

Interatomic potentials for mixed oxide and advanced nuclear fuels

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We extend our recently developed interatomic potentials for UO_2 to the fuel system $(\text{U,Pu,Np})\text{O}_2$. We do so by fitting against an extensive database of *ab initio* results as well as to experimental measurements. The applicability of these interactions to a variety of mixed environments beyond the fitting domain is also assessed. The employed formalism makes these potentials applicable across all interatomic distances without the need for any ambiguous splining to the well-established short-range Ziegler-Biersack-Littmark universal pair potential. We therefore expect these to be reliable potentials for carrying out damage simulations (and molecular dynamics simulations in general) in nuclear fuels of varying compositions for all relevant atomic collision energies.

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The interest in using mixed oxide (MOX) and advanced nuclear fuels comprising $(\text{U,Pu,MA})\text{O}_2$ (where $\text{MA} = \text{Np}$, Am , and Cm) in fast breeder and transmutation reactors is ever increasing. Since this complex fuel experiences a high burn-up ratio with large quantities of fission products and materials defects, it becomes crucial to understand the evolution and statistics of atomic displacement cascades due to high energy radiation that the material faces.^{1,2} Classical molecular dynamics (MD) with its ability to simulate fairly long length scales, although still retaining the fine atomic structure of the material, is ideally suited for such studies. However, the complexity of the interatomic interactions for radiation damage simulations cannot be fully represented by simple classical forms due to the disparate scales of energies involved. Interactions corresponding to equilibrium conditions are traditionally found by fitting to a variety of thermodynamic data, while for description of the short-range behavior, the Ziegler-Biersack-Littmark (ZBL) universal pair potential³ developed in the 1980s is well-accepted. These two “pieces” then need to be smoothly connected via somewhat arbitrarily applied splines. We recently proposed a methodology for developing interatomic potentials that is valid for all interatomic separations, without the need for any ambiguous splines.⁴ In this article, we apply this formalism to a more general case of nuclear fuels of varying composition. In addition to capturing high temperature thermodynamic properties, as done by available potentials,^{5–9} we also incorporate the correct treatment of point defects. Created due to irradiation, these are critical for the understanding of a variety of phenomena such as fuel swelling, fission gas release, and burn-up structure formation.^{10–13} A key test of any developed energy surface lies in its ability to adequately represent systems/configurations that were not included in the fitting procedure.¹⁴ We here fit the potential parameters to *ab initio* and experimental data for the oxides PuO_2 and NpO_2 , and then check for their transferability by comparing against *ab initio* data for $(\text{U}_x\text{Pu}_{1-x})\text{O}_2$ and $(\text{U}_x\text{Np}_{1-x})\text{O}_2$ configurations that were not included in the fit.

In the present study we employ the generalized potential formalism⁴ that behaves correctly in both short-range and long-range limits. The only component in this potential that

remains to be determined is a correction term for intermediate distances associated with chemical bonding. We find this correction term by fitting to an extensive database of generalized gradient approximation $\text{GGA} + U$ *ab initio* calculations¹⁵ on PuO_2 and NpO_2 . The potential’s applicability in a mixed environment pertinent to MOX and advanced fuels is further verified by testing against $\text{GGA} + U$ data for $(\text{U}_x\text{Pu}_{1-x})\text{O}_2$ and $(\text{U}_x\text{Np}_{1-x})\text{O}_2$. $\text{GGA} + U$ is known to provide electronic and magnetic behaviors of the actinide oxides¹⁶ that are consistent with experiments. In this approximation, the spin-polarized GGA potential is supplemented by a Hubbard-type term to account for the localized and strongly correlated $5f$ electrons. Our database comprises results obtained from $\text{GGA} + U$ calculations with the projector augmented wave method and collinear antiferromagnetic moments as implemented in the VASP package.¹⁷ Dudarev’s rotationally invariant approach^{18,19} to $\text{GGA} + U$ is employed wherein the parameter $U-J$ is set to 3.99, 3.25, and 3.40 for U, Pu, and Np, respectively.^{20–22} These are the generally accepted values for reproducing the correct band structures of the corresponding oxides. Energy cutoff for the plane waves was kept at 400 eV. Since $\text{GGA} + U$ overestimates the lattice parameter, a common scaling factor (the same as that used⁴ for UO_2) was employed to get experimentally correct lattice parameters. $\text{GGA} + U$ is known to give rise to many metastable solutions in correlated systems,²³ which can be problematic for predicting the properties of such materials. To assure that our DFT database is not stuck in such a metastable minima, we use the recently proposed U -ramping method,²³ wherein the U parameter is slowly increased and the occupation matrices of previous calculations are iteratively reapplied. The *ab initio* database so obtained for fitting comprises the following:

