8.3 AN INITIAL ATOMISTIC-BASED EQUATION OF STATE FOR HELIUM IN IRON - R. E. Stoller and Y. N. Osetskiy (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this research is to determine the equation of state of helium in radiation-induced bubbles in iron-based alloys. Properties of He-bubbles significantly affect the evolution of the microstructure and mechanical properties under radiation damage conditions.

SUMMARY

An equation of state that accurately reproduces the pressure-volume relationship of helium is necessary to understand and predict the behavior of He-vacancy defects in irradiated materials. We have used *ab initio* calculations to determine the energetics of helium-vacancy clusters and applied the results to develop a new three-body interatomic potential that describes the behavior of helium in iron. The potential was employed in molecular dynamics simulations to determine the conditions for mechanical equilibrium between small helium-stabilized bubbles and an iron matrix, and to systematically map the pressure-volume relationship for the bubbles at a range of temperatures. These atomistic results are compared to an existing equation of state and a modification is proposed for bubbles with high helium densities.

PROGRESS AND STATUS

Introduction

The helium produced in irradiated metals and alloys by (n,α) transmutation reactions strongly influences microstructural and mechanical property changes. Helium is a particular concern for DT fusion reactor conditions because this environment will lead to significantly higher levels of He production than in fission reactor irradiation experiments where most data on radiation effects has been obtained. A prominent result of high He levels is the formation of very high densities of small He-vacancy clusters that can evolve into larger bubbles and voids. A computational model capable of predicting the behaviour of these small cavities requires an accurate equation of state to reproduce the pressure-volume relationship. Previous research has employed equations of state of varying complexity, including the ideal gas, van der Waals, and hard sphere models. Recent advances in high performance computing have made it possible to employ ab initio calculations to determine the energetics of larger and more complex atomic systems. Such calculations were used as the basis for development of a new three-body interatomic potential that accurately describes the behaviour of helium as either a substitutional or interstitial impurity in iron [1,2]. Molecular dynamics simulations employing this potential have been used to determine the conditions for mechanical equilibrium between small helium-stabilized bubbles and the iron matrix, and to systematically map the pressure-temperature relationship for He-filled bubbles. These atomistic results build on our previous research [3,4], and are compared to a hard-sphere equation of state we have used previously [5,6]. A modification of the hard-sphere model is proposed for bubbles with high helium densities.

Simulation Method

Molecular dynamics (MD) simulations were carried out at constant volume using a bcc iron system size of 128,000 iron atoms (40 lattice parameters cubed) containing helium-filled bubbles consisting of 9 to 44,399 vacancies, corresponding to nominal radii (r_b) from ~0.25 nm to ~5.0 nm. The appropriate lattice parameter was used for each simulation temperature in the range from 300 to 1000 K. The helium density in the bubbles was the primary simulation variable, with the density expressed as either the helium-to-vacancy ratio or the number of helium atoms per unit volume. Note that when the bubble volume is required, it is calculated based on the number of vacancies in the bubble and the atomic volume, i.e. $V_b = n_v\Omega$, and not as a sphere of radius r_b. This distinction is particularly important for small bubbles. The interatomic potentials employed were those of Ackland and co-workers for iron [7] and the ORNL three-body He-Fe potential [2]. For each simulation condition, the simulations were carried out long enough (see below) to obtain an accurate determination of the bubble pressure. There is a slight linguistic ambiguity in the following discussion. When carrying out MD simulations, it is common to use the term "equilibration" to describe the process of carrying out a simulation long enough for the total system energy to be equally distributed between kinetic and potential energy. We follow this convention here. However, we also wish to determine the equilibrium state of bubbles as discussed in the next paragraph. The latter we refer to as a condition of mechanical equilibrium. Although the MD simulations do not account for any influence of quantum effects that may occur with helium at high densities, previous work indicated that these effects are not significant above about 50 K even for very high pressures [8].

