The development and validation of a combined interatomic potential for the description of Xe in γU-Mo fuels

Benjamin Beeler[a,b,*], Shenyang Hu[c], Yongfeng Zhang[b], Yipeng Gao[b]

[a] *North Carolina State University, Raleigh, NC 27607*
[b] *Idaho National Laboratory, Idaho Falls, ID 83415*
[c] *Pacific Northwest National Laboratory, Richland, WA 99354*

Abstract

1. Introduction

2. Computational Details

3. Results

3.1. Surface, formation and binding energies of voids and bubbles

$$E_{surf} = \frac{(E^* - E)}{A} \times N \tag{1}$$

*Corresponding author
Email address: benjamin.beeler@inl.gov (Benjamin Beeler)

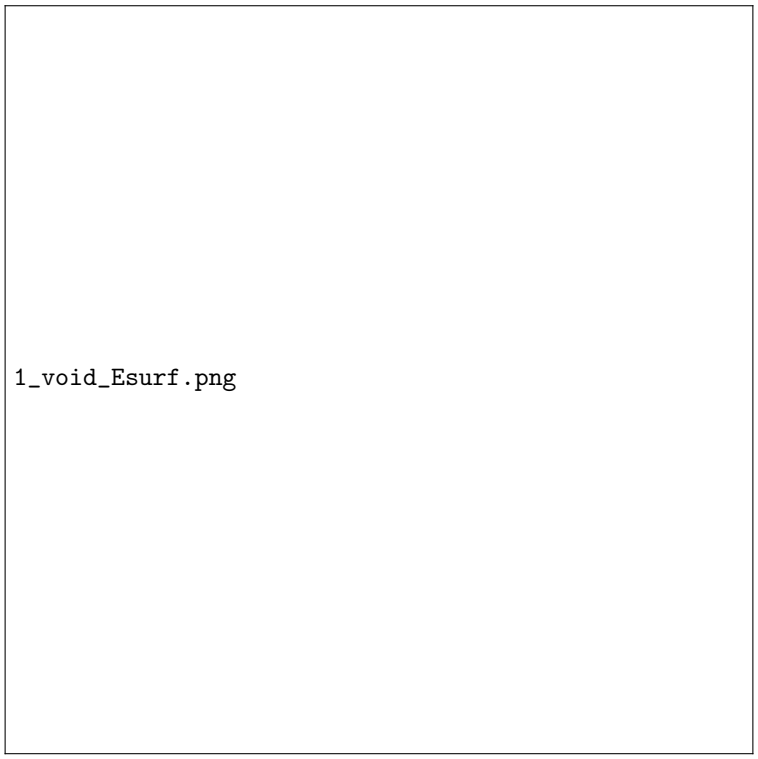

Figure 1: Void surface energy as a function of radius for voids in U-10Mo from 400 K to 700 K.

