

Molecular Dynamics Simulations of Thermal Properties of Solid Uranium Dioxide

LI Jiu-Kai(李久楷)*, TIAN Xiao-Feng(田晓峰)

Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065

(Received 15 September 2009)

Molecular dynamics simulations are performed with the recently developed empirical interaction potential by Morelon et al. Thermodynamics properties of solid UO_2 that have been assessed include melt point, density, enthalpy, heat capacity, lattice parameter variation with temperature, mean-square-displacement and diffusion coefficients of oxygen ion. The results are compared with the data in literature and it is suggested that the rigid ionic potential provides perfect results below the superionic range. The data showing thermodynamics properties will become unacceptable when the temperature is higher than 2500 K. Compared with the previous empirical potentials, the empirical potential developed by Morelon et al. improves the agreement of these data with the recommend ones.

PACS: 65.40.-b, 02.70.Ns, 07.05.Tp

DOI: 10.1088/0256-307X/27/3/036501

Uranium dioxide (UO_2) is the key nuclear fuel in pressurized water reactor and has been the subject of numerous experimental and theoretical studies. The melting point and thermal properties of UO_2 , especially for high temperature, is of great interest for the safety of the nuclear reactor. Due to the high temperature condition and radioactive toxicities, it is somewhat difficult to experimentally evaluate the melt point and thermal properties with accuracy of such oxide fuels. The properties of the material will be strongly affected by ionic disorder on the oxygen sublattice (superionic conduction) and electronic excitations in high temperature in solid.^[1]

So far, for evaluating the various thermal properties and melt point of UO_2 , many molecular dynamics simulations have been performed.^[1–3] Molecular computer simulations have become extremely helpful in providing an atomic perspective on various properties of materials.^[4] The successful application of any computational molecular modeling technique requires the use of interatomic potential that can correctly describe the interactions of all atoms in the simulation system.^[5,6] A number of interatomic potentials for UO_2 have been developed before.^[3,7] Generally, there are two main categories of interatomic potentials for UO_2 , the first model is the shell-model which takes polarization effects into account and the second one is the rigid ion model considering the ions as massive point charges.

Recently, Morelon et al.^[2] have developed a rigid model potential of UO_2 , the new empirical potential more correctly describes the experimental energies of formation and migration of point defects. In this Letter, we perform molecular dynamics using the interatomic potentials developed by Morelon et al. to evaluate the melt point and thermal properties of UO_2 . Firstly, we briefly introduce the employed computational methodology, and then our results are pre-

sented, compared to previous studies and discussed in detail.

This rigid-ion potential improved by Morelon et al. has been used in the simulation of displacement cascades in UO_2 lattices.^[2,8] The U-U and U-O interaction conserve the Born–Meyer–Huggins (BMH) analytic form to describe the short range interactions. The short-rang U-U interaction is neglected, which is explained by Morelon et al. that the U-U distances are always so large that the results are unaffected by short-rang potential.^[2]

The interaction of O-O follows the model of Jackson et al.^[9] and is defined by intervals with two splines, which is described in detail elsewhere.^[1,2] This rigid model potential requires the computational cost to be lower than shell-model potential because the shell motion is absent.^[7] For the calculation of the Coulombic interaction energy, the uranium and oxygen atoms are both assumed to be fixed, but fractional charges. The comparatively long-rang Coulombic energy is computed by Ewald's^[10] summation.

Recently, Schwen et al.^[11] employed this rigid-ion potential to investigate the re-resolution of Xe fission gas bubbles in UO_2 , and interesting results have been obtained.

The LAMMPS code,^[12] developed at Sandia National Laboratories, is employed to perform the molecular dynamics simulations in the present work. We test one-phase simulations (OPS) and two-phase simulations (TPS) to evaluate the melt point of UO_2 . Very recently, Arima and his co-workers^[3] have used these two types' simulations to estimate the melt point of UO_2 using three different rigid ionic potentials, and they obtained that the OPS gives the melt point much higher than the experimental values. On the other hand, TPS's results are acceptable.

Perfect crystalline UO_2 is simulated using a $6 \times 6 \times 6$ supercell of the fluorite structure as the starting con-

*To whom correspondence should be addressed. Email: txf8378@163.com

© 2010 Chinese Physical Society and IOP Publishing Ltd

figuration for the one-phase simulations. When we perform the two-phase simulation, a supercell consisting of solid and liquid phases is used and both the solid and liquid cell sizes are $6 \times 6 \times 6$. The systems are simulated for at least 100 ps for equilibrium using an isobaric-isothermal (NPT) ensemble in which the temperature and pressure are maintained via a Nosé-Hoover thermostat.^[13–15] All of the simulations are carried out at zero pressure with a time step of 0.001 ps.

