Available online at www.sciencedirect.com
ScienceDirect
Journal of Nuclear Materials 372 (2008) 89–93
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Molecular dynamics simulation of the pressure–volume–temperature data of xenon for a nuclear fuel

Jae-Yong Oh *, Yang-Hyun Koo, Jin-Sik Cheon, Byung-Ho Lee, Dong-Seong Sohn

Korea Atomic Energy Research Institute, P.O. Box 105, Yuseong, Daejeon 305-600, Republic of Korea

Received 6 October 2006; accepted 19 February 2007

Abstract

The exact equation of state for the fission gas is necessary for the accurate prediction of the fission gas behavior in a nuclear fuel. However, certain kinds of extrapolating data are used to construct and verify the equations of state for the fission gas because experimental data are very limited at high temperatures and pressures that are encountered in the nuclear fuel. To fill the lack of experimental data for the fission gas, the behavior of Xe gas atoms was investigated by molecular dynamics simulation assuming an exponential-six potential. The molecular dynamics simulation produced reasonable pressure–volume–temperature data for Xe and the simulation results were compared with existing equations of state for Xe.

PACS: 31.15.Qg; 51.30.+i

1. Introduction

The fission gas products in nuclear fuels have various significant effects on the fuel rod integrity in a nuclear reactor. They can release to the free volume of the fuel rod and lead to a high fuel rod overpressurization and a clad lift-off by a thermal feedback effect [1,2]. The fission gas products in a fuel pellet can also affect the fuel swelling and the thermo-mechanical properties of the fuel pellet [3]. Hence, an accurate prediction of the fission gas behavior is necessary for the assessment of the integrity and performance of a fuel rod.

The basic foundation for an accurate prediction of the fission gas behavior is the equations of state of the fission gas. As the fission gas mostly consists of inert gas elements, either the Van der Waals equation or the ideal gas law has traditionally been used due to their simple forms [3]. Since the internal rod pressure and the estimated equilibrium pressure of a sufficiently large gas bubble in a fuel pellet are not so high, the Van der Waals equation is in this case adequate.

However, there is a possibility that the Van der Waals equation would not be applicable to possibly overpressurized gas bubbles in the rim structure, which has been observed at the periphery of high burnup UO_2 fuel pellets [4,5]. As the in-pile temperature in the rim structure is markedly lower than that in the central part of a pellet, the atomic diffusivity in the rim is very low and an elastic equilibrium state in the gas bubbles cannot be achieved. The overpressure of the rim bubbles is therefore predicted to be tens to hundreds MPa [4,6,7], which is much higher than the equilibrium pressure, and thus exceeding the applicable range of the Van der Waals equation. The reliability of the equations of state can only be confirmed with experimental data over a wide range of temperatures and pressures. Unfortunately the experimental data for fission gas are very limited at high temperatures and pressures, and certain kinds of interpolating and extrapolating data are in some cases to be used.

The Xe element was selected as the representative of fission gas products in this paper because it was a major

* Corresponding author. Tel.: +82 42 868 2944; fax: +82 42 864 1089.
E-mail address: tylor@kaeri.re.kr (J.-Y. Oh).

0022-3115/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2007.02.009

element of fission gas products [3]. The pressure–volume–temperature (PVT) relationship for Xe was therefore evaluated by the molecular dynamics (MD) simulation with a refined interatomic potential. The results were compared with existing equations of state for Xe.

2. Equations of state for Xe

Before simulating the behavior of Xe gas atoms, the PVT data and the equations of state for Xe published in the literatures were reviewed to get information for the MD simulation. Although the Xe density was measured at room temperature under several GPa pressure [8], the experimental data at the nuclear fuel operating high temperatures are rare and also restricted to a low pressure range [9]. To fill the lack of experimental data for Xe, the equations of state for Xe were developed by extrapolating data of Ar or theoretical backgrounds [10–13].

