A stochastic differential equations approach for the description of helium bubble size distributions in irradiated metals.

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Abstract

A rate theory model based on the theory of nonlinear stochastic differential equations (SDEs) is developed to estimate the time-dependent size distribution of helium bubbles in metals under irradiation. Using approaches derived from Itô's calculus, rate equations for the first five moments of the size distribution in helium-vacancy space are derived, accounting for the stochastic nature of the atomic processes involved. In the first iteration of the model, the distribution is represented as a bivariate Gaussian distribution. The spread of the distribution about the mean is obtained by white-noise terms in the second-order moments, driven by fluctuations in the general absorption and emission of point defects by bubbles, and fluctuations stemming from collision cascades. This statistical model for the reconstruction of the distribution by its moments is coupled to a previously developed reduced-set, mean-field, rate theory model. As an illustrative case study, the model is applied to a tungsten plasma facing component under irradiation. Our findings highlight the important role of stochastic atomic fluctuations on the evolution of helium-vacancy cluster size distributions. It is found that when the average bubble size is small (at low dpa levels), the relative spread of the distribution is large and average bubble pressures may be very large. As bubbles begin to grow in size, average bubble pressures decrease, and stochastic fluctuations have a lessened effect. The distribution becomes tighter as it evolves in time, corresponding to a more uniform bubble population. The model is formulated in a general way, capable of including point defect drift due to internal temperature and/or stress gradients. These arise during pulsed irradiation, and also during steady irradiation as a result of externally applied or internally generated non-homogeneous stress fields. Discussion is given into how the model can be extended to include full spatial resolution and how the implementation of a path-integral approach may proceed if the distribution is known experimentally to significantly stray from a Gaussian description.

Keywords: Rate Theory, Helium-Vacancy Clustering, Size Distribution, Stochastic Differential Equations

1. Introduction

In neutron irradiated ferritic/martensitic steels, helium bubbles form homogeneously in the matrix, and heterogeneously in close proximity to nano precipitates, dislocations, and grain boundaries. It is well-known that the size distribution of bubbles depends on the local environment, such as the proximity to precipitate interfaces, grain boundaries, external surfaces, and dislocations. The stress field thus plays a significant role in determining whether a bubble has an equilibrium number of gas atoms, or that its gas atom composition is out of equilibrium.

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The challenge here is to predict not only the size distribution of helium bubbles at any spatial point in the material, but also the ratio of helium atoms to vacancies inside each bubble. Such information is crucial to controlling the effects of generated helium atoms during irradiation on the overall swelling and grain boundary fracture of irradiated steels.

Near the surface region in the tungsten (W) divertor region of tokamaks, the material is bombarded with low energy deuterium and helium plasmas, making the situation more complicated. Steep temperature and stress gradients exist near the surface, forcing bubbles to migrate and coalesce and lead to local material deformation. The literature is rich with experimental data on the response of tungsten to ion irradiation. Over a very large temperature range, tungsten samples exposed to lower energy (< 50 keV) helium implantation exhibit severe surface damage as helium bubbles coalesce at the surface [1, 2]. Prolonged exposure leads to the formation of a coral-like surface morphology, risking contamination of the fuel mixture [3]. An extensive review of experimental findings can be found in [4].

In general, bubbles may contain both vacancies and helium atoms, as well as hydrogen isotopes. Presently, there is no computational method that can describe the space-time-size-composition characteristics of such complex distribution functions. Density functional theory (DFT) calculations and Molecular Dynamics (MD) simulations can be useful in obtaining the energetics and parameterizations for more coarse grained models, but their reach is not adequate for the spatial and temporal requirements of the problem. Kinetic Monte Carlo (KMC) methods are not only extremely computationally intensive, but also limited to very small spatial regions and short time scales [4, 5, 6]. Similar limitations exist with current phase field models of bubble nucleation and growth [7, 8, 9]. Limitations on simulation domain sizes specifically create severe difficulties in gathering statistics of the bubble size distribution, which is of utmost importance in predicting the true internal bubble microstructure, and thus, the state of the material.