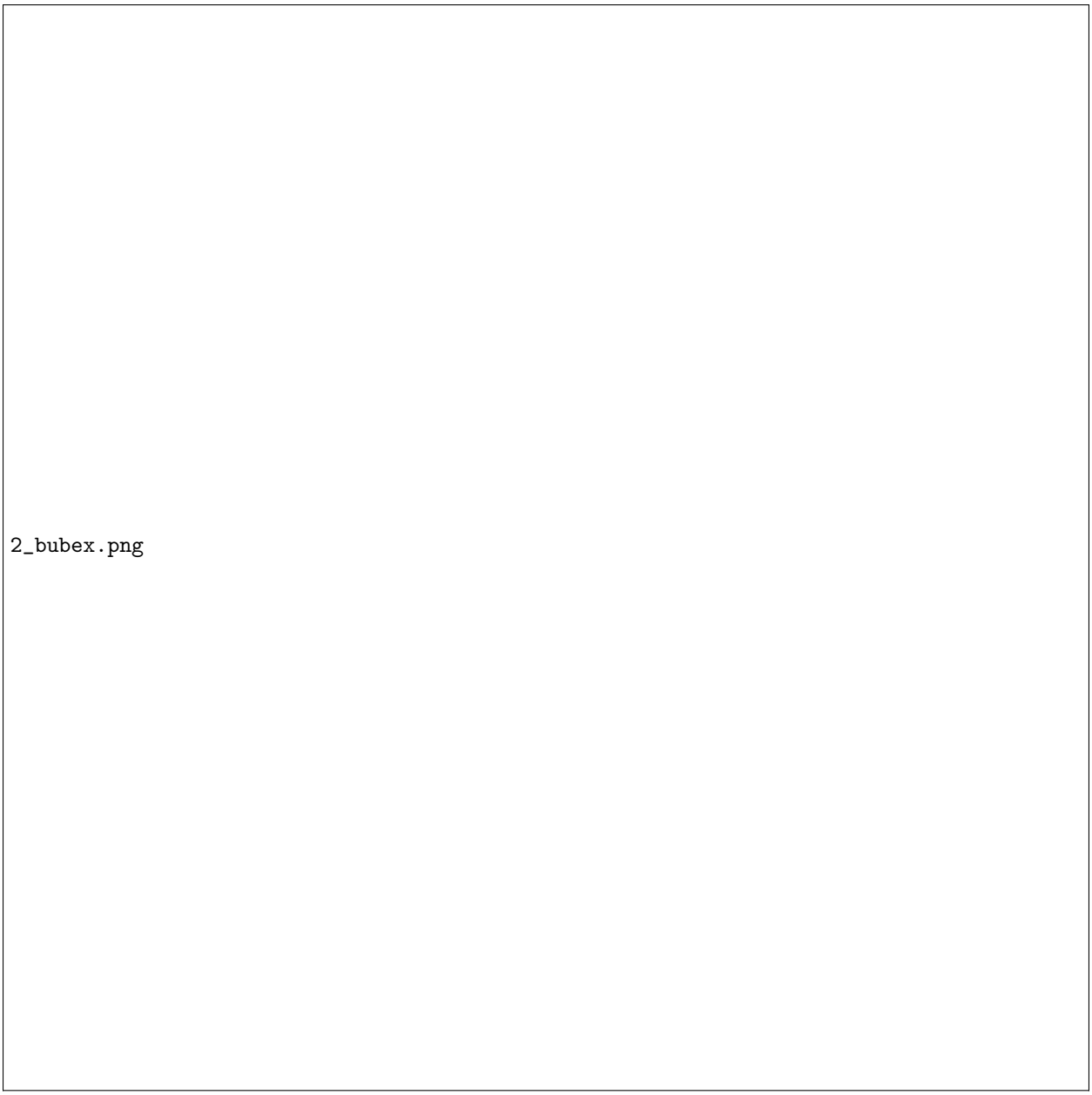

Figure 2: A Xe bubble at 500 K with a diameter of 7.1 nm in U-10Mo as a function of time. Starting from a void (a), to a Xe/vacancy ratio of 0.16 (b), and a Xe/vacancy ratio of 0.32 (c). Red atoms are U, blue atoms are Mo and green atoms are Xe.