As the pressure increases, the repulsive Van der Waals force between the Xe atoms starts to play an important role and produce a deviation from the ideal gas law. Because the Van der Waals equation of state considers the repulsive force and has a very simple equation form, it is widely used for the Xe gas [3]. It is expressed as

$$p(V-B)=RT, \tag{1}$$

where p is the pressure of the volume per mole V at temperature T, R is the gas constant and B is the volume occupied by the atoms. Although B is a function of the pressure and temperature, it is usually taken as a constant [3].

Harrison [10] proposed an extrapolated equation of state for Xe from the existing argon equation of state for higher pressures and temperatures. Data were not fitted into the equation of state but summarized in a table form. Kaplun and Meshalkin [13] proposed the equation of state for Xe with a consideration of the Van der Waals force as

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

where a, b and c are fitted coefficients. And a similar equation based on the same concept was also developed by Juza and Sifner [11].

Ronchi [12] took a different approach. The theoretical equation of state for rare gases was constructed starting from a hard sphere model and applying the perturbation method. It was very useful to extrapolate data at a low temperature and high pressure into those at a high temperature and pressure. However a recent measurement [8] shows that the pressure predicted by Ronchi is higher than the measured one. For example, the measured pressures at room temperature are 0.95 GPa in 53.33 Å^3/atom and 2.39 GPa in 45.70 Å^3/atom [8], but the pressure predicted by Ronchi were about 1.8 GPa and 4.2 GPa, respectively [12]. It means that the Xe atoms in a few GPa pressure range are softer than predicted.

Ronchi used the Lennard-Jones (L-J) interatomic potential which is

$$U(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^n-\left(\frac{\sigma}{r}\right)^m\right], \tag{3}$$

where ε and σ are the L-J energy and length parameters, and r is the interatomic distance. The n and m are exponents for the L-J potential. Although the L-J potential is generally used for the inert gas model, it may be less accurate in the high pressure range where the repulsive force is more dominant. This explains the discrepancy between the measurement and the prediction mentioned above. Hence a more flexible interatomic potential is necessary for more accurate predictions.

3. Condition for molecular dynamics simulation

For an interatomic potential, we choose the exponential-six potential [14]

$$U(r)=\varepsilon\left\{\frac{6}{\alpha-6}\exp\left[\alpha\left(1-\frac{r}{\sigma}\right)\right]-\frac{\alpha}{\alpha-6}\left(\frac{\sigma}{r}\right)^6\right\}, \tag{4}$$

where α is the fitting parameter for the exponential-six potential; $\alpha=13.0$, $\varepsilon/k=243.1$ K, $\sigma=4.37$ Å are used for the calculation [15], where k is the Boltzmann constant. The exponential-six potential is compared with the L-J potential for Xe in Fig. 1. The gradient of the exponential-six potential is less stiff than that of the L-J potential at the short interatomic distances where the repulsive force is dominant, and ε is also smaller in the exponential-six potential. Considering the reason of the discrepancy mentioned in the previous section, the softer exponential-six potential is suitable for this study.

The MD simulation was performed in the NVT ensemble (constant N-number of atoms, V-volume, T-temperature) with the modified MXDORTO program [16]. The number of Xe atoms was 2000 and they were distributed randomly. The time step (Δt) was 0.002 ps and the number of time steps was 10000. The simulation stability was checked by using a variable number of atoms in the range of 100–2000. Although 500 atoms resulted to be enough for most cases, the condition of 2000 atoms was selected to reduce the deviation.

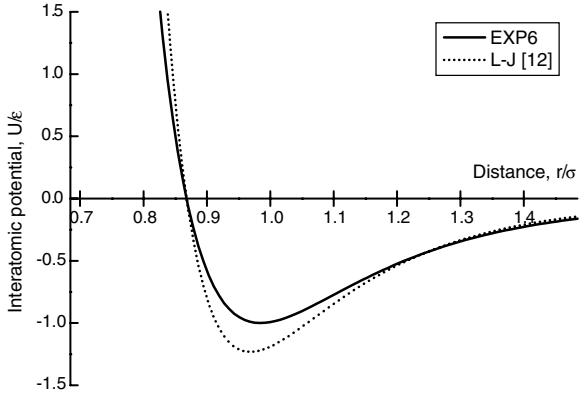

Fig. 1. Comparison of the exponential-six interatomic potential with the Lennard-Jones' for Xenon [12].