Results

The helium density is a useful parameter for determining the helium inventory in irradiated materials, and is a critical parameter in any equation of state. The helium-to-vacancy ratio for equilibrium bubbles is shown in Fig. 1. The temperature dependence in the ratio is not strong, except for the 0.25 nm

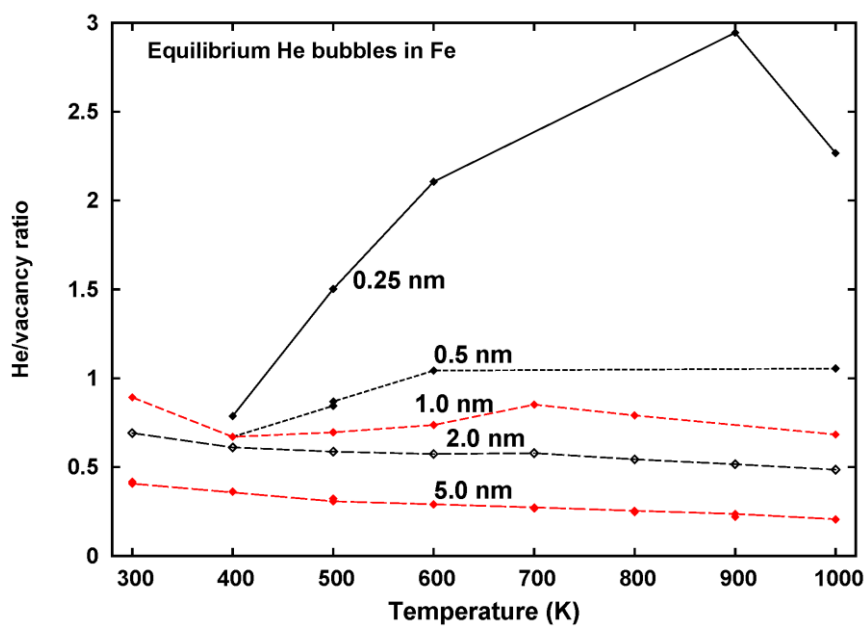

Figure 1. Helium-to-vacancy ratio for bubbles with radius shown, in mechanical equilibrium with the iron lattice for the indicated conditions.

bubbles. The ratio varies from 0.69 to 0.48 and 0.4 to 0.2 between the temperatures of 300 and 1000 K for 2 and 5 nm bubbles, respectively. There is a stronger dependence on bubble radius, ranging from 0.4 to 0.9 and from 0.2 to 1.0 between 5 nm and 0.5 nm at 300 and 1000 K, respectively. The results for 0.25 nm bubbles exhibit a stronger temperature dependence and higher values than the bubbles with larger radii. This may be related to a He phase change within the bubbles as discussed by other researchers [9-11]. In an initial assessment of the pair correlation functions obtained for He in these small bubbles, the He appears to be in the gas phase for 2 and 5 nm bubbles at all temperatures and in 1 nm bubbles at high temperatures. For the 0.25 and 0.5 nm bubbles and 1 nm bubbles at low temperatures the structure observed in the pair correlations is consistent with liquid or solid-like behavior. A more detailed analysis of the pair correlations and He diffusion behavior is underway and will be reported elsewhere. Note that there are two closely spaced data points at 500 K for the 0.5 nm radius. Only this very small difference was observed between MD equilibrations that started at different points to assess of the accuracy of the calculated values.

The He compressibility is defined as the ratio of the bubble pressure obtained from the MD simulations to the ideal gas pressure for the same bubble size, temperature, and helium content. The compressibility of bubbles in mechanical equilibrium with the iron lattice is shown as a function of bubble radius in Fig. 2a and as a function of the He/vacancy ratio in 2b. All temperatures are included for each radius and the line connects values at 500 K as a guide to the eye. There is a clear increase in scatter for He/vacancy ratios greater than about 0.7 (compressibilites greater than about 8) in Fig. 2b. This may be related to the He phase change mentioned above. Additional analysis of bubble behavior for higher He/vacancy ratios is underway and will be published elsewhere.