Current rate-theory approaches allow for both larger length and timescales, but must balance the cost-savings of a crude treatment of the rich variety of physics involved, with a potentially enormous set of rate equations. Direct integration of ($> 10^6$) rate equations [10], each representing one combination of a bubble's helium-vacancy content, is extremely computationally demanding and even more so when attempting to account for spatially varying drift-inducing internal forces on bubbles and point-defects. Significant reduction of the number of these equations by grouping methods that average over specified regions of the distribution [11] also face crippling computational requirements when spatial-resolution is to be applied and multiple species considered. One major limitation to the description of bubble size distributions in irradiated materials is that all existing approaches do not account for the physics of inhomogeneous point defect fluctuations introduced by displacement collision cascades. In other words, where one solves an enormous number of discrete rate equations, or group them into a smaller set, no mention is given in the model of how collision cascades affect the size distribution. That is a critical limitation, since we need to be able to extrapolate experimental results from one type of particle (e.g. electron, or ion) to another (e.g. fission or fusion neutrons).

In the following, we present a novel approach to solving this complex problem. The approach is based on the utilization of nonlinear Stochastic Differential Equations (SDE) to describe the time-dependence of the size distribution, not as a deterministic quantity, but as a probability distribution function that evolves in time in the material. The primary advantage of the method is the minimal number of required evolution equations that can describe the size distribution. In what follows, a previously developed reduced-set rate theory model is first reviewed, followed by a description of the SDE approach that we have developed to determine the size distribution. Then, a presentation of the results of a simulation of irradiated tungsten using the model is found in Section 3. Finally, a conclusion with discussion of potential future developments of this approach is given in Section 4.

2. Helium-Vacancy Cluster Size Distribution

Our objective is to describe the evolution of the helium-vacancy size distribution, $p(x_1, x_2, t)$, as a function of time, where we represent the average number of helium atoms and average number of vacancies in a bubble, by x_1 and x_2 , respectively. In a previous study by Ghoniem and co-workers [12], a reduced set of rate equations for the concentrations of vacancies (C_v), self-interstitials (C_i), helium interstitials (C_g), helium substitutionals (C_{gv}), di-helium interstitials (C_{2g}), di-helium mono-vacancy (C_{2gv}) and the critical nucleus (C^*) were developed. The critical nucleus here is taken as any cluster containing three helium atoms. These equations are conservation of mass rate equations for various species, where the rates of change in concentrations are to the sum of all production and loss rates, stemming from physical atomic processes (trapping/de-trapping, recombination, etc). We note that spatial variations due to defect diffusion were not considered, and the model follows the mean-field assumption for illustrative purposed. Under the approximation that the number of vacancies times the atomic volume equals the total bubble volume, we can express the rate equations for the average number of helium atoms per bubble (x_1), and the average number of vacancies per bubble (x_2) as [13]

$$\frac{\partial x_1}{\partial t} = 4\pi R\Omega^{-1}(D_g C_g) - x_1 b \quad (1)$$

$$\frac{\partial x_2}{\partial t} = \frac{4\pi R}{\Omega} \left(D_v C_v - D_i C_i - D_v C_v^e \left\{ \exp \left[\frac{\Omega}{kT} \left(\frac{2\gamma}{R} - p \right) \right] - 1 \right\} \right) \quad (2)$$

where the average bubble radius and pressure are given as

$$R = \left(\frac{3\Omega}{4\pi} \right)^{\frac{1}{3}} x_2^{\frac{1}{3}} \quad \text{and} \quad p = \frac{x_1 kT}{(4/3)\pi R^3 - x_1 B} \quad (3)$$

For equation (1), the first term on the right hand side represents the rate at which helium atoms impinge on bubbles of radius R , while the second represents their rate of re-solution into the matrix. In equation (2), the number of vacancies in bubbles is governed by three processes: (1) growth by the capture of diffusing vacancies, and shrinkage by (2) the capture of SIAs, and (3) the thermal emission of vacancies from pressurized bubbles.

Solution of the coupled equations introduced thus far provides knowledge of the time dependence of average sized bubbles, effectively representing a single point on the helium-vacancy size distribution, located at (x_1, x_2) . In this work, however, we wish to construct the full size distribution surface in helium-vacancy space. To accomplish this, we begin under the assumption that the distribution can be assumed to be a two-dimensional Gaussian. While this assumption provides good approximation for stochastic processes that are governed purely by white noise, path integral approaches may be implemented in more general applications, where the distribution function is known to be non-Gaussian, or even bimodal [14]. To construct the distribution, our first task is calculate the means and variances. For this, we use a nonlinear stochastic differential equations (SDE) approach with Itô's rule [15]. In what follows, we describe the method of differential equations for stochastic processes and apply it to the helium-vacancy cluster size distribution problem.