4. Results and discussion

4.1. Verification

As there were no proper experimental data for Xe at high temperatures and pressures, experimental data at room temperature [8] were used for a verification of the high pressure conditions. Table 1 shows that the calculated pressures are in good agreement with the measured data at room temperature.

The calculated pressures are compared with the measured ones at 573 K [9] in Fig. 2 to verify the calculation results in the pressure range below 40 MPa. The MD simulation results agree well with experimental data though they tend to slightly underestimate the pressure.

Hence it is thought that the exponential-six potential can describe the behavior of Xe atoms up to several GPa pressure at a high temperature. This pressure range covers the overpressure of a rim bubble in a nuclear fuel up to several hundreds MPa [5].

4.2. Comparison with other equations of state for Xe

The PVT data for Xe from 300 K to 2300 K simulated by MD were shown in Fig. 3. The range of temperatures and pressures in Fig. 3 covers the conditions of the nuclear fuels in reactors. The simulated pressures agree with Ronchi's data [12] at low pressures, but they are 40–50% lower than Ronchi's data at high pressure where the effect of interatomic potential is large. Fig. 4 shows a magnification of Fig. 3 at high pressures.

The MD simulation results were also compared with the equations of state for Xe at selected temperatures in Figs. 5 and 6. The temperature of 900 K is the typical temperature

Table 1
Comparison of the calculated pressures with the measured ones [8] at room temperature

Volume (cm^3/mol)	Measured pressure (GPa)	Calculated pressure (GPa)
32.10	0.80	0.83
31.53	0.95	0.93
27.51	2.39	2.04
25.98	3.02	2.83

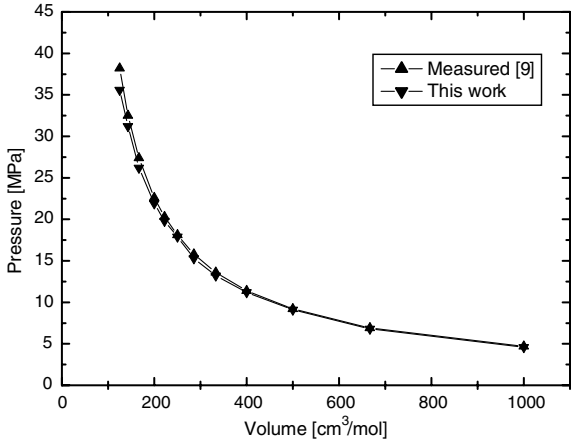

Fig. 2. Comparison of the calculated pressures with the measured data at 573 K [9].

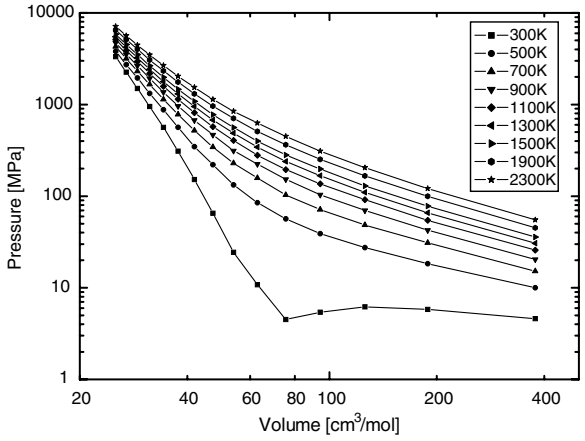

Fig. 3. Results of molecular dynamics simulation from 300 K to 2300 K.