The melt point of UO_2 is estimated in the investigation of the variation of density of the simulated system with temperature. It is well known that the density of UO_2 is discontinuous at the melt point. We present the results of OPS and TPS in Figs. 1 and 2, respectively. The experimental data^[16–19] and the MD results by Arima *et al.*^[3] are also employed for comparison. All the data show that the density decreases gradually with the increasing temperature, and there is a jump at the melt point. In our simulations, the densities are obtained at intervals of 50 K near the melt point, so the error of estimation of the melt point is ± 25 K. Our OPS gives a value 4325 ± 25 K of the melt point, which can be compared with the previous MD results of 4225 ± 25 K and 4550 ± 25 K obtained by Basak and Arima potential respectively. From Fig. 1, we can see that the densities are slightly higher than the experimental data^[17–19] for the liquid phase, although our data are much better than those obtained by Basak potential. Additionally, both our and previous OPS results are not acceptable and they are much higher than the INSC recommended data of 3120 ± 30 K.

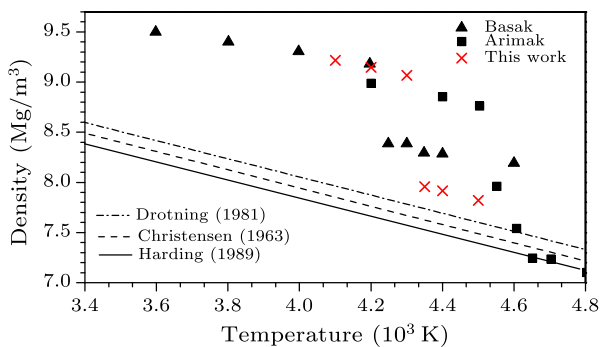


Fig. 1. Relationship between UO_2 density and temperature for OPS. Experimental data for liquid phase were given by Drotning,^[17] Christensen^[18] and Harding *et al.*^[19]

The TPS is performed using a supercell consisting of both solid and liquid phases. The liquid phase cell is obtained from a simulation of $6 \times 6 \times 6$ supercell of the fluorite structure starting configure at 5000 K in an NPT ensemble. Figure 2 shows that all the results of TPS have significant improvement compared with OPS. Our TPS estimates the melt point temperature to be 3425 ± 25 K, which is comparable to the experimental data. Basak and Arima potentials give the results of 3325 ± 25 and 3675 ± 25 K, respec-

tively. The disorder phase in the liquid phase plays a role as trigger for melting, this is discussed in detail in Ref. [3].

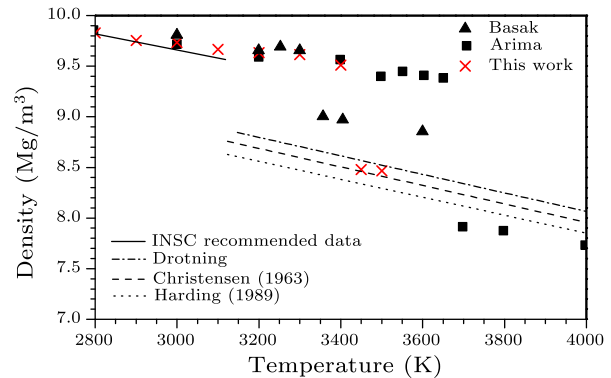


Fig. 2. Relationship between UO_2 density and temperature for TPS. Experimental data for the solid phase was recommended by INSC.^[16] Other literature data are the same as those in Fig. 1.

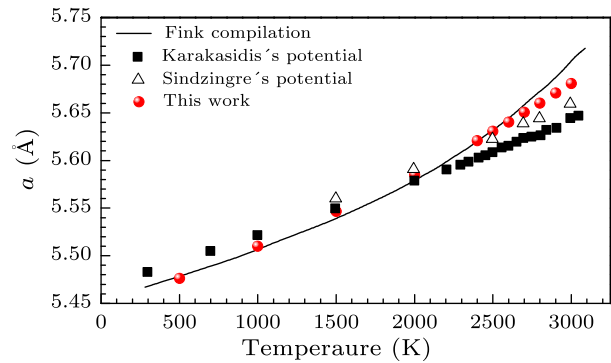


Fig. 3. Comparison of the present simulated and the previous values of grid parameter versus temperature. The literature data were analytic expression recommended by Fink,^[20] the simulated results using the Karakasidis-Lindan^[21] potential and the Sindzingre-Gillan^[22] potential.