Brearley and MacInnes developed a hard-sphere equation of state (HSEOS) for helium based on the formalism of Carnahan and Starling [12]. Although the simple form of the equation neglects some of the potentially significant correction terms discussed by Wolfer, et al. [13] and Trinkaus, et al. [14,15], their model predicted compressibilities (Z) in good agreement with a somewhat limited amount of relatively low temperature (~65°C), high pressure helium data [5]. The equation of state has the following form:

$$Z = \frac{PV}{mkT} = \frac{(1 + y + y^2 - y^3)}{(1 - y)^3} \quad (1)$$

where y is proportional to the helium density: $y=(\pi d_g^3/ 6)\cdot(m_{He}/V_b)$, d_g is the effective hard sphere diameter of the He atoms, m_{He} is the number of He atoms, and V_b is the bubble volume in nm^3. The hard sphere diameter is determined by the interatomic potential assumed; Brearley and MacInnes employed a modified Buckingham potential leading to a four-parameter expression for $d_g=0.3135\ [0.8542 - 0.03996\ ln(T/9.16\ K)]$ nm. This equation of state was adopted previously for use in models of bubble evolution and void swelling [6]. For comparison with the hard-sphere equation of state, compressibilities were calculated as the ratio of the bubble pressure obtained from the MD simulations to the ideal gas pressure for the same bubble size, temperature, and helium content. Because the values cover a range of discrete conditions (radii, helium densities, and temperatures), they are plotted as individual data points in Fig. 3a. Perfect agreement between the HSEOS and MD results would follow the 1:1 in Fig. 3a.