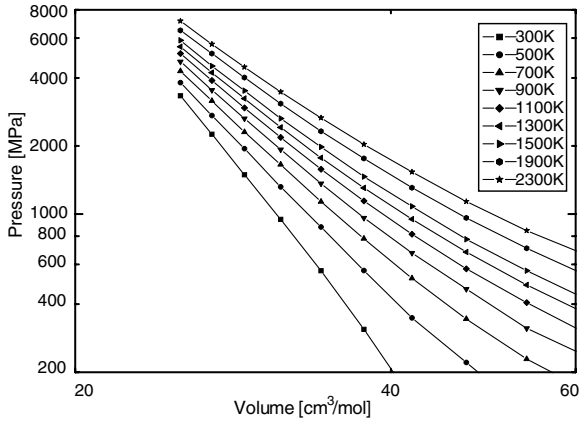

Fig. 4. High pressure range of Fig. 3.

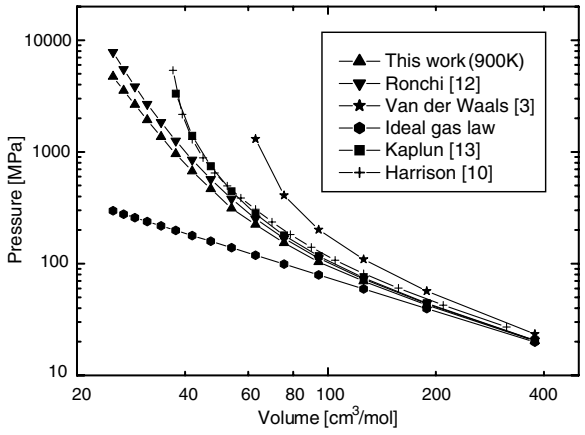

Fig. 5. Comparison of the MD data with the equations of state for Xe at 900 K.

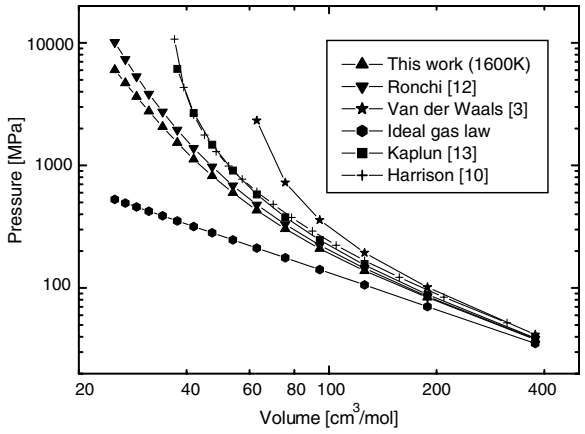

Fig. 6. Comparison of the MD data with the equations of state for Xe at 1600 K.

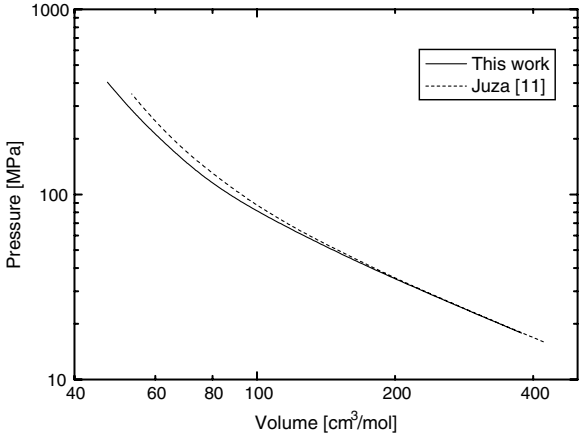

Fig. 7. Comparison of the MD data with Juza's equation of state for Xe at 800 K.

for the in-pile rim structure and the temperature of 1600 K for the centerline temperature in the a LWR fuel pellet. As there are no experimental data in the high temperature and MD simulation was verified in the previous section, our MD simulation results were used as a reference for the comparison of equations of state for Xe. Equations of state were assumed to be acceptable if the difference between equations of state and MD simulation results were lower than 15%. In the low pressure range where the effect of the Van der Waals force is small, all the equations of state and MD results converge to the ideal gas law.