$$E_f^{bub} = E^{bub} - \frac{N^{void}}{N^{sys}} E^{sys} \tag{2}$$

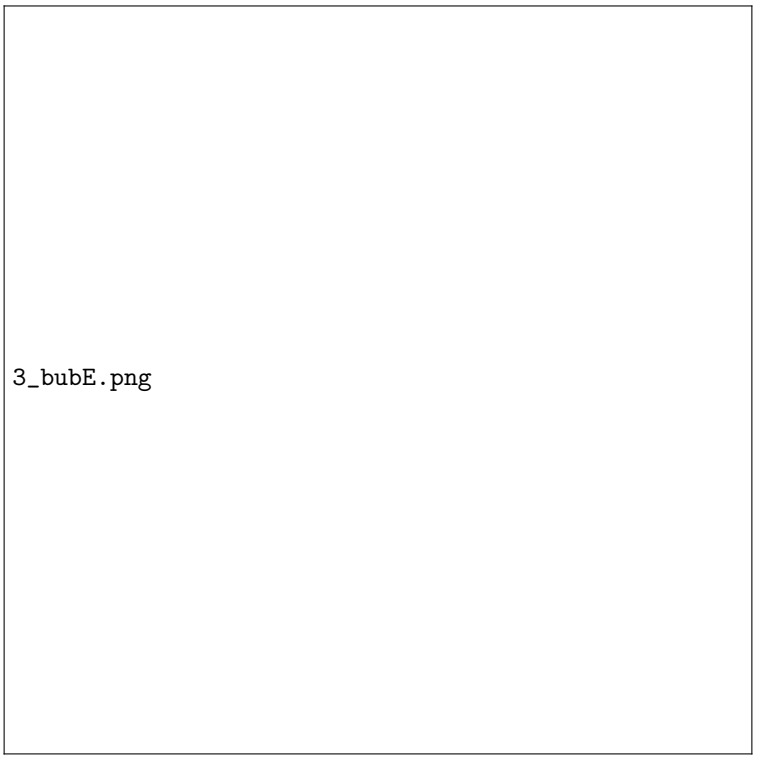

Figure 3: Relative bubble energy at 500 K as a function of Xe/vacancy ratio for bubbles of five unique sizes. Bubble diameters labeled, units in nm.

$$E^{bind} = E(n) - E(n-1) - E_{Xe}^{Sub} + E_{Vac} \tag{3}$$

$$E_f^{def} = E_F^{def} - E_F^{alloy} \tag{4}$$

$$E_F = E_{Tot} - E_U \times N_U - E_{Mo} \times N_{Mo} \tag{5}$$

Table 1: Point defect formation energies and binding energies in U-10Mo at 400 K. Units in eV.

Defect Type	Formation Energy	Binding Energy
Vacancy	1.6	-
Interstitial	1.1	-
Xe substitutional	6.1	-
Divacancy	2.1	-1.2
Xe sub-vac pair	7.4	-0.4

Figure 4: Binding energy of the nth Xe atom in a bubble as a function of the Xe/vacancy ratio.

3.2. Bubble pressurization transition

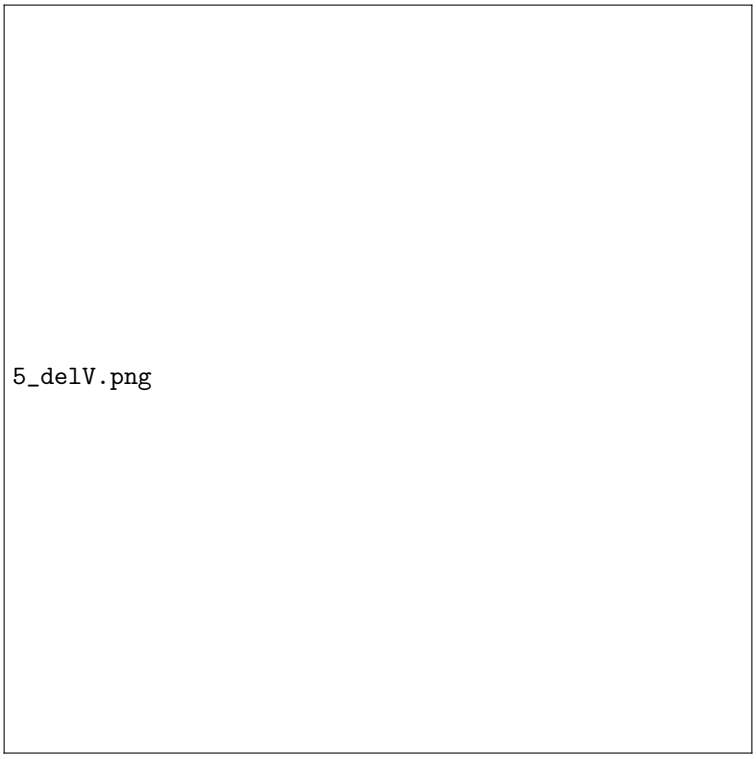

Figure 5: The normalized volume of a system with a bubble as a function of Xe/vacancy ratio for five unique bubble sizes. Bubble diameters labeled, units in nm.

$$P = \frac{2\gamma}{R} \tag{6}$$

Table 2: Predicted pressure based on Eq. 6, calculated pressure, and the subsequent difference. Units of pressure in GPa.