(1) Isochoric relaxed runs on a 12 atom unit cell, which was isometrically contracted and expanded by various amounts (i.e., equation of state calculations wherein each data point was calculated under the constraint of constant cell volume) and for which an $8 \times 8 \times 8$ k -point grid was taken after ascertaining k -point convergence. Ionic relaxations were carried out until residual forces were less than 0.01 eV/Å.

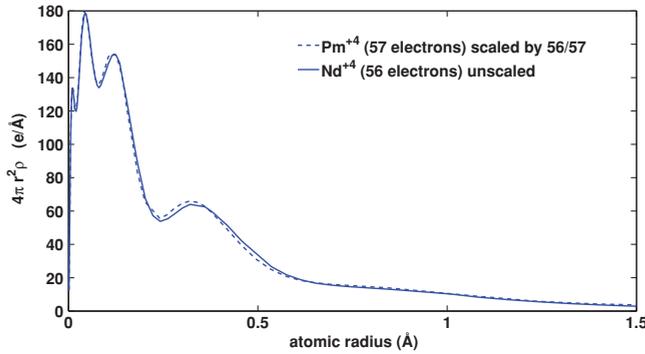


FIG. 1. (Color online) Test of approximation validity of $f_{\text{PuPu}} = (90/88)f_{\text{UU}}$ and $f_{\text{NpNp}} = (89/88)f_{\text{UU}}$ by looking at the applicability of similar relations for cations of members of the previous row of the periodic table with similar shell structure, viz., Pm and Nd. The dashed line denotes the result from this approximation while the solid line is the actual charge density³ for Nd⁴⁺.

(2) Static (i.e., no ionic relaxation) runs on a 96 atom $2 \times 2 \times 2$ supercell in which one atom at a time (O or Pu or Np) was perturbed from its equilibrium position by varying distances (on the order of 1 Å or less from the equilibrium positions) in different directions. Sampling of the gamma point only was found to be satisfactorily accurate for this.

(3) A 96 atom $2 \times 2 \times 2$ supercell for the formation energies of stoichiometric defects, namely, the oxygen Frenkel pair, neptunium Frenkel pair, and plutonium Frenkel pair. Several vacancy-interstitial distances were considered to ascertain the separation between these corresponding to the minimum defect formation energy (excluding the case of nearest neighbor distances, which was found to lead to vacancy-interstitial recombination). Correct prediction of these energies has been given great importance in generating interatomic potentials for cascade simulations in UO₂.^{1,2,10-12,24-26}

A total of approximately 50 *ab initio* configurations were thus used in the fitting. For equation of state and defect configurations, relaxed state forces (corresponding respectively to relaxation under constant cell volume and full relaxation) were

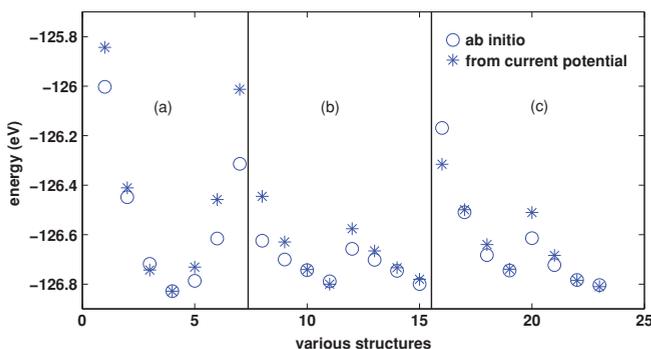


FIG. 2. (Color online) Quality of fit from our fitted potential (asterisks) for various *ab initio* energies (circles) for PuO₂. (a) Equation of state, (b) oxygen atom perturbation, and (c) plutonium atom perturbation. For each of oxygen and plutonium, the first four perturbations are along the $\langle 100 \rangle$ direction, while the second four are along the $\langle 110 \rangle$ direction. The perturbations are on the order of 1 Å or lower from the equilibrium positions.