A comparison of the equations of state for Xe at 900 K is shown in Fig. 5. Though the Van der Waals equation generally overestimated the pressure, it matched the MD results reasonably well up to 23 MPa. The data of Harrison agreed with the MD results up to 70 MPa. Kaplun's equation can be applied up to 150 MPa. And Ronchi's results showed a good agreement for the MD results up to 280 MPa.

As the bubble pressure in the rim structure is predicted to range from several tens MPa to several hundreds MPa [4,6,7], the Van der Waals' equation and Harrison data are not suitable for describing rim phenomena. Other equations of state for Xe should be used with a careful check of the calculated pressure with the applicable pressure range.

A comparison of the equations of state for Xe at 1600 K is shown in Fig. 6. The Van der Waals equation matched the MD results reasonably well up to 65 MPa. The data of Harrison agreed with the MD results up to 100 MPa. Kaplun's equation can be applied up to 210 MPa. And Ronch's results showed a good agreement for the MD results up to 730 MPa. As the temperature increases and Xe approaches the ideal gas law behavior, the applicable pressure range of the equations of state increased.

Another equation of state for Xe is compared at 800 K in Fig. 7. Juza proposed the extrapolated equation of state of Xe based on experimental data fitting [11]. This equation of state agreed well with the results calculated by MD. However, as its application range is restricted up to 800 K and 350 MPa [11], the application range is too low to apply it to the gas bubbles in nuclear fuels.

5. Conclusions

Assuming an exponential-six interatomic potential, the pressure–volume–temperature data for Xe were calculated by a molecular dynamics simulation for temperatures encountered in the LWR fuel under operating conditions. The comparison with experimental data indicated that the MD simulation showed good agreement with data. The simulation results were compared with existing equations of state for Xe to check the applicable pressure range of equations of state.

Acknowledgments

The Ministry of Science and Technology (MOST) of the Republic of Korea has sponsored this work through the Mid- and Long-term Nuclear R&D Project.

References

[1] Y.H. Koo, J.Y. Oh, B.H. Lee, D.S. Sohn, J. Nucl. Mater. 321 (2003) 249.
[2] W. Wiesenack, B.H. Lee, D.S. Sohn, Nucl. Eng. Technol. 37 (2005) 317.
[3] D.R. Olander, Fundamental Aspects of Nuclear Reactor Fuel Elements, Technical Information Center, Springfield, 1976.
[4] J. Spino, K. Vennix, M. Coquerelle, J. Nucl. Mater. 231 (1996) 179.
[5] G.L. Hofman, Y.S. Kim, Nucl. Eng. Technol. 37 (2005) 299.
[6] Y.H. Koo, B.H. Lee, J.S. Cheon, D.S. Sohn, J. Nucl. Mater. 295 (2001) 213.
[7] J.Y. Oh, Y.H. Koo, J.S. Cheon, B.H. Lee, D.S. Sohn, in: Proceedings of 2005 Water Reactor Fuel Performance Meeting, AESJ, Kyoto, Japan, 2005, p. 1161.
[8] A.N. Zisman, I.V. Aleksandrov, S.M. Stishov, Phys. Rev. B 32 (1985) 484.
[9] J.A. Beattie, R.J. Barriault, J.S. Brierley, J. Chem. Phys. 19 (1951) 1219.
[10] J.W. Harrison, J. Nucl. Mater. 31 (1969) 99.

[11] J. Juza, O. Sifner, ACTA Tech. CSAV 22 (1977) 1.
[12] C. Ronchi, J. Nucl. Mater. 96 (1981) 314.
[13] A.B. Kaplun, A.B. Meshalkin, Thermophys. Prop. Mater. 41 (2003) 373.
[14] M. Ross, A.K. McMahan, Phys. Rev. B 21 (1980) 1658.
[15] V. Schwarz, H. Juranek, R. Redmer, Phys. Chem. Chem. Phys. 7 (2005) 1990.
[16] K. Kawamura, K. Hirao, Material Design Using Personal Computer, Shokabo, Tokyo, 1994.