Diameter (nm)	Predicted	Calculated	Difference
3.1	1.39	0.24	1.15
4.4	1.07	0.31	0.77
5.7	0.82	0.43	0.38
7.1	0.65	0.43	0.22
8.5	0.55	0.43	0.13

$$P = \frac{2\gamma}{R} - A \times exp(-B \times R) \tag{7}$$

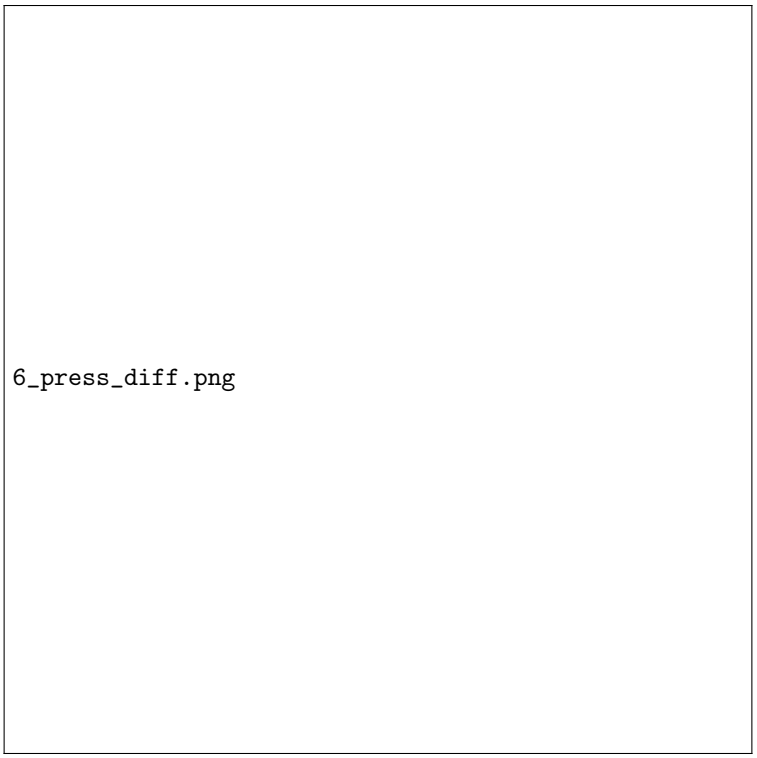

Figure 6: Predicted bubble pressure from Eq. 6 minus the calculated pressure from molecular dynamics as a function of bubble size.

3.3. Xe bubble equation of state in U-Mo

3.3.1. Kaplun EOS

$$P = \frac{RT}{v}\left(1 + \frac{c}{v-b}\right) - \frac{a}{v^2} \tag{8}$$

3.3.2. Virial EOS

A virial equation of state is utilized, expanded to the third order with respect to volume and the second order with respect to temperature, as is shown in equation 9,

$$P = \frac{RT}{v}\left(A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3}\right) \tag{9}$$

where A=1, and B, C and D are temperature dependent Taylor series of 1/T (B=b_0 + b_1/T + b_2/T^2, C=c_0 + c_1/T + c_2/T^2 and D=d_0 + d_1/T + d_2/T^2), leading to nine unique fitting parameters. The virial equation is a general function relating pressure, molar volume and temperature that can be directly derived from statistical mechanics [**?**].

The subsequent fit, with and without molecular dynamics data, is shown in Fig. 8 and Fig. 9, respectively.