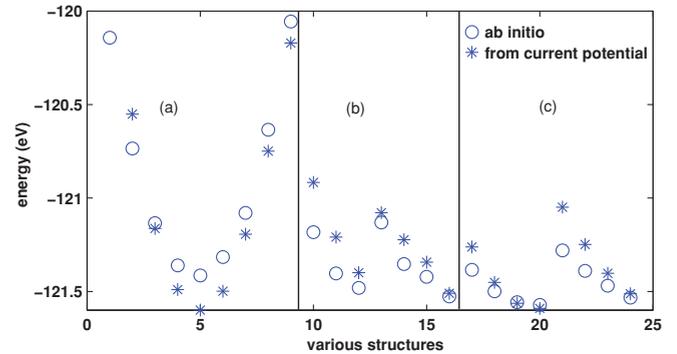


FIG. 3. (Color online) Quality of fit from our fitted potential (asterisks) for various *ab initio* energies (circles) for NpO₂. (a) Equation of state, (b) oxygen atom perturbation, and (c) neptunium atom perturbation. For each of oxygen and neptunium, the first four perturbations are along the $\langle 100 \rangle$ direction, while the second four are along the $\langle 110 \rangle$ direction. The perturbations are on the order of 1 Å or lower from the equilibrium positions.

also included in the fitting.²⁷ The total number of observables used in the fitting is therefore on the order of thousands. Note that in the above calculations, any interactions between atoms and their periodic images do not systematically bias the fit of the potentials because the same supercell geometry is used in both the *ab initio* and the empirical potential energy calculations. It would be beneficial to include liquid state configurations as well in our database. However, this has not been done due to the exceptional computational requirements when studying magnetic actinide oxides. These difficulties are related to (i) the supercell size (since a minimum cell size is required to model the liquid state), (ii) the large number of *ab initio* ionic steps needed to do an equilibrated MD run, and (iii) the spin-degeneracy problem. The *U*-ramping method²³ that avoids the problems from metastable spin-degenerate states is easy to implement on a set of relaxed or “frozen-phonon” geometries as in our *ab initio* database above, but rather cumbersome and computationally demanding to do within *ab initio* MD.

The *ab initio* database employed for validation and for testing transferability includes equation of state runs similar to those in the fitting database, for oxides of U₃₁Pu, U₃₀Pu₂, U₃₁Np, and U₃₀Np₂, each with 64 oxygens. These mixed environment data points were not included in the fit itself and were used only after the fitting was complete for validating

TABLE I. Defect energy comparisons.

	<i>ab initio</i> (Current Work)	Potential (Current Work)	Potential (Previous Works ^{5,7})
O Frenkel pair formation energy in PuO ₂ (eV)	3.9	4.9	7.0
O Frenkel pair formation energy in NpO ₂ (eV)	4.5	5.8	10.0
Pu Frenkel pair formation energy (eV)	11.9	24	17
Np Frenkel pair formation energy (eV)	12.2	26.7	17.5

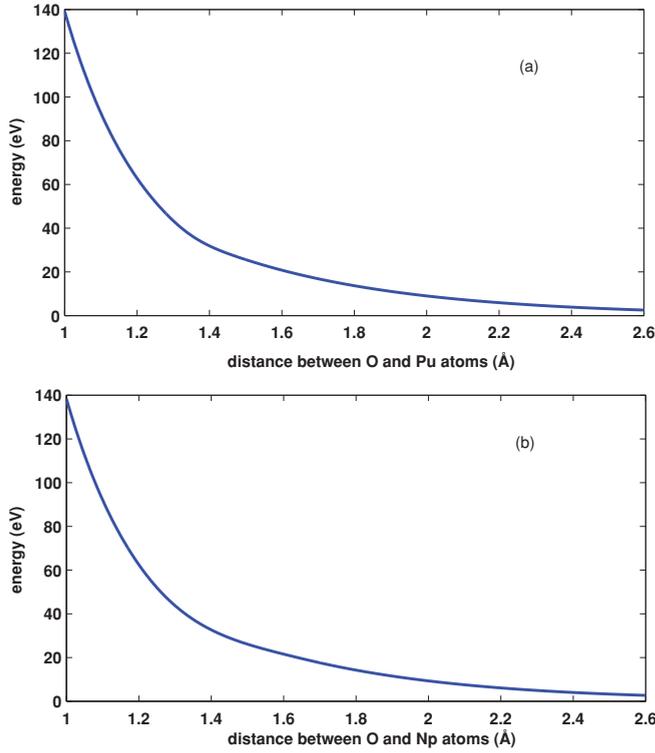


FIG. 4. (Color online) (a) Fitted O-Pu interaction, and (b) fitted O-Np interaction.

the robustness of the potentials with respect to use in mixed environments.