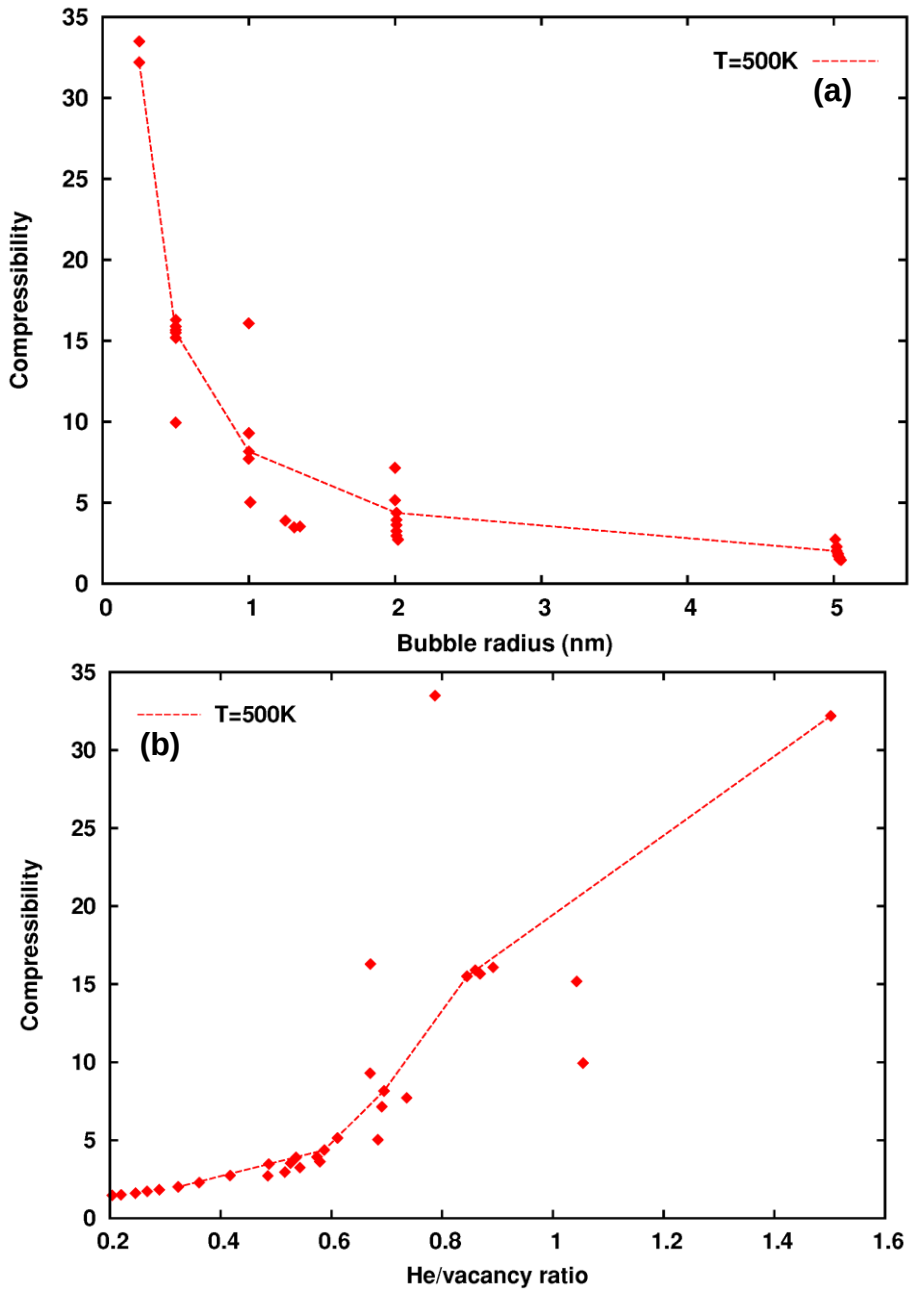

Figure 2. Compressibility of bubbles in mechanical equilibrium with the iron lattice as a function of bubble radius (a) and He/vacancy ratio (b), all temperatures are shown for each radius and line connects values at 500 K. Compressibility defined as the pressure from MD simulations divided by ideal gas pressure.

For compressibility values less that about 2, there is reasonable agreement between the MD and HSEOS results. However, the MD-based compressibilities are significantly greater for higher helium densities. Moreover, the results become increasingly scattered as the bubble radius decreases. This appears to be a result of two aspects mentioned previously: (1) the statistical difficulties associated with small

