A modified equation of state for Xe at high pressures by molecular dynamics simulation*

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The exact equation of state (EOS) for the fission gas Xe is necessary for the accurate prediction of the fission gas behavior in uranium dioxide nuclear fuel. However, the comparison with the experimental data indicates that the applicable pressure ranges of existing EOS for Xe published in the literature cannot cover the overpressure of the rim fission gas bubble at the typical UO_2 fuel pellet rim structure. Based on the interatomic potential of Xe, the pressure–volume–temperature data are calculated by the molecular dynamics (MD) simulation. The results indicate that the data of MD simulation with Ross and McMahan's potential [M. Ross and A. K. McMahan 1980 *Phys. Rev. B* **21** 1658] are in good agreement with the experimental data. A preferable EOS for Xe is proposed based on the MD simulation. The comparison with the MD simulation data shows that the proposed EOS can be applied at pressures up to 550 MPa and 3 GPa and temperatures 900 K and 1373 K respectively. The applicable pressure range of this EOS is wider than those of the other existing EOS for Xe published in the literature.

Keywords: equation of state, fission gas, molecular dynamics simulation

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1. Introduction

Uranium dioxide is the most commonly used nuclear reactor fuel.[1] It has been a subject of numerous experimental and theoretical studies for over half a century.[2,3] The mechanical stability of nuclear reactor fuel pins during reactor irradiation is to a large extent dependent on the thermodynamical state of the fission gas Xe retained in the fuel.

The fission gas Xe has various significant effects on the fuel rod integrity in a nuclear reactor; it can release the free volume of the fuel rod, leading to over pressurization and clad lift-off by a thermal feedback effect.[4,5] The fission gas products in a nuclear fuel pellet can also affect the fuel swelling and the thermo-mechanical properties of the fuel pellet.[6] Hence, an accurate prediction of the fission gas behavior is very necessary for the assessment of the integrity and performance of a nuclear fuel rod in the nuclear reactor.

The basic foundation for an accurate prediction of the fission gas behavior is the EOS of the fission gas Xe. As the fission gas mostly consists of inert gas elements, the van der Waals EOS has been used traditionally due to its simple form.[6] However, there is a possibility that the van der Waals EOS would not be applicable to over-pressurized gas bubbles, which has been observed at the rim of high burn-up UO_2 fuel pellets.[7–10] The over-pressure of the rim bubbles is therefore predicted to be in a range from tens of MPa to several hundreds of MPa.[9–12]

Ronchi[13] has extrapolated confidently the high temperature and high density pressure–volume–temperature data of Xe using a Leonard–Jones (LJ) interatomic potential based on a perturbation hard sphere model with the MD simulation. However, recent experimental data[14] show that the pressure predicted by Ronchi is higher than the experimental values. Oh[15] used the exponential-6 interatomic potential to investigate the behaviors of Xe gas atoms with MD simulation. He obtained the reasonable pressure–volume–temperature data for Xe but did not propose an applicable EOS for Xe. Unfortunately, the experimental data at very high pressures and high temperatures are very limited, so a modified EOS for Xe at high pressures by MD simulation would be useful and enable extrapolations to higher temperatures and pressures.

The rest of the paper is organized as follows. In Section 2, we review the EOS for Xe published in the literature. In Section 3, we introduce the method of MD simulations of Xe. In Section 4, we discuss the results of MD simulations and then establish an improved EOS for Xe in detail. Finally, some conclusions are drawn in Section 5.

2. EOS for Xe

There have been numerous theoretical attempts to predict the EOS for gases at high pressure. First of all, the van der Waals EOS is widely used for the Xe gas and other gases

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due to its consideration of repulsive force and very simple form.[16,17] The van der Waals EOS is expressed as

$$\left(P+\frac{N^2a}{V^2}\right)(V-Nb)=NkT, \tag{1}$$

where P is the pressure, V the volume, N the number of atoms, T the absolute temperature, k Boltzmann's constant and a and b are constants. For applying it to the fuel behavior models,[18] this equation is often simplified into

$$P(V-Nb)=NkT, \tag{2}$$

which is known as the reduced van der Waals EOS.

Harrison[19] proposed an extrapolated EOS for Xe from the existing argon EOS for higher pressures and temperatures. Data were not fitted into the EOS but summarized in table form.