In addition to the *ab initio* data, we also included experimental thermal expansion behavior²⁸ of PuO₂ and NpO₂ in the fit. We found that including experimental thermal expansion data (which is readily available) is a very effective way to ensure reasonable thermal expansion behavior in this system. To make the calculation of high temperature lattice parameters computationally tractable during the fitting procedure, we employed the quasiharmonic approximation (QHA),²⁹ in which atoms are treated as pure harmonic

TABLE II. Coefficients of fitted potentials.

	PuO ₂	NpO ₂
A (eV)	597.304	597.605
ρ (Å)	0.475 712	0.484 948
B (eV/Å ⁶)	0.311 87	0.311 87
C (eV/Å ⁵)	0.000 3375	-0.073 5556
D (eV/Å ⁴)	0.029 085	0.0489 72
r_1 (Å)	1.42	1.17
r_2 (Å)	1.7	1.7
r_3 (Å)	2.85	2.94

oscillators whose frequencies depend on the cell volume. The so-called zero static internal stress approximation (ZSISA)³⁰ to QHA, as implemented in the package GULP, was used.³¹ QHA involves a full relaxation with respect to external (cell parameters) and internal (atom positions within the cell) coordinates. ZSISA ignores the dependence on internal coordinates of the vibrational part of the free energy. We found that for the materials studied and potential forms used in this communication, the lattice parameter through NPT (constant number, pressure, and temperature) MD was slightly lower than that through ZSISA. As such, an empirical adjustment to the ZSISA lattice parameter had to be included in the fitting. Thus, several independent fits were done using ZSISA lattice parameter values equal to the experimental lattice parameter multiplied by η , with η varying between 1 and 1.01. NPT MD was carried out with these potentials (the details of MD are provided later) to find the η that led to MD values matching the experimental data the best. We found that η equals 1.0006 and 1.0008 for PuO₂ and NpO₂ respectively, for a best match in the least squares sense between experimental and NPT MD lattice parameters.

The potential forms thus used for fitting to the *ab initio* and experimental data are similar to those proposed previously⁴ and are summarized below for Pu-Pu and Pu-O interactions (with similar forms for other interactions):

$$\begin{aligned}
 V_{\text{PuPu}}(r) &= \text{ZBL}_{90,90}(r) + \frac{(4)(4)e^2}{4\pi\epsilon_0 r} + \frac{8e^2}{4\pi\epsilon_0} \left[\frac{90}{r} - \frac{4\pi}{e} f_{\text{PuPu}}(r) \right] \forall 0 < r, \\
 V_{\text{OPu}}(r) &= \frac{(-2)(4)e^2}{4\pi\epsilon_0 r} + \begin{cases} \text{ZBL}_{90,10}(r) + \frac{4e^2}{4\pi\epsilon_0} \left[\frac{10}{r} - \frac{4\pi}{e} f_{\text{OO}}(r) \right] - \frac{2e^2}{4\pi\epsilon_0} \left[\frac{90}{r} - \frac{4\pi}{e} f_{\text{PuPu}}(r) \right] & 0 < r \leq r_1, \\ \text{5th order polynomial} & r_1 < r \leq r_2, \\ A \exp(-r/\rho) - B/r^6 + (r - r_3)^2 (Cr^3 + Dr^2) & r_2 < r \leq r_3, \\ A \exp(-r/\rho) - B/r^6 & r_3 < r. \end{cases}
 \end{aligned} \tag{1}$$

The UO₂ family of interactions is kept the same as in Ref. 4. Here $\text{ZBL}_{Z_1+q_1, Z_2+q_2}(r)$ denotes the ZBL form of interaction between two neutral atoms having atomic numbers $Z_1 + q_1$ and $Z_2 + q_2$, but using the screening length for Z_1 and Z_2 , as explained in Ref. 4. The functions f in the above are

related to the charge densities of the respective atoms. Detailed coefficients of f_{OO} and f_{UU} can be found in Ref. 4, while f_{PuPu} and f_{NpNp} can be calculated from the relations $f_{\text{PuPu}} = (90/88)f_{\text{UU}}$ and $f_{\text{NpNp}} = (89/88)f_{\text{UU}}$. This was needed since Np⁺⁴ and Pu⁺⁴ charge densities $\rho(r)$ are not available in