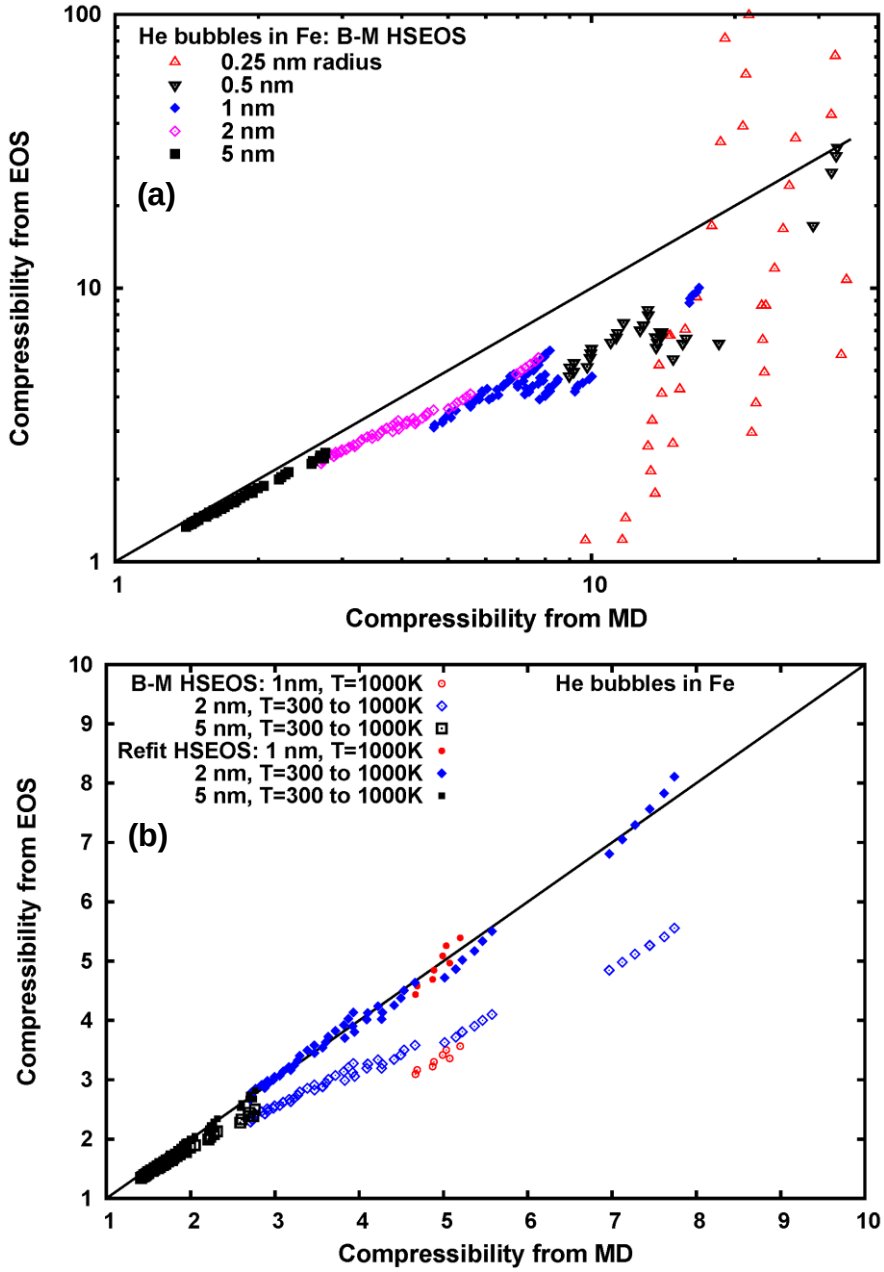

Figure 3. Comparison of compressibility obtained from MD simulations with those calculated using the Brearley-MacInnes hard-sphere equation of state [4]: (a) original parameters for all conditions, and (b) comparison of original parameters with those obtained from the non-linear fitting process as discussed in the text, see Table 1.

numbers of vacancies and He atoms in the smallest bubbles, and (2) the apparent phase change associated with the highest pressures. In addition, as reported previously [2,3], He atoms do not uniformly fill the bubble volume due to a strong, short-range Fe-He repulsion. A small radial gap is observed between the time-averaged position of the outermost He atoms and the bubble surface. This effectively reduces the active bubble volume and increases the pressure. Since the gap is nearly independent of the bubble radius, the relative impact is larger for smaller bubbles.

In order to provide an improved description of the MD results, the data was used as the basis for refitting the parameters in the HSEOS. The non-linear generalized reduced gradient method implemented in the Microsoft Excel *Solver* function was employed in the fitting process. The fitting parameters were the four coefficients in the hard sphere diameter d_g listed above and the size of the radial gap (Δr) between the He atoms and the bubble surface. As discussed above, the bubble volume in the HSEOS is determined by the number of vacancies rather than the nominal radius. The impact of Δr was accounted for in the context of an effective change in the atomic volume of the bubble which scaled as the cube of the corrected to nominal radius: $V_b^{eff} / V_b = (r_b - \Delta r)^3 / r_b^{\ 3}$. Based on the systematic trends on the MD results that have already been discussed, the fitting database included all results for 2.0 and 5.0 nm bubbles and the 1000 K results for 1.0 nm bubbles. The results of the fitting process are shown in Fig. 3b, which clearly demonstrates the improved agreement. The applicable range of the compressibilities in Fig. 3b includes most conditions of interest to reactor materials. Future work will examine scenarios for extrapolating the HSEOS to higher compressibilities. The coefficents obtained in the fitting process are listed in Table 1.

Table 1. Coefficients obtained from fitting the HSEOS to the MD results

Fitting Parameter	**Original HSEOS**	**Refit HSEOS**
a_1	*0.3135*	0.319332
a_2	*0.8542*	0.865456
a_3	*0.03996*	0.041802
a_4	9.16	9.228038
Δr	n/a	0.057389
Hard-sphere gas atom diameter: $d_g = a_1 [a_2 - a_3 \ln(T(K)/a_4)$, *T= temperature in K*		
Effective reduced bubble volume: $V_b^{eff} / V_b = (r_b - \Delta r)^3 / r_b^{\ 3}$		

Comparison with Experiments

The MD simulations employing the ORNL three-body He-Fe potential [1] indicate that the helium-to-vacancy ratio for equilibrium bubbles large enough to be visible in the transmission electron microscope is in the range of 0.3 to 1.0. Values greater than 1.0 are obtained only for bubbles with radii less than 1 nm. This result is consistent with recent experimental measurements using electron energy loss spectroscopy to determine the helium-to-vacancy ratio for small helium bubbles in ferritic-martensitic steels [16,17]. The helium density results of Wu et al. for a 1.3 nm bubble lead to a He/vacancy ratio ~0.6 [17], and earlier measurements by Frechard et al. for bubbles between 2 and 5 nm for which the He/vacancy ratio was in the range of 0.25 to 0.85 [16].

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