The system densities in solid phase presented in Fig. 2 are well in agreement with the INSC recommended data below 3120 K. Additionally, our results are similar to the data obtained by the Basak potential. While in liquid range, the present theoretical results lies perfectly in the experimental line of Christensen.^[18] The results by Basak and Arima potentials overrate and underate the liquid UO_2 densities, respectively.

Now, we present the thermodynamic properties of solid UO_2 arising from a series of MD simulations performed in NPT ensemble using the Morelon potential. A lot of potentials have been employed to estimate the variation in the lattice parameter. We make a comparison between the results performed in the present work and the previous theoretical results^[20–22] in Fig. 3. Overall, the calculated lattice parameters are very close to the analytic data recommended by Fink.^[20] Our MD results is in quit satisfactory agreement with the data by Fink up to 2700 K, and our results

slightly underestimate Fink's data at higher temperature. Both the values of lattice parameters estimated by Karakasidis's potential and Sindzinger's potential overestimate Fink's results below 2000 K and underestimate those when the temperature is higher than 2000 K.

We then calculate the enthalpy variation with temperature at constant pressure. The simulated values of enthalpy increase slowly and the curve of enthalpy variation with temperature is nearly linear. We can see from Fig. 4 that the present MD simulations underestimate the relative enthalpy values although our estimation improves the data in the literature.^[21,22] The divarication between the MD results and the data recommended by Fink^[20] becomes serious with the increase of temperature. Sindzinger^[22] and Morelon *et al.*^[2] concluded that this cannot simply attribute to the fact that the value of expansion coefficient or the lattice parameter in the simulated system is lower than the experimental results at high temperature. The error of estimation of enthalpy introduced by poor simulation of lattice parameter at this temperature range is very small.^[2,22] Morelon pointed out that the superionic transition plays a key role in the poor agreement with experiment at high temperature.^[2] Thus, we will discuss the superionic transition and oxygen-ion diffusion coefficients in the following.

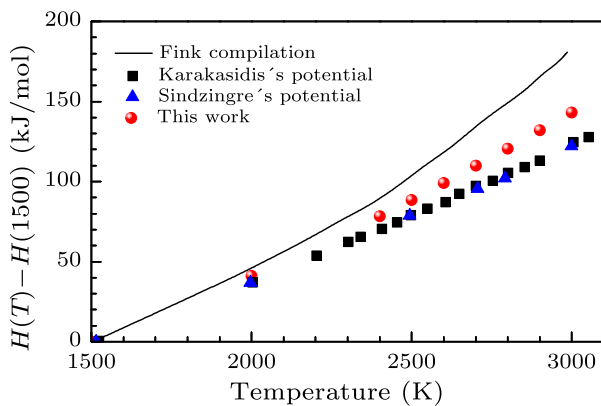


Fig. 4. Comparison of the present simulated and previous values of relative enthalpy variation between 1500 and 3000 K. The literature data are the same as those in Fig. 5.

Figure 5 compares the heat capacity data with those taken from the literature and shows that our results calculated using the relative enthalpy curves presented in Fig. 4 agree better with the interpretation of the experimental observation^[23] and the recommended data by Fink^[20] than other MD results. Our fitted data agree very well with the data deduced by Ralph and Hyland^[23] and those recommended by Fink^[20] up to 2300 K. The agreement becomes poor in the superionic range.

We can see from Fig. 5 that all the simulated heat capacity data fall below the recommend data when the temperature is higher than 2500 K. Ronchi and Hyland^[24] found that the increase of heat capacity

is due to the formation of lattice and electronic defects mainly introduced by Frenkel defects from 1500 to 2670 K. While above the λ -phase transition, the Schottky defects play an important role. Thus, we guess that the deviation between the heat capacity data obtained by molecular dynamics simulation and those recommend in literature may attribute to the fact that the rigid model potentials are developed for the perfect fluorite structure of UO_2 and can not yet well estimate the attribution on the thermodynamic properties introduced by the defects at the superionic range.