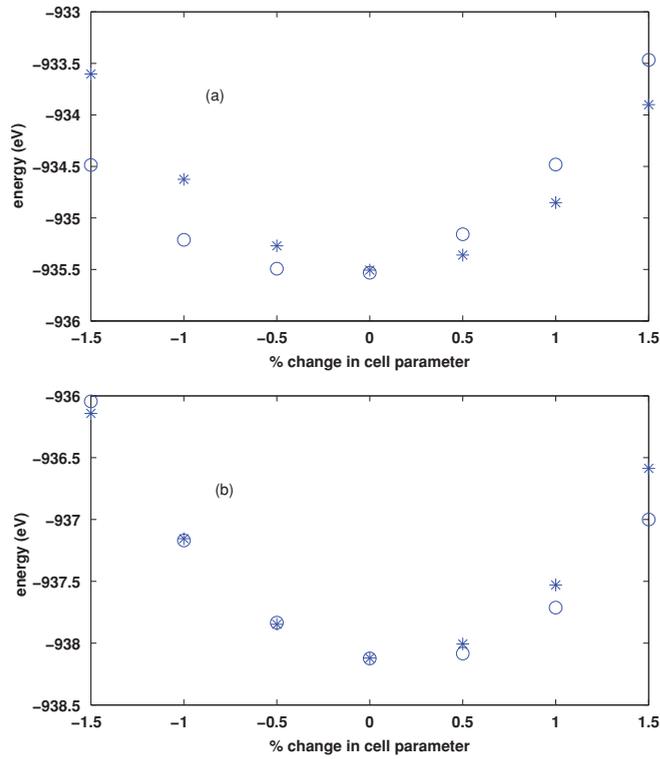


FIG. 5. (Color online) Equation of state for (a) $U_{31}PuO_{64}$ and (b) $U_{30}Pu_2O_{64}$. Circles denote *ab initio* data while asterisks are the values predicted (not fitted) with current potential.

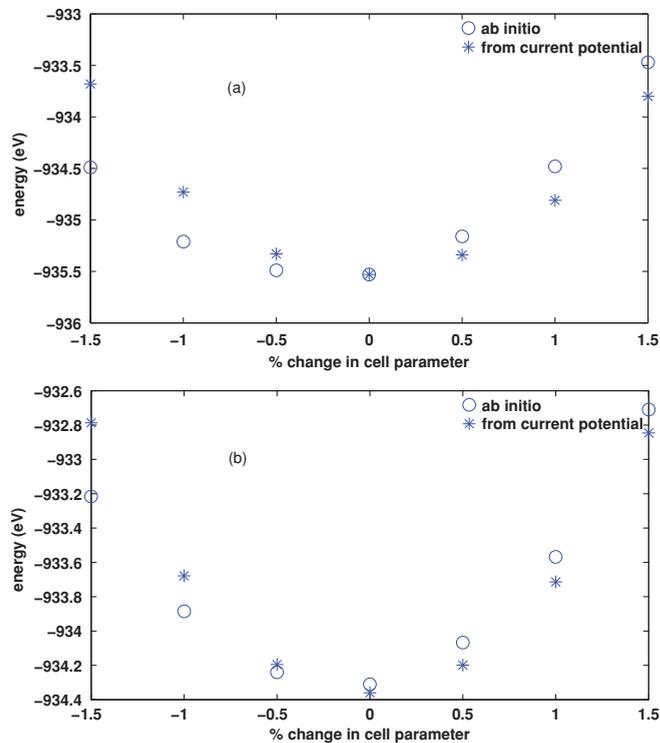


FIG. 6. (Color online) Equation of state for (a) $U_{31}NpO_{64}$ and (b) $U_{30}Np_2O_{64}$. Circles denote *ab initio* data while asterisks are the values predicted (not fitted) with current potential.