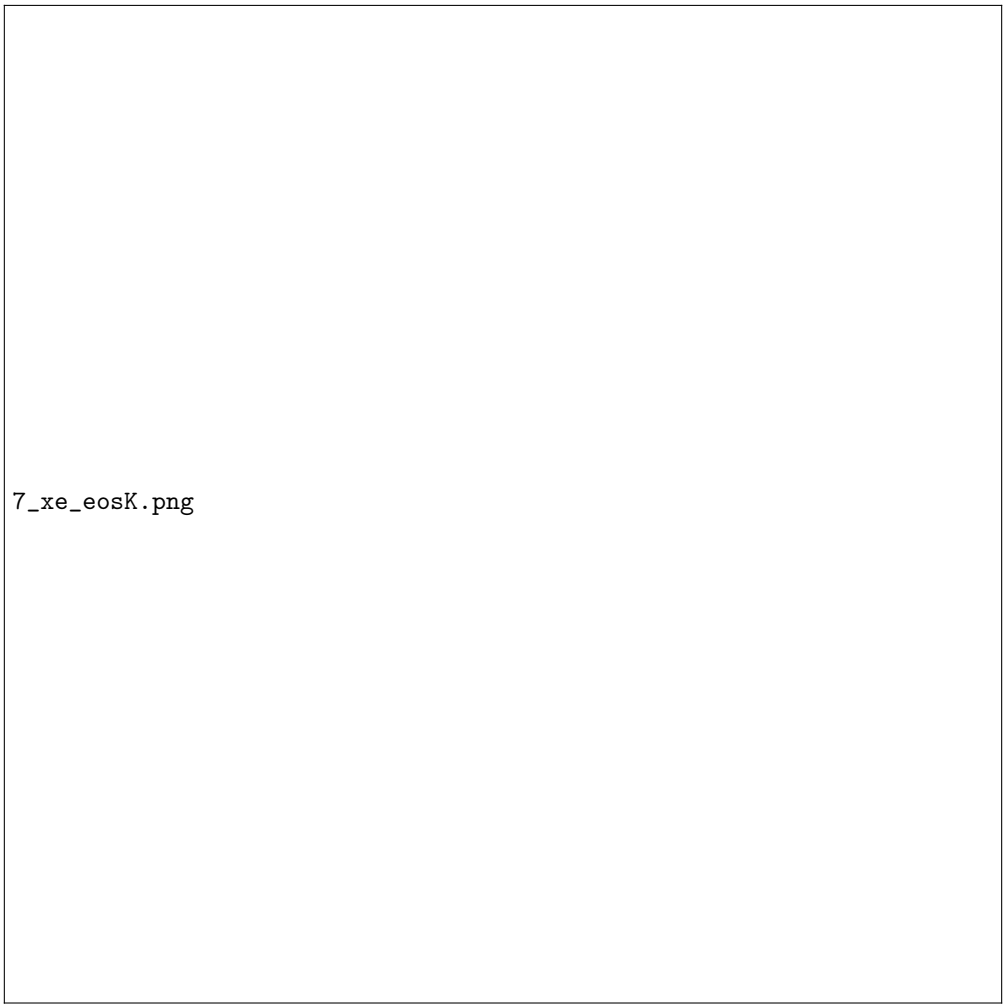

Figure 7: An equation of state (EOS) based on a modified Van der Waals equation from Kaplun for Xe bubbles in U-10Mo from 400 K to 700 K (a) compared to molecular dynamics data and (b) without molecular dynamics data.

Table 3: Virial equation of state (Eq. 9) parameters for Xe bubbles in U-Mo.

Parameter	Value
b_0	197.229 cm^3/mol
b_1	120307.145 cm^3-K/mol
b_2	60.555 cm^3-K^2/mol
c_0	-22038.723 cm^6/mol^2
c_1	2292.793 cm^6-K/mol^2
c_2	-117.564 cm^6-K^2/mol^2
d_0	1030015.045 cm^9/mol^3
d_1	-5.200 cm^9-K/mol^3
d_2	-280.677 cm^9-K^2/mol^3