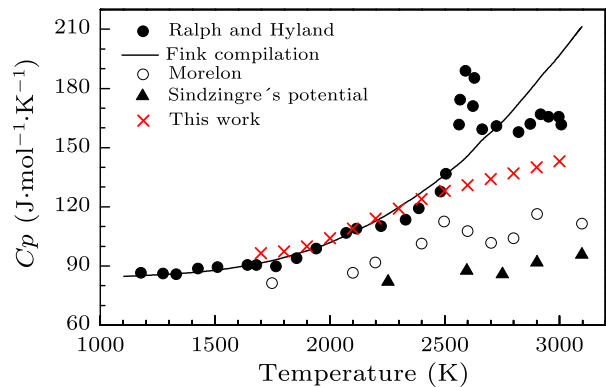


Fig. 5. Heat capacity variations of solid UO_2 at high temperature. The literature data are the values deduced by Ralph and Hyland from an analysis of the experimental data,^[23] analytic recommended by Fink,^[20] MD results by Morelon,^[2] the data obtained using Sindzinger's potential.^[22]

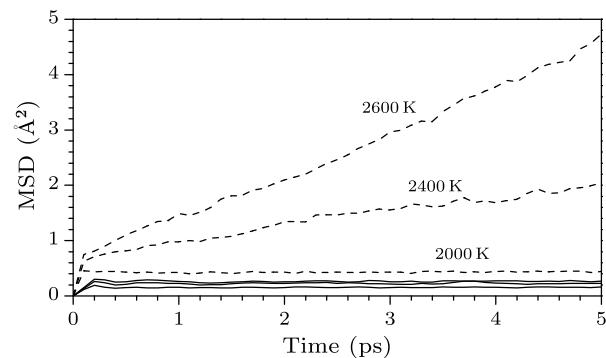


Fig. 6. Mean square displacement curves for uranium (solid) and oxygen (dashed) ions. No diffusion is visible in uranium sublattice, even at high temperature. Diffusion appears in the oxygen sublattice above 2000 K.

The λ -phase transition, which is an important contribution to the enthalpy and capacity in high temperature range, is investigated experimentally by Clausen^[25] and Hutchings.^[26] It reveals that this superionic phase is mainly due to the highly mobile oxygen ions. Experimental measures suggested that the oxygen sublattice becomes disordered in the range 2000–3000 K, that is, the defect concentration increases in this temperature range.

The cation and anion diffusion coefficients D_α have been obtained from the time-depend mean-square-

displacement (MSD) of the ions. The diffusion coefficients D_α are simply related to MSD by the Einstein relation defined as

$$\langle [\Delta r_\alpha(t)]^2 \rangle \xrightarrow{t \rightarrow \infty} B_\alpha + 6D_\alpha t. \quad (1)$$

Figure 6 displays the MSD of oxygen ions and uranium ions at three temperatures: 2000 K, 2400 K and 2600 K. It clearly shows that the superionic conduction appears at high temperature. The slope of the oxygen ion's MSD is zero at 2000 K, indicating that the disorder of oxygen sublattice does not appear below this temperature. The MSDs at 2400 K and 2600 K suggest that the slope of oxygen ion's MSD increases rapidly between 2000 K and 3000 K. The zero slope for the uranium ions confirms that the system is indeed in the solid phase.

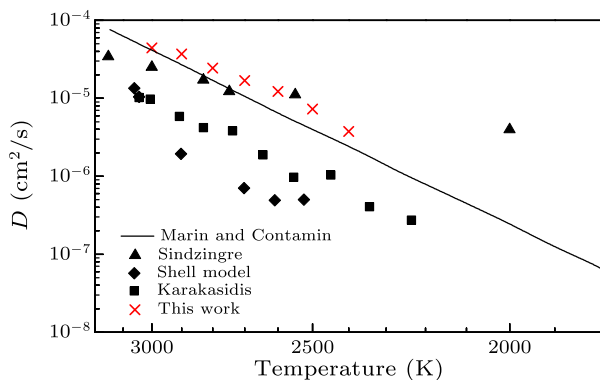


Fig. 7. Comparison of the present simulated and the previous values of oxygen diffusion coefficients. The literature data are the simulated results using the Karakasidis–Lindan^[21] potential, Sindzingre–Gillan^[22] potential and the shell model potential by Lindan and Gillan.^[28] The experimental data are taken from Marin and Contamin.^[27]

In Fig. 7, we present our results for the oxygen ion diffusion coefficients. These results can be compared with the extrapolated experimental data^[27] and other simulated results. The results obtained by the shell model^[28] and the Karakasidis–Lindan^[21] potentials are relatively close and underestimate the extrapolated experimental data by a factor of 5–10. We can obtain that the present simulations overestimate the diffusion coefficients slightly but still in good agreement with the recommended data. The Sindzingre–Gillan potential also reaches satisfactory results although the diffusion coefficients are overestimated clearly below 2500 K. Summarily, all the results of diffusion coefficients at high temperature presented in the figure are comparable with the recommended data with values 10^{-6} – 10^{-5} cm²s⁻¹.