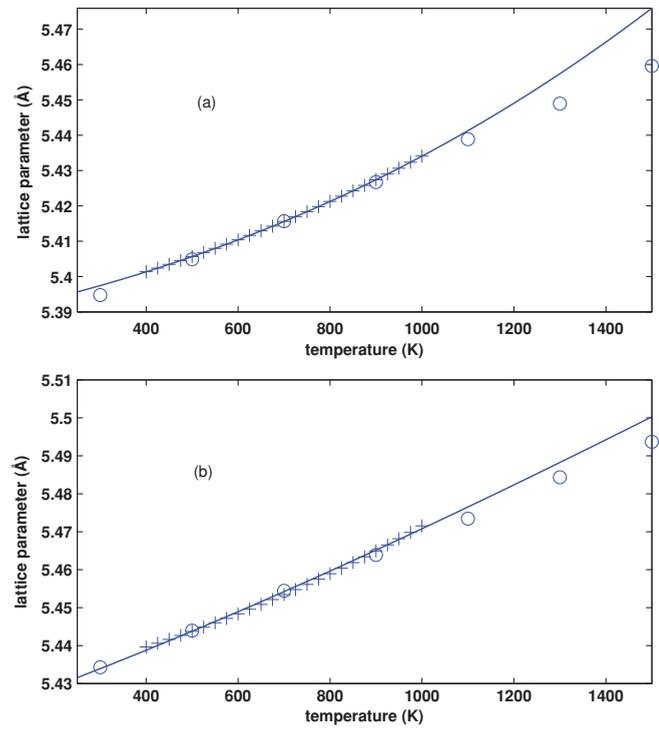


FIG. 7. (Color online) Lattice parameter at various temperatures for (a) PuO_2 and (b) NpO_2 . Straight lines are the experimental values²⁸ valid between 400 and 1000 K, while circles denote values obtained from MD simulations using current potentials. Plus signs represent $(1/\eta)$ times the experimental values actually used in fitting to account for the observation that ZSISA slightly overestimates the MD lattice parameters. Details of the calculation of this adjustment factor η (equaling 1.0006 and 1.0008 for PuO_2 and NpO_2 , respectively) can be found in the text.

Ref. 3. We tested this approximation using cations of elements in the previous row of the periodic table where actual ZBL charge densities are available, viz., Nd, Pm, and Sm. As can be seen from Fig. 1, the approximation satisfactorily captures the electronic shell structure of $4\pi r^2 \rho(r)$, which is the quantity of interest to us. Note that we have removed altogether any splines for cation-cation interactions. The downhill simplex method of Nelder-Mead was then used to carry out the potential fitting.³² The fitting involved minimizing an objective function equal to the sum of the squares of the differences between the *ab initio*/experimental data (weighted since they denote different quantities) and that predicted by the potential for all the classes of data as detailed above. GULP was used for energy calculations and for atomic-positions optimization.³¹

Figure 2 shows the quality of fit for the PuO_2 equation of state and single atom perturbation data, while Fig. 3 shows the same for NpO_2 . Table I shows the defect formation energies as obtained by us in the GGA + U calculations, along with the corresponding values from the current potential and from the previous potentials published for these systems. We excluded the Pu and Np cation defect formation energies entirely from the fitting objective function. This can be justified by considering that (i) these energies as per *ab initio* are already very high—upward of 12 eV; (ii) it is expected that

experimental observations and *ab initio* calculations both underestimate these energies,^{10,25,35} and thus they are even less likely to form; and (iii) Pu and Np concentrations are lower than U concentrations, while their formation energies are around 2 eV higher. It has been argued^{33,34} though that uranium Frenkel pairs and Schottky trios might play an important role in the diffusion of noble gas impurities formed after fission; as such, our library of potentials does provide a much better match for the uranium Frenkel pair and Schottky trio formation energy since it is based on the potentials in Ref. 4.

The potentials so obtained are plotted in Fig. 4, while the fitted coefficients are detailed in Table II. Note that since there was no spline in any cation-cation interaction [see Eq. (1)], they do not find a mention in the above list. The aforementioned 5th order polynomial is uniquely determined by the provided cutoffs and potentials. The detailed potentials are available as a GULP library file.³⁷

The performance of the potential against the validation data, i.e., equations of state for oxides of $U_{31}Pu$, $U_{30}Pu_2$, $U_{31}Np$, and $U_{30}Np_2$, can be seen from Figs. 5 and 6. The match is satisfactory and it improves with more Pu or Np content in the respective cases (in a least squares deviation sense). Since the potential was fit to the limiting cases of pure PuO_2 and NpO_2 , we expect it to be valid in more concentrated systems as well.

The generated potentials were verified through NPT MD simulations on $3 \times 3 \times 3$ unit cells (324 ions). The system was equilibrated for 10 ps while production runs were carried out for 100 ps with time steps between 0.001 and 0.0005 ps (depending on temperature). Apart from the lattice parameter, we also considered the enthalpy as a function of the temperature.

