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Comparison of interatomic potentials for UO_2 Part II: Molecular dynamics simulations

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Abstract

An improved knowledge of nuclear fuel can be gained from a better description of atomic-scale processes such as point defects behaviour under irradiation. In these perspectives, computer simulation techniques involving semi-empirical potentials can play a major role as they allow studying some of these processes separately. The range of applicability in static calculations of the available interatomic potentials for UO_2 has been previously assessed by the authors. This study complements the static calculations by including dynamical simulations of the temperature evolution of different elastic properties (lattice parameter, specific heat, bulk modulus and Gruneisen parameter) and by calculations of bulk melting temperature.

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1. Introduction

The evolution of the nuclear fuel, under irradiation or in storage repository, is affected by many phenomena that cannot always be isolated experimentally. Computer simulations are a way to avoid such complications, as isolated processes can be simulated. Techniques involving interatomic potentials are in this context very promising. They allow determining structure information, such as defect properties working at 0 K with a limited number of atoms, but they can also be used to determine the evolution of a larger system under different conditions of pressure, volume or temperature.

In a previous article [1] we already estimated the range of applicability of the different potentials developed for UO_2 using static calculations. We could determine various elastic and defect properties, at zero temperature. With this article, we will complete this study including the dynamical behaviour of UO_2. Molecular dynamics simulations have been performed under different conditions of temperature and volume in order to analyze the temperature evolution of several thermodynamic properties up to 3000 K: lattice parameter, specific heat, bulk modulus and Gruneisen parameter. The second stage of this study was the analysis of the predicted melting temperature. For computation time reasons, shell–core MD being about ten times slower than MD with rigid ion potentials, this stage was only performed for five rigid ion potentials: *Basak*, *Karakasidis*, *Morelon*, *Walker*, *Yamada*. For clarity, rigid ion potentials will be written in italic, shell–core potentials in bold in the text; on the figures, crosses will be used for rigid ion potentials with non-formal charges, open symbols for rigid ion potentials with formal charges and full symbols for shell–core potentials.

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2. Calculation technique

2.1. Interatomic potentials

A molecular dynamics (MD) simulation allows determining the time-evolution of a system of atoms. In order to perform such a simulation the forces acting on each atom are derived from an effective interatomic potential, describing in a simple way atomic interactions. The same formalism is used in energy minimisation techniques (cf. the first part of this work [1]) but in that case the interatomic potential serves to find configurations presenting a local minimum of energy.

Two models accounting for atomic description have been considered by the different authors having developed potentials for UO_2 [2–16]. The first one is the rigid ion model, which describes atoms as massive point charges interacting by electrostatic interactions and a short-range potential. The second model is the shell–core model [17] which describes atoms as one massive point charge – representing the nucleus and the inner electron shells – bound by a spring to a massless shell – representing the valence electron shell. In this model the electrostatic interactions act between both species, but the short-range potential acts between shells only. With both models, interactions between ions have been formulated in terms of a short-range potential in addition to the long-range coulombic interactions. Three different forms of short-range potentials have been used by these authors: Buckingham, Buckingham-4-ranges and Buckingham + Morse potentials.

The most used was the Buckingham potential

$$V_{ij}(r) = A_{ij}\exp\left(-\frac{r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6}, \tag{1}$$

where r is the distance between atoms i and j. The Buckingham form yields unphysical attraction at very short distance because of the $1/r^6$ term. This zone is separated from the 'conventional' zone by an energy barrier whose location and height depends on the potential parameters. These short distances being potentially reached in MD runs at high temperature, care has to be taken in order to avoid entering this unphysical zone.

The problem of entering the unphysical region appeared in some of our simulations – with the following potentials: **Catlow1**, **Catlow2**, **Jackson1**, **Jackson2**, *Karakasidis*, *Lewis_a*, **Meis2**, *Sindzingre*, *Tharmalingam1*, *Walker* – at higher than they were initially developed for. To overcome this problem, we 'hardened' the potentials by the addition of a strong repulsive term at very short distance to the O–O and/or O–U interactions of the problematic potentials, with the form

$$V_{\text{repuls}}(r) = A\cdot\exp\left(\frac{r}{\rho}\right) \tag{2}$$

where we used the following values: $A = 1.0\times10^{12}$ eV and $\rho = 0.06$ Å. This additional term provides a sufficiently high energy barrier at small separation and, at the same time, does not affect the potential at 'normal' distances (see Fig. 1), in perfect lattice and defect configurations. This has been checked by repeating the static calculations of lattice parameter, elastic constants and defect properties with the modified potential. Less than 1% difference with the original potential predictions (see [1]) was observed.

An interesting point to note is that previous authors [9,18] made simulations at high temperatures with the *Karakasidis* and **Jackson2** potentials and did not encounter this problem. It has been suggested by Karakasidis [19] that a too large timestep or a too low number of reciprocal-space vectors used in the Ewald summation can be responsible for it, but modifications of these parameters did not result in any improvement of our simulations.

Different authors avoided this problem during the potential development using a 'Buckingham-4 ranges' potential, defined by intervals

$$V_{ij}(r) = \begin{cases} A_{ij}\exp\left(-\frac{r}{\rho_{ij}}\right) & \text{if} r \leqslant r_1, \\ \text{5th-degree polynomial} & \text{if} r_1 < r \leqslant r_{\min}, \\ \text{3rd-degree polynomial} & \text{if} r_{\min} < r \leqslant r_2, \\ -\frac{C_{ij}}{r^6} & \text{if} r > r_2. \end{cases} \tag{3}$$

The two splines are such that the potential and its two first derivatives are continuous and that $r_{\min}$ is the potential minimum. This form was used only for the O–O interactions, and the above-mentioned hardening of potential had in some cases (**Jackson1**, **Jackson2**, *Karakasidis*, *Sindzingre*, *Walker*) to be done for the O–U interactions.

The last form of potential found in MD simulations of UO_2, consists into the addition of a Morse potential, used in order to describe a covalent bond, to a Buckingham potential. A partial ionization is generally assumed with such a model. The potential is expressed by

$$V_{ij}(r) = f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r}{b_i + b_j}\right) - \frac{c_i c_j}{r^6} + D_{ij}\left\{\left[1 - \exp\left(\beta_{ij}(r - r^*_{ij})\right)\right]^2 - 1\right\} \tag{4}$$

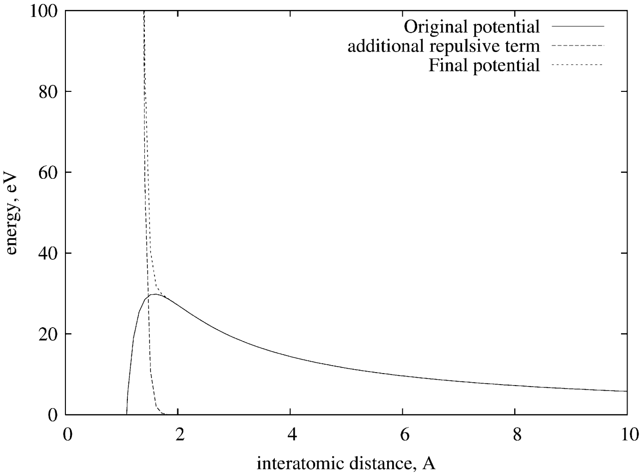

Fig. 1. Addition of a repulsive term to the O–O potential. The coulombic term is included in the potential function.