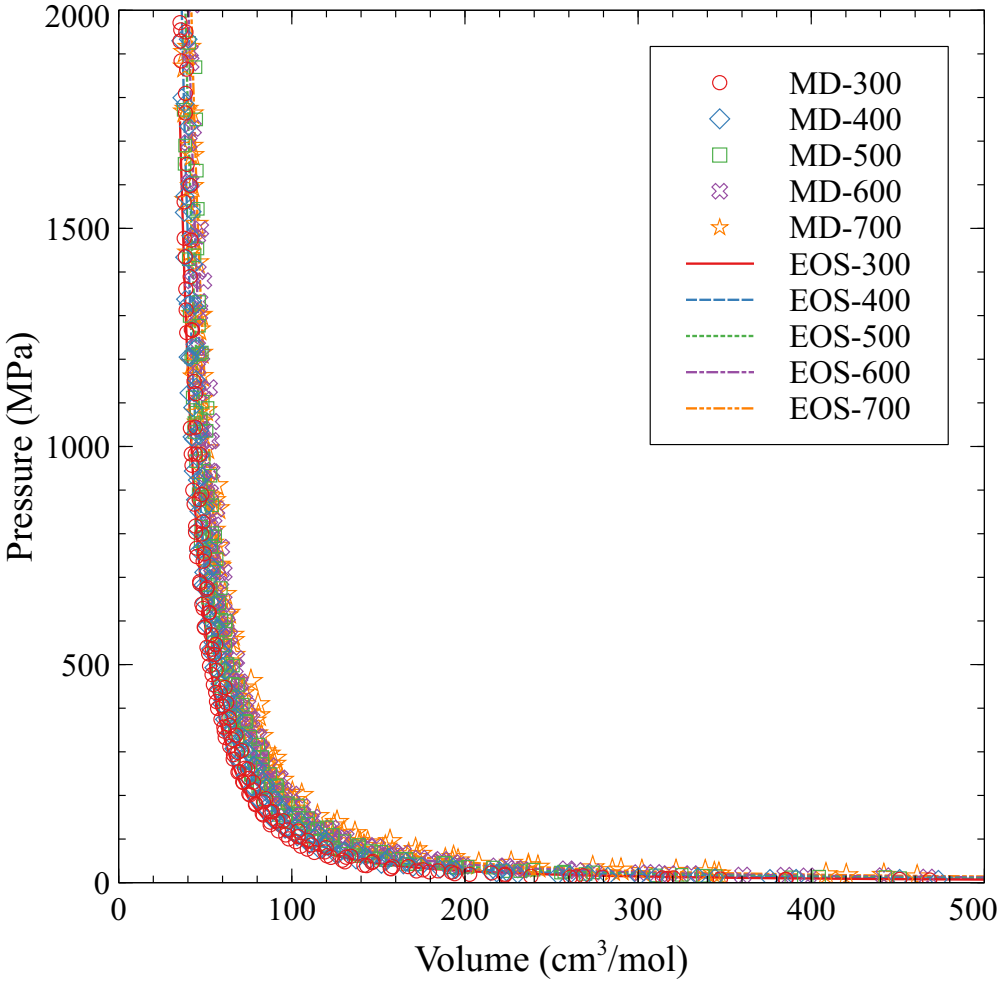

Figure 8: An equation of state (EOS) based on a virial expansion for Xe bubbles in U-10Mo from 400 K to 700 K (a) compared to molecular dynamics data and (b) without molecular dynamics data.