Figure 7 compares the lattice parameter as obtained from the MD simulations with experimental values for PuO_2 and NpO_2 .²⁸ Figure 7 also shows the corresponding ZSISA values as obtained from the potentials. The overestimation adjustment factor η used on the ZSISA values can be seen here. After this adjustment to ZSISA, the match for the lattice parameters between NPT MD and experiments is excellent. The experimental values²⁸ are valid only up to 1300 K. Nevertheless, in Fig. 7 we extend the polynomial fit to experimental data as reported by these authors up to 1500 K. The match is still excellent (0.23% and 0.15% error between MD and extrapolated experimental value at 1500 K for PuO_2 and NpO_2 , respectively). The quality of the enthalpy values compared between experiments³⁶ and those predicted from NPT MD with current potential is also very good (see Fig. 8). The fluorite structure remained stable during all the runs we performed, up to temperatures of 2500 K.

To summarize, we have developed fixed charge interatomic potentials for the MOX and advanced fuel systems

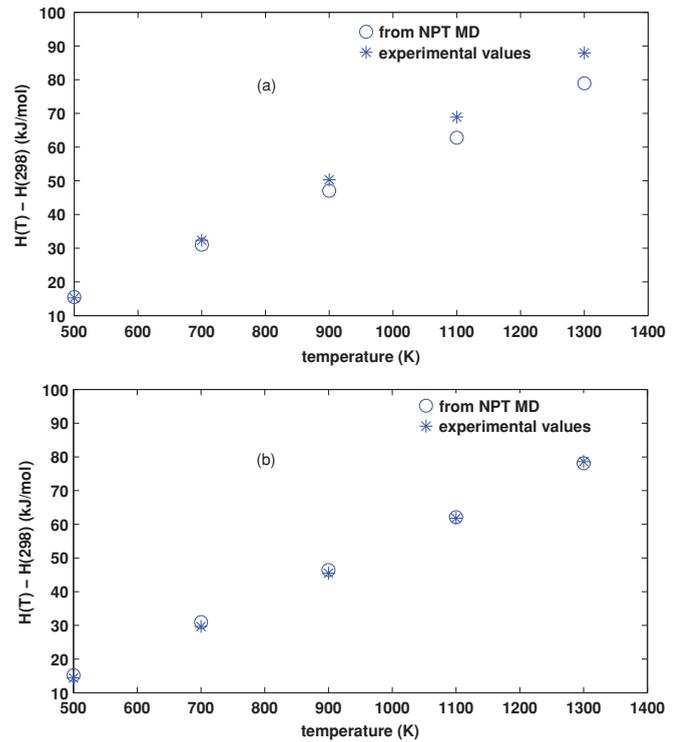


FIG. 8. (Color online) Enthalpy at various temperatures (relative to room temperature enthalpy) for (a) PuO_2 and (b) NpO_2 . The circles denote values from NPT MD (predicted and not fitted values) while the asterisks are the known experimental values.³⁶

(U,Pu,Np) O_2 by fitting to an extensive *ab initio* database and to available experimental observations using a formalism that has been shown to be capable of dealing in a self-contained manner with conditions ranging from thermodynamic equilibrium to very high energy collisions relevant for fission events, as long as there is not much significant charge transfer between cationic species in the fuel. The potentials capture known experimental measurements on these oxides as well as a rich database of *ab initio* GGA + U results. The applicability of these potentials in scenarios not included in the fitting is also explicitly demonstrated.

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¹R. Devanathan, L. Van Brutzel, A. Chartier, C. Gueneau, A. Mattson, V. Tikare, T. Bartel, T. Besmann, M. Stan, and P. Van Uffelen, *Energy Environ. Sci.* **3**, 1406 (2010).

²W. J. Weber *et al.*, *J. Mater. Res.* **13**, 1434 (1998).

³J. F. Ziegler, J. P. Biersack, and U. Littmark (Pergamon, New York, 1985).

⁴P. Tiwary, A. van de Walle, and N. Grønbech-Jensen, *Phys. Rev. B* **80**, 174302 (2009).

⁵K. Kurosaki, K. Yamada, M. Uno, S. Yamanaka, K. Yamamoto, and T. Namekawa, *J. Nucl. Mater.* **294**, 160 (2001).

⁶T. Arima, S. Yamasaki, Y. Inagaki, and K. Idemitsu, *J. Alloys Compd.* **400**, 43 (2005).

