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A comparison of empirical potential models for the simulation of dislocations in uranium dioxide

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ABSTRACT

The presence of dislocations, resulting from high levels of irradiation, in nuclear fuel may have a profound effect on the fuel's properties. Here atomistic simulations, employing empirical pair potentials, are used to examine the core structures of a series of dislocations in UO_2 with Burgers vector $1/2\langle 110\rangle$ and their relative stabilities are assessed by comparing their line energies. As there are a large number of empirical pair potential models available for UO_2 a critical assessment of the efficacy of the potential models is also presented. There is a high level of agreement between the different pair potential models with all those tested predicting the same ordering of the dislocation stabilities i.e. screw $<\{100\}\langle 110\rangle<\{111\}\langle 110\rangle<\{110\}\langle 110\rangle$ which is in excellent agreement with experiment.

1. Introduction

The interaction of radiation with nuclear fuel during reactor operation leads to the formation of dislocation loops in the fuel matrix. As the burn-up of the fuel is increased there is a marked increase in the dislocation density (Nogita and Une, 1994; Degueldre et al., 2011; Mieszczynski et al., 2011), which can in turn have a significant effect on the fuel's properties, for example the creep rate and the thermal conductivity (Deng et al., 2013). Additionally, dislocations can provide trap sites for point defects and fission products (Nerikar et al., 2011a) as well as providing pathways for enhanced diffusion through the fuel grains via processes such as pipe diffusion. The reorganisation of dislocations into "sub-boundary" domains is thought to lead to the subdivision of the original fuel grains into the smaller grains that make up the high-burn structure found at the pellet rim (Rondinella and Wiss, 2010; Jonnet et al., 2006).

Consequently, it is essential to develop a mechanistic understanding of how these dislocations form and how they affect the fuel matrix. Dislocations are often discussed within the framework of linear elastic theory, which provides an excellent description of the region surrounding a dislocation, however, within the core region of the dislocation this theory breaks down. The limited extent of the core region ensures that it is currently difficult to perform direct observations (although it is noted that modern microscopic techniques may help assess the stresses generated around dislocations). Atomistic simulation techniques are therefore of particular value in providing a detailed description of the dislocation core.

Ab initio simulation techniques such as density functional theory (DFT) have been widely employed to study nuclear fuels, such as UO_2. DFT determines the forces on atoms based on the underlying electronic structure; however, they are also computationally demanding. Consequently, the number of atoms that can be included in any simulation supercell is restricted. This limitation renders DFT unsuitable for the simulation of dislocations, where the large strain fields surrounding the dislocations mean that supercells containing hundreds of thousands of atoms are more appropriate. Such large simulation supercells may be achieved by adopting the classical Born interpretation of a crystal, whereby the lattice is treated as an array of point charges and the interactions between ions are modelled using a long range charge interaction and a short range isotropic interaction.

There have been a large number of potential models developed for the UO_2 system as shown in Fig. 1. In all cases the interactions of the ionic charges are modelled using the standard Coulombic term:

$$E_{ij}^{\text{Coulomb}} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \tag{1}$$

where, q_i and q_j are the charges on ions i and j, ε_0 is the permittivity of free space and r_{ij} is the separation between i and j. For a fully ionic system the values taken for q_i and q_j will equal the formal valence charges on the ions (i.e. for UO_2 $q_U = 4.0$ |e| and $q_O = -2.0$

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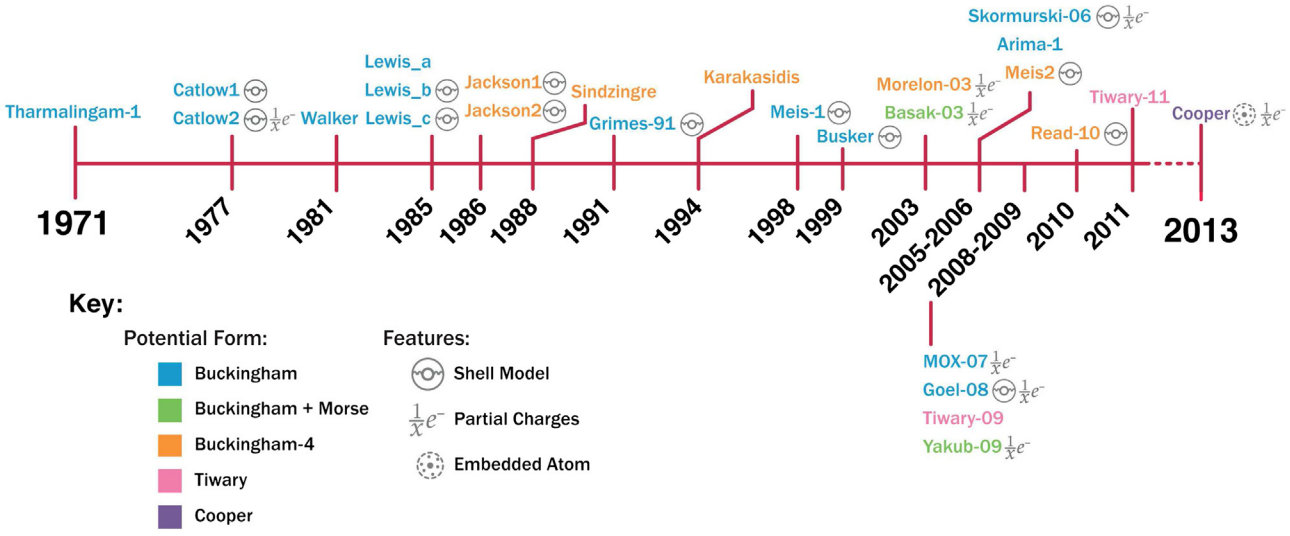