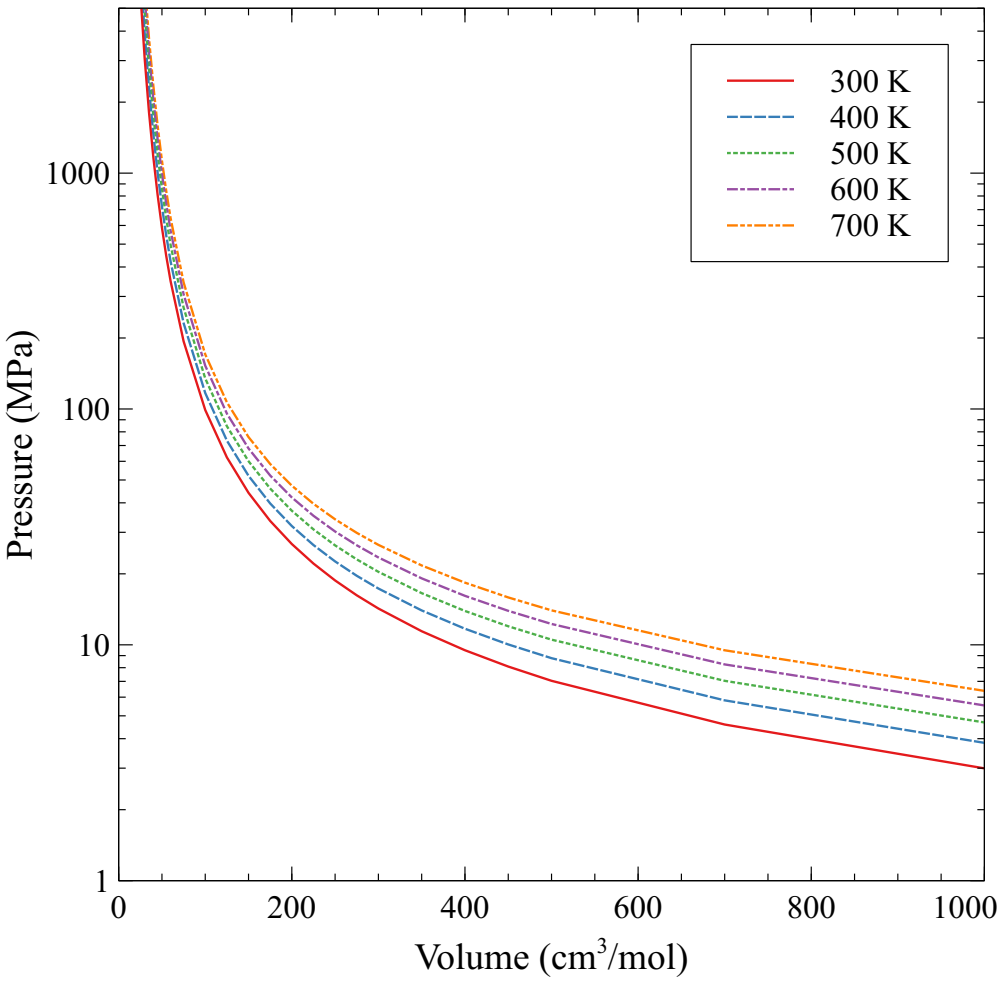

Figure 9: An equation of state (EOS) based on a virial expansion for Xe bubbles in U-10Mo from 400 K to 700 K (a) compared to molecular dynamics data and (b) without molecular dynamics data.

4. Conclusions

This work investigated Xe bubbles in γU-Mo from a diameter of 3 nm up to 8.5 nm and from 400 K up to 700 K. The energetic relationship of Xe bubbles with regard to voids and Xe point defects is described. The relative energy of a bubble increases quadratically as a function of Xe/vacancy ratio, with larger bubbles exhibiting a more rapid increase in energy. The binding energy of Xe atoms is negative, indicating attraction, for all bubbles and all Xe/vacancy ratios investigated. This shows that the energy of a Xe atom in the U-Mo lattice is sufficiently high, such that Xe will always want to reside in the bubble, regardless of bubble pressure investigated in this work. The under- to over-pressurized transition for bubbles is determined. This transition is below a Xe/vacancy ratio 0.2 for all bubbles in this work. A modification of the Young-Laplace equation is suggested to determine the equilibrium volume pressure of Xe bubbles in U-Mo. Finally, two distinct equations of state were fit to the pressure as a function of molar volume and temperature for Xe in U-Mo bubbles. The virial EOS variant represents an improvement in accuracy and extended applicability compared to a previously developed EOS.

The knowledge that the Xe/vacancy ratio depends on the bubble size and optimally decreases with increasing bubble diameter is valuable, in that the assumption is typically made of a constant Xe/vacancy ratio, regardless of bubble size. Also, the examined Xe/vacancy ratios in this study are somewhat lower than the previous estimate of fission gas densities in bubbles in U-Mo, although the pressures are similar in magnitude. A modification to the Young-Laplace equation will dramatically modify the suggested equilibrium state for small fission gas bubbles. The information provided in this work regarding bubble energetics, under- to over-pressurization transition, and an updated equation of state for Xe bubble in U-10Mo can be directly utilized to improve the fidelity of mesoscale models that describe fission gas induced swelling in U-Mo fuels.

5. Acknowledgement

This work was supported by the U.S. Department of Energy, Office of Material Management and Minimization, National Nuclear Security Administration, under DOE-NE Idaho Operations Office Contract DE-AC07-05ID14517. This manuscript has been authored by Battelle Energy Alliance, LLC with the U.S. Department of Energy. The publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for U.S. Government purposes. This research made use of the resources of the High Performance Computing Center at Idaho National Laboratory, which is supported by the Office of Nuclear Energy of the U.S. Department of Energy and the Nuclear Science User Facilities.