- ⁷K. Kurosaki, M. Imamura, I. Sato, T. Namekawa, M. Uno, and S. Yamanaka, *J. Alloys Compd.* **387**, 9 (2005).
- ⁸J. H. Harding, *J. Chem. Soc., Faraday Trans. 2* **83**, 1177 (1987).
- ⁹A. Cleave, R. W. Grimes, and K. Sickafus, *Phil. Mag.* **85**, 897 (2005).
- ¹⁰N. D. Morelon, D. Ghaleb, J.-M. Delaye, and L. Van Brutzel, *Philos. Mag.* **83**, 1533 (2003).
- ¹¹L. Van Brutzel, A. Chartier, and J.-P. Crocombette, *Phys. Rev. B* **78**, 024111 (2008).
- ¹²C. R. A. Catlow, *J. Chem. Soc., Faraday Trans. 2* **83**, 1065 (1987).
- ¹³R. A. Jackson, C. R. A. Catlow, and A. Dixon Murray, *J. Chem. Soc., Faraday Trans. 2* **83**, 1171 (1987).
- ¹⁴A. van de Walle and G. Ceder, *J. Phase Equilib.* **23**, 348 (2002).
- ¹⁵V. I. Anisimov, J. Zaanen, and O. K. Andersen, *Phys. Rev. B* **44**, 943 (1991).
- ¹⁶K. T. Moore and G. van der Laan, *Rev. Mod. Phys.* **81**, 235 (2009).
- ¹⁷G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ¹⁸S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, *Phys. Rev. B* **57**, 1505 (1998).
- ¹⁹S. L. Dudarev, G. A. Botton, S. Y. Savrasov, Z. Szotek, W. M. Temmerman, and A. P. Sutton, *Phys. Status Solidi A* **166**, 429 (1999).
- ²⁰H. Y. Geng, Y. Chen, Y. Kaneta, M. Iwasawa, T. Ohnuma, and M. Kinoshita, *Phys. Rev. B* **77**, 104120 (2008).
- ²¹H. Y. Geng, Y. Chen, Y. Kaneta, and M. Kinoshita, *Phys. Rev. B* **75**, 054111 (2007).
- ²²D. A. Andersson, J. Lezama, B. P. Uberuaga, C. Deo, and S. D. Conradson, *Phys. Rev. B* **79**, 024110 (2009).
- ²³B. Meredig, A. Thompson, H. A. Hansen, C. Wolverton, and A. van de Walle, *Phys. Rev. B* **82**, 195128 (2010).
- ²⁴R. Devanathan, J. Yu, and W. J. Weber, *J. Chem. Phys.* **130**, 174502 (2009).
- ²⁵K. Govers, S. Lemehov, M. Hou, and M. Verwerft, *J. Nucl. Mater.* **366**, 161 (2007).
- ²⁶K. Govers, S. Lemehov, M. Hou, and M. Verwerft, *J. Nucl. Mater.* **376**, 66 (2008).
- ²⁷F. Ercolessi and J. B. Adams, *Europhys. Lett.* **26**, 583 (1994).
- ²⁸T. Yamashita, N. Nitani, T. Tsuji, and H. Inagaki, *J. Nucl. Mater.* **245**, 72 (1997).
- ²⁹A. van de Walle and G. Ceder, *Rev. Mod. Phys.* **74**, 11 (2002).
- ³⁰N. L. Allan, T. H. K. Barron, and J. A. O. Bruno, *J. Chem. Phys.* **105**, 8300 (1996).
- ³¹J. D. Gale, *J. Chem. Soc. Trans.* **93**, 629 (1997).
- ³²J. A. Nelder and R. Mead, *Comput. J.* **7**, 308 (1965).
- ³³A. Chartier, L. Van Brutzel, and M. Freyss, *Phys. Rev. B* **81**, 174111 (2010).
- ³⁴R. W. Grimes and C. R. A. Catlow, *Philos. Trans. R. Soc. London A* **335**, 609 (1991).
- ³⁵J. P. Crocombette, F. Jollet, T. N. Le, and T. Petit, *Phys. Rev. B* **64**, 104107 (2001).
- ³⁶H. Serizawa, Y. Arai, and K. Nakajima, *J. Chem. Thermodyn.* **33**, 615 (2001).
- ³⁷See supplemental material at [<http://link.aps.org/supplemental/10.1103/PhysRevB.83.094104>] for potentials.