A theoretical EOS has been calculated for non-attracting rigid spheres.[20] By using the Virial theorem of classical mechanics and assuming the total potential energy to result from the additive contributions of pairs of molecules, it is possible to relate the EOS to the radial distribution function, $g(r)$, by the following equation: [21]

$$\frac{PV}{NkT}=1-\frac{2\pi N}{3kTV}\int_0^\infty g(r)\frac{\mathrm{d}u(r)}{\mathrm{d}r}r^3\,\mathrm{d}r. \tag{3}$$

Here, the radial distribution function $g(r)$ describes the average density of atoms at a distance r from another atom located at $r=0$, divided by the overall density of atoms; $u(r)$ is the interatomic potential.

By making an appropriate approximation[22,23] for $g(r)$, the Percus–Yevick EOS may be derived as the following equation:

$$\frac{PV}{NkT}=(1+y+y^2)(1-y)^{-3}, \tag{4}$$

where

$$y=\pi d^3N/(6V),$$

d is the diameter of the atom. For $y<0.4$, the Percus–Yevick EOS is in good agreement with the results from Monte–Carlo and MD simulation; however, for $y\geq 0.4$, this EOS deviates from the simulation data.[16]

Carnahan and Starling[20] have calculated an EOS that reproduces the simulated data at a value of y up to 0.49, i.e., $y=0.49$ and so it is an improvement on the Percus–Yevick EOS in this high density region. The Carnahan–Starling EOS is expressed as

$$\frac{PV}{NkT}=(1+y+y^2-y^3)(1-y)^{-3}, \tag{5}$$

where as before,

$$y=\pi d^3N/6V.$$

Proceeding from strict thermodynamic equations, a three-parameter EOS for Xe is established by Kaplun and Meshalkin.[24,25] The EOS for Xe, considering the van der Waals force, is given as

$$P=\frac{RT}{V}\left(1+\frac{c}{V-b}\right)-\frac{a}{V^2}, \tag{6}$$

where a, b and c are fitting coefficients. It is shown that in a wide range of density of Xe, the proposed three-parameter EOS adequately describes the experimental data up to a high pressure.[25]

3. Method

The interatomic potentials for Xe–Xe, for which we choose the three most recent and widely used interatomic potentials given by Ross and McMahan,[26] Geng *et al.*[27] and Tang and Toennies,[28] are assessed by reproducing the high pressures of Xe at room temperature, 573 K and 800 K respectively.

The MD simulation program, GULP (general utility lattice program, version 6.0)[29] is employed for all the simulations. The simulations are performed in the NVT ensemble (constant N-number of atoms, V-volume, T-temperature) using a Nose/Hoover temperature thermostat.[30]

The number of Xe atoms is 8000 and they are distributed randomly. The MD runs in steps of 0.001 ps and the number of time steps is 6×10^4. The simulation stability is checked by using a variable number of atoms in a range from 500 to 8000. Although 1000 atoms are enough for most cases of the three potentials, the condition of 8000 atoms was selected to reduce the deviation.

4. Results and discussion

4.1. Comparison of simulated values with experimental data

As there have been no proper experimental data for Xe at high temperatures and pressures, experimental data at room temperature[14] are used for assessing the three potentials under high pressure conditions. Table 1 shows the comparison between the pressures calculated by three potentials with the experimental data[14] at room temperature. It is shown that the calculated pressures by Ross and McMahan's potential[26] are in good agreement with the experimental data at room temperature. The pressures predicted by the Geng *et al.* potential[27] and the Tang and Toennies potential[28] are all higher than experimental data.

Table 1. Comparison of the pressures calculated by three potentials with the experimental values[14] at room temperature.

Volume/(cm^3/mol)	Experimental pressure/GPa	Calculated pressure/GPa		
		Ross potential	Geng potential	Tang potential
32.10	0.80	0.86	1.49	1.15
31.53	0.95	0.96	1.61	1.29
27.51	2.39	2.09	3.00	3.19
25.98	3.02	2.89	4.01	4.56

The calculated pressures by three potentials are compared with the experimental values at 573 K;[31] the comparison results are shown in Fig. 1. It is shown that the MD simulation results from the Ross and McMahan potential[26] and the Tang and Toennies potential[28] accord well with experimental data in the pressure range below 40 MPa. Most of the calculated pressures by the Geng *et al.* potential[27] obviously deviate from the experimental data.