In summary, MD simulations have been employed to evaluate the melting point and thermal properties of UO₂ using the interatomic potential developed by Morelen. For evaluating the melt point, two different types of simulations are applied, which are OPS and TPS. The results show that the OPS's estimate of melt point is too high to be acceptable, while the re-

sults of TPS are in agreement with the experimental measures, which indicates that the disordered liquid phase in the TPS plays a key role for melting.

Turning to thermodynamic properties, Morelen's rigid ionic potential can provide reasonable densities, values of lattice parameter versus temperature, relative enthalpy and heat capacity variations with temperature, but these results become poor in the superionic range. Thus, the rigid ionic potential can not yet correctly estimate the effect introduced by superionic conduction on the thermodynamic properties. New types of potentials are urgently needed to accurately estimate the thermodynamic properties for superionic phase. Lastly the MSD of oxygen and uranium ions are calculated and the oxygen ion diffusion coefficients are obtained. This rigid potential can describe the disorder of oxygen sublattice and can give us accurate diffusion coefficients for oxygen.

References

- [1] Sindzingre P and Gillan M J 1988 *J. Phys. C* **21** 4017
- [2] Morelon N D, Ghaleb D, Delaye J M and Brutzel L V 2003 *Philos. Mag.* **83** 1533
- [3] Arima T, Idemitsu K, Inagaki Y, Tsujita Y, Kinoshita M and Yakub E 2009 *J. Nucl. Mater.* **389** 149
- [4] Sun T Y, Long X G, Wang J and Hou Q 2008 *Chin. Phys. Lett.* **25** 1784
- [5] Cygan R T, Liang J J and Kalinichev A G 2004 *J. Phys. Chem. B* **108** 1255
- [6] Zou Y, Huai X L and Liang S Q 2009 *Chin. Phys. Lett.* **26** 013101
- [7] Govers K, Lemehov S, Hou M and Verwerft M 2007 *J. Nucl. Mater.* **366** 161
- [8] Karakaidis T and Lindan P J D 1994 *J. Phys.: Condens. Matter* **6** 2965
- [9] Jackson R A, Murray A D, Harding J H and Catlow C R 1986 *Philos. Mag. A* **53** 27
- [10] Ewald P P 1921 *Ann. Phys.* **64** 253
- [11] Schwen D, Huang M, Bellon P and Averbach R S 2009 *J. Nucl. Mater.* **392** 35
- [12] Plimpton S J 1995 *J. Comput. Phys.* **117** 1
- [13] Hoover W G 1985 *Phys. Rev. A* **31** 1695
- [14] Hoover W G 1986 *Phys. Rev. A* **34** 2499
- [15] Melchionna, Ciccotti and Holian 1993 *Mol. Phys.* **78** 533
- [16] International Nuclear Safety Centre (INSC), Material Properties Database, Argonne National Laboratory, Illinois, USA, <http://www.insc.anl.gov/matprop/>.
- [17] Drotning W D 1981 *Proceedings of the 8th Symposium on Thermophysical Properties, National Bureau of Standard* (Gaithersburg, Maryland 15–18 June 1981)
- [18] Christensen J A 1963 *J. Am. Ceram. Soc.* **46** 607
- [19] Harding J H, Martin D G and Potter P E 1989 *Commission of European Communities Report* EUR 12402
- [20] Fink J K 2000 *J. Nucl. Mater.* **279** 1
- [21] Karakasidis T and Lindan P J 1994 *J. Phys.: Condens. Matter.* **6** 2965
- [22] Sindzingre P and Gillan M 1988 *J. Phys. C* **21** 4017
- [23] Ralph J and Hyland G J 1985 *J. Nucl. Mater.* **132** 76
- [24] Ronchi C and Hyland G J 1994 *J. Alloys Compd.* **213/214** 159
- [25] Clausen K, Hayes W, Macdonald J E and Osborn R 1984 *Phys. Rev. Lett.* **52** 1238
- [26] Hutchings M T 1987 *J. Chem. Soc. Faraday Trans. II* **83** 1083
- [27] Marin J E and Contamin P 1969 *J. Nucl. Mater.* **30** 16
- [28] Lindan P J and Gillan M 1994 *Philos. Mag. B* **69** 535