Fig. 1. Timeline showing the development of the empirical pair potential models for UO_2.

|e|). In order to introduce a degree of covalency many authors choose to reduce the charges on the ions thereby creating a partial charge model. The choice of ionic charge states is a fundamental design choice when creating a pair potential model as these charges remain fixed during all future simulations.

A further important consideration is the choice of short range potential form. Nearly all of the potential models used for the simulation of UO_2 employ one of the following three potential forms. The first is the Buckingham potential, which consists of a repulsive term and an attractive term to represent van der Waals interactions (Buckingham, 1936):

$$E_{ij}^{sr} = A_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \tag{2}$$

where, A_{ij}, ρ_{ij} and C_{ij} are parameters specific to the pairs of interacting species. The attractive $-C_{ij}/r_{ij}^6$ term can lead to unphysical attractive interactions at very short interatomic separations, sometimes referred to as the Buckingham catastrophe. In order to overcome this problem a form called the Buckingham-4 form was developed:

$$E_{ij}^{sr} = \begin{cases} A_{ij}\exp\left(\frac{r_{ij}}{\rho_{ij}}\right) & r_{ij} \le r_1 \\ \text{5th order polynomial} & r_1 < r_{ij} \le r_{\min} \\ \text{3rd order polynomial} & r_{\min} < r_{ij} \le r_2 \\ -\frac{C_{ij}}{r_{ij}^6} & r > r_2 \end{cases} \tag{3}$$

where, $r_{\min}$ is the potential minimum and the two splines are parameterized such that the potential is continuous in its 1st and 2nd derivatives.

The last of the commonly employed potential forms has all cation–cation and anion–anion interactions modelled using the normal Buckingham form shown in Equation (2). The anion–cation interaction differs from the Buckingham form by the addition of a Morse term as shown in Equation (4),

$$E_{ij}^{sr} = f_0(b_i+b_j)\exp\left(\frac{a_i+a_j-r_{ij}}{b_i+b_j}\right) - \frac{c_i c_j}{r_{ij}^6} + D_{ij}\left\{\left[1-\exp\left(\beta\left(r_{ij}-r_{ij}^*\right)\right)\right]^2 - 1\right\} \tag{4}$$

where, D_{ij} and β_{ij} are parameters and r_{ij}^* is the equilibrium bond length.

Potential parameters are normally obtained by fitting to either experimental or DFT data, such as lattice parameters, thermal expansion, elastic constants and dielectric constants. The result is that different potential models tend to be capable of faithfully replicating the property values to which they were fitted, however, this does not ensure that they are reliable when predicting properties not included in the original fitting database. Previous studies (Govers et al., 2007, 2008; Devanathan et al., 2009; Potashnikov et al., 2011; Chernatynskiy et al., 2012) have shown that the choice of potential can have a significant influence on the outcomes of the simulations; a good example of this is the large variation in the predicted activation energies for oxygen diffusion (Govers et al., 2007, 2008; Potashnikov et al., 2011). Consequently, it is prudent to perform a reliability test of the different potentials with a specific focus on the properties of interest in a given study.

The aim of the present work is to investigate the applicability of the different potential models to the study of dislocations in UO_2. Specifically, the structure and stabilities of different dislocations are predicted using a number of the more popular empirical potential models, including those of Arima et al. (2005), Basak et al. (2003), Busker (Abramowski et al., 1999), Catlow (1977), Goel et al. (2008), Grimes and Catlow (1991), Jackson et al. (1986), Meis and Charier (2005), Morelon et al. (2003), MOX07 (Potashnikiov et al., 2007), Read and Jackson (2010), Skormurski et al. (2006) and Yakub et al. (2007). In addition a new potential of Cooper et al. (2013) that is currently in development and employs a potential form that represents a departure from the potential forms discussed above.

2. Methodology

All simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package (Plimpton, 1995). Simulation supercells containing four dislocations were generated using a modified version of the “mismatch”