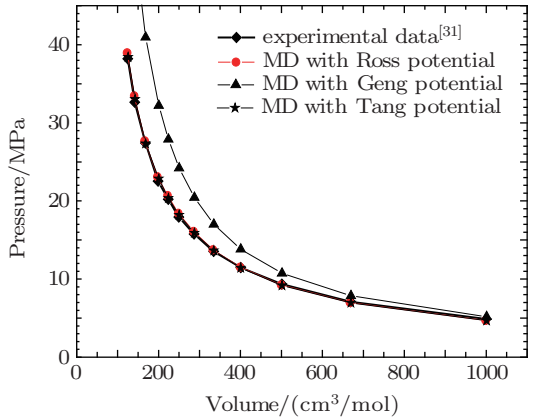


Fig. 1. (color online) Comparison of the pressures calculated by MD with the experimental data for Xe at 573 K.[31]

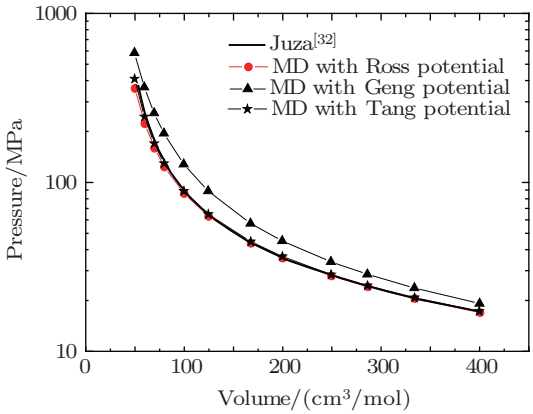


Fig. 2. (color online) Comparison of the calculated pressures by MD with Juza and Sifner's EOS fitted by experimental data for Xe at 800 K.[32]

The MD simulations pressures at 800 K by the three potentials are compared with the results extrapolated from EOS of Xe based on experimental data fitting by Juza and Sifner;[32] the comparison results are shown in Fig. 2. The calculated results by MD with the Ross and McMahan potential[26] and the Tang and Toennies potential[28] accord well with the results from the extrapolated EOS at pressures up to 400 MPa. However, all of the calculated pressures calculated by the Geng *et al.* potential[27] are higher than the experimental data obviously.

Hence it is thought that only the potential taken from the work by Ross and McMahan[26] can describe the behavior of Xe atoms at up to several GPa pressure and a high temperature. This pressure range covers the overpressure of the rim fission gas bubble in the UO_2 nuclear fuel up to several hundreds of MPa.[9–12]

4.2. Modified EOS for Xe

Figure 3 shows the temperature dependences of pressure. It is shown that the pressures calculated by MD vary linearly with temperature from 500 K to 1300 K for the cases of three different Xe densities (60 cm^3/mol, 80 cm^3/mol, and 100 cm^3/mol) obviously. So it is thought that the behaviors of Xe atoms can be described admirably by an EOS which has the characteristic that pressure varies linearly with temperature.

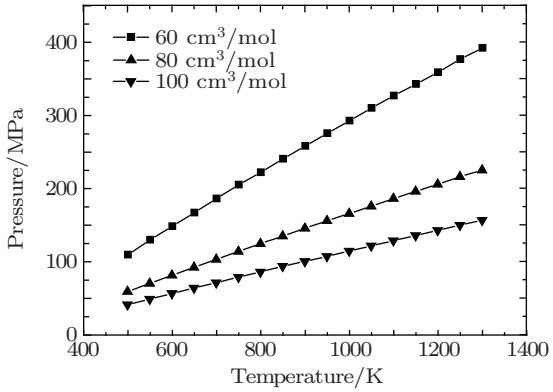


Fig. 3. Variations with temperature of the pressures as calculated from MD by the Ross and McMahan potential.[26]

Kaplun and[25] have proposed an EOS, in which only three parameters are used to describe the thermal properties of Xe and other gas atoms. The form of the EOS is shown in Eq. (6). From Eq. (6), it can be observed that the pressure varies linearly with temperature, which is the same as the result of this work. So, equation (6) is proposed to describe the behavior of Xe atoms in this paper and the three parameters a, b and c are fitted by MD data in Fig. 3. The parameters values of Eq. (6) in this work are given in Table 2.

Table 2. Values of parameters used in Eq. (6) in this work.

