribution by Brand *et al*. (this volume).

Applicability to diffusion creep: At very low strain rates, such as obtain in planetary interiors, solid-state flow is most likely to be dominated by diffusion creep processes, controlled by molecular or atomic volume diffusion and grain-boundary diffusion. These diffusion coefficients have the general form of an Arrhenius law, $D = D_0\exp(-E/kT)$, where E is the activation energy, typically ~ 20 $kJmol^{-1}$. In water ice, laboratory creep rates are - necessarily - measured at much larger strain rates, where the deformation is controlled by other processes (such as grain boundary sliding). Due to grain growth, and the practical difficulties involved, it is thought unlikely that pure diffusion creep in water ice can be measured in the laboratory [3]. Note that much of the contemporary discussion pertains only to the low-pressure phase ice Ih; data on the diffusion creep of high-pressure ice phases is equally relevant (ice VI, for example may form layers up to 400 km thick in the largest icy moons), and considerably more difficult to measure. Creep measurements upon other planetary hydrates and ice-rock mixtures are fairly sparse (see contributions by Grindrod *et al.,* and Middleton *et al*., this issue).

Volume diffusion in ice might normally be expected to occur by atomic diffusion (H and O), but spectroscopic measurements indicate identical rates for both species, leading to the conclusion that the mechanism in ice Ih is *molecular* interstitial diffusion [4]. Given the relatively large voids in the structure of low-pressure ices, it is likely that molecular diffusion is also important in ices II and III. The increasing tendency towards interpenetrating hydrogen bonds in ices IV, V, and VI, means that pathways for molecular interstitial diffusion are blocked [e.g., 5]. Thus, in the high-pressure ices, atomic diffusion is likely to dominate. However, only in ice VII has the proton diffusion coefficient been measured [6]. In sulfate hydrates, volume diffusion of H_2O may be related to the availability of non cation-coordinated water molecules, of which there is one in epsomite ($MgSO_4{\cdot}7H_2O$), two in mirabilite ($Na_2SO_4{\cdot}10H_2O$), and five in meridianiite ($MgSO_4{\cdot}11H_2O$); the sparse data suggest a rheological trend from rock-like strength in epsomite through to ice-like strength in meridianiite. Sulfuric acid hydrates (6½ and $8H_2O$), which are plausibly of relevance in the icy crust of Europa, are molecular sandwiches containing layers with ice-like structure [7,8], and are therefore likely to be relatively weak.

Dealing with grain-boundary diffusion is potentially more difficult, although it has been suggested that a good proxy is the self-diffusion coefficient of supercooled water [9]. This has interesting implications for the rheological behaviour of high-pressure ices, since supercooled water actually becomes more fluid at high-pressure [10].

An early *ab initio* approach to calculating absolute diffusion coefficients employed static DFT to determine the activation-energy term (by exploring the energy surface surrounding an atomic defect), and then used a statistical theory to determine the rate at which defects attempt to 'jump' the activation-energy barrier. This methodology met with success for simple oxides, employing Vineyard theory [11] to determine the pre-exponential frequency factor [e.g., 12,13]. However, the static *ab initio* calculations do not account for important contributions from vibrational entropy or anharmonicity (which must be addressed by corrections to Vineyard theory). Furthermore, the technique requires some *a priori* knowledge of diffusion pathways through the structure, which is relatively straightforward in simple close-packed ionic crystals, but becomes increasingly intractable in complex molecular crystals.

A dynamic rather than a static computational technique is therefore more desirable, in which no *a priori* knowledge of diffusion paths or mechanism are necessary, and the system evolves over time (i.e., atoms and/or molecules diffuse) according to the classical- or quantum-chemical rules imposed upon it. This is the basis of molecular dynamics (MD) calculations, which are capable of yielding both the activation energy and the pre-exponential term. In MD, atoms are moved according to a force matrix obtained from either classical interatomic potentials, or quantum mechanical *ab initio* calculations [14] - so-called 'on-the-fly' DFT. MD is well suited to the study of diffusion in liquids, since the rates are rapid and the calculation timescales are short (order 10^{-11} s). In solids, we are faced with the twin problems of needing to simulate large supercells, possibly containing many hundreds of atoms, and extremely long - for MD - simulated timescales (order 10^{-7} s) for determination of slow diffusive processes. It is for this reason that computationally cheap classical MD studies of solid-state diffusion are primarily carried out. A number of researchers have employed classical MD to investigate self-diffusion in water-ice and clathrates and the diffusion of small molecules through the ice lattice [15-17]. However, interatomic potentials are notoriously difficult to transfer from one structure to another, and only *ab initio* MD offers the certainty of obtaining reliable diffusion coefficients, despite the very considerable computational expense, since the dynamics naturally incorporate vibrational entropy and anharmonic effects. The most popular implementation of *ab initio* MD is the Car-Parinello method [18], which nonetheless suffers from poor scaling (the size of the calculation scales as N^3, where N is the number of atoms in the system), although more efficient algorithms - which scale linearly in N - are becoming available [19]. To date, *ab initio* MD studies of diffusion have been limited to liquids [20].

Summary: The substantial experimental obstacles associated with the measurement of diffusion creep processes in water ice and related planetary hydrates, means that calculations are able to make a significant contribution to understanding the creep of solids under planetary conditions. Some of the techniques described here have already borne fruit in determining the rheology of terrestrial mantle minerals [e.g., 21], and we will make similar strides in advancing understanding of ice diffusion creep at a range of pressures and temperatures relevant to icy moon interiors. Advances in computer technology mean that the extension of *ab initio* MD to the study of diffusion in solids is becoming tractable, and offers the hope that diffusion creep in ice can be determined *in silico* if not in the laboratory.

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