Parameters	Value
a/(J·cm^3/mol^2)	259780
b/(cm^3/mol)	23.9276
c/(cm^3/mol)	55.6583

4.3. Comparison with other EOS for Xe

Figure 4 shows the comparison of the pressure values derived from Eq. (6) in this work with those from the EOS for Xe published in the literature and MD simulation results with the Ross and McMahan potential[26] at selected temperatures of 900 K. The temperature of 900 K is the typical temperature for the in-pile rim structure in the LWR UO_2 fuel pellet. As there are no available experimental data at high temperature and MD simulation was verified in the previous section, our MD simulation results with the Ross and McMahan potential[26] are used as a reference for the comparison of EOS for Xe. The EOS was assumed to be acceptable if the difference between EOS and MD simulation results is lower than 15%. In the low pressure range where the effect of the van der Waals force is very small, the EOS and MD results both converge to the ideal gas law. Though the van der Waals EOS generally overestimates the pressure in the low pressure range, it matches the MD results reasonably well at pressures up to 23 MPa. The data of the Kaplun equation can be applied at pressures up to 150 MPa, while Ronchi's results accord well with the MD results at pressures up to 280 MPa. It is also shown in Fig. 4 that the pressure values derived from Eq. (6) in this work with the parameters values in Table 2 are in good agreement with the MD results at pressures up to 550 MPa.

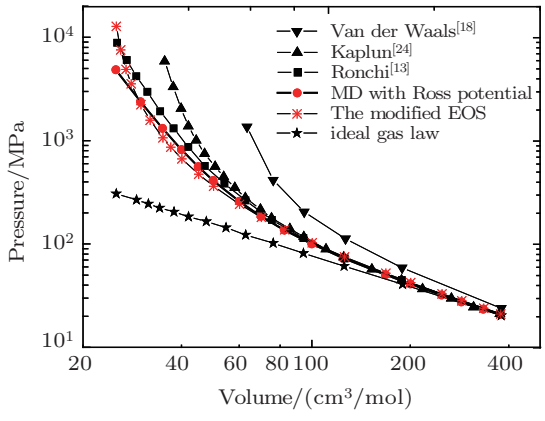


Fig. 4. (color online) Comparison of the MD data with the results from the EOS for Xe at 900 K.

A comparison of MD data with the results from the EOS for Xe at 1373 K is shown in Fig. 5. The temperature of 1373 K is the highest for the in-pile rim structure region in the LWR UO_2 fuel pellet.[7] The results from the van der Waals EOS match the MD results reasonably well at pressures up to 60 MPa. The data of the Kaplun equation can be applied at pressures up to 190 MPa, while Ronchi's results accord well with the MD results at pressures up to 650 MPa. It is also shown in Fig. 4 that the pressure values derived from Eq. (6) in this work using the parameter values in Table 2 are in good agreement with the MD results at pressures up to 3 GPa. As the temperature increases and Xe approaches to the ideal gas law behavior, the applicable pressure range of the EOS increases.

As the bubble pressure in the rim structure is predicted to range from tens of MPa to several hundreds of MPa,[9–12] the van der Waals EOS is not suitable for describing rim phenomena. The application ranges of the other EOSs for Xe are restricted up to some temperatures and pressures, but fortunately, the applicable temperature and pressure range of the EOS proposed by Eq. (6) in this work are wide enough to describe the behavior of Xe atoms in the rim structure of the LWR UO_2 fuel pellet.

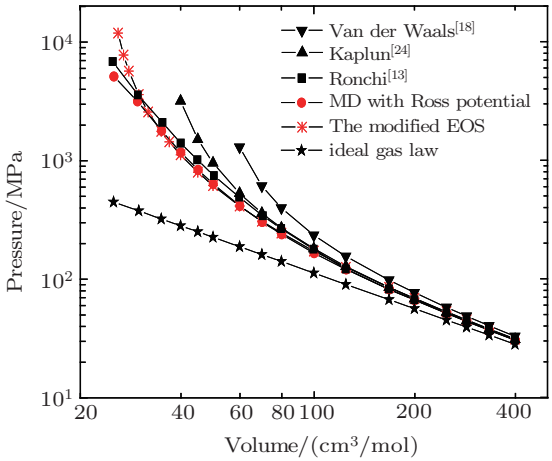


Fig. 5. (color online) Comparison of the MD data with the results from the EOS for Xe at 1373 K.

5. Conclusions

Proceeding from interatomic potentials presented by Ross and McMahan,[26] Geng *et al.*[27] and Tang and Toennies,[28] the pressure–volume–temperature data of Xe are calculated by MD simulation. The comparison with experimental data indicates that the MD simulation results with the interatomic potential of Ross and McMahan[26] are in good agreement with the experimental data. A modified EOS for Xe at high pressures based on the MD simulation results with the interatomic potential of Ross and McMahan[26] is proposed. The modified EOS can be applied at pressures up to 550 MPa and 3 GPa at 900 K and 1373 K respectively. The applicable pressure range of this EOS is wider than those of the other existing EOS for Xe published in the literature.

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