2.1. Stochastic Differential Form Representation of the Cluster Evolution Equations

When an otherwise deterministic variable, $x_i(t)$, is excited by a stochastic Brownian process, $dW(t)$, in general differential form, $x_i(t)$ can be expressed as [15]:

$$dx_i(t) = f_i(x_i(t), t)dt + g_i(x_i(t), t)dW_i(t) \quad (4)$$

where $dW(t)$ is a time continuous Wiener process representing Brownian fluctuations in the variable $x_i(t)$, and $g_i(x_i(t), t)$ is its variable coefficient. By adding the product of these stochastic terms to (1) and (2), and performing basic algebraic manipulations, we can re-express them in a simplified stochastic differential form as

$$dx_1 = \left(c_1 x_2^{1/3} - c_2 x_1 \right) dt + g_1(x_1, x_2, t) dW_1(t) \quad (5)$$

and

$$dx_2 = \left[c_3 x_2^{1/3} - c_4 x_2^{1/3} \exp \left(c_5 x_2^{-1/3} - \frac{c_6 x_1}{c_6 x_2 - c_7 x_1} \right) \right] dt + g_2(x_1, x_2, t) dW_2(t) \quad (6)$$

where the following parameters are defined:

$$\begin{aligned} c_1 &= \left(\frac{4\pi\sqrt{3}}{\Omega} \right)^{2/3} (D_g C_g) & c_4 &= \left(\frac{4\pi\sqrt{3}}{\Omega} \right)^{2/3} C_v^e D_v \\ c_2 &= b & c_5 &= \frac{2\gamma}{kT} \left(\frac{4\pi\Omega^2}{3} \right)^{1/3} \\ c_3 &= \left(\frac{4\pi\sqrt{3}}{\Omega} \right)^{2/3} (C_v D_v - C_i D_i + C_v^e D_v) & c_6 &= \Omega \\ & & c_7 &= B. \end{aligned} \quad (7)$$

We note here that the factors c_1 , c_3 , c_4 , and c_5 are (in general) spatially and temporally dependent, due to varying concentrations and temperature fields.

2.2. Itô's Rule for Obtaining Moments of Stochastic Differential Equations

Given the differential equation for a stochastic variable $x_i(t)$, we can compute any function of $x_i(t)$, such as $Y(t) = \phi(x_i(t), t)$, using Itô's rule [15]. Itô's rule provides the equivalent of the chain rule of calculus for the analysis of stochastic processes. For correlated stochastic processes, such as equations (5) and (6), the traditional Itô's rule takes a slightly modified form. Suppose we want to obtain an arbitrary function, $Y(t) = \phi(x_1(t), x_2(t), t)$, where x_1 and x_2 are correlated stochastic processes of the form in equation (4). Then we can express the SDE for $Y(t)$ as

$$dY(t) = \tilde{f}(x_1, x_2, t) dt + \phi_{,x_1} g_1(x_1, x_2, t) dW_1(t) + \phi_{,x_2} g_2(x_1, x_2, t) dW_2(t) \quad (8)$$

where

$$\tilde{f}(x_1, x_2, t) = \left[\phi_{,t} + \phi_{,x_1} f_1 + \phi_{,x_2} f_2 + \frac{1}{2} \phi_{,x_1 x_1} g_1^2 + \frac{1}{2} \phi_{,x_2 x_2} g_2^2 + \rho g_1 g_2 \phi_{,x_1 x_2} \right] \quad (9)$$

and f_i and g_i represent the coefficient terms of the incremental change in time and white noise for species i , obtained from its SDE. Commas denote derivatives and dW_1 and dW_2 are correlated Brownian terms with correlation coefficient ρ , defined by $E[dW_1 dW_2] = \rho dt$, where $E[X]$ is the expectation value of X . Denoting m_{ij} as the i^{th} moment in x_1 and the j^{th} moment in x_2 , we can obtain the moments of $x_i(t)$ in a straightforward way. For example, for the second moment in helium, m_{20} , we choose $Y(t) = \phi(x_1, x_2, t) = x_1^2$. Then we have

$$\tilde{f}(x_1, x_2, t) = \frac{\partial}{\partial x_1} [\phi(x_1, x_2, t)] f_1(x_1, x_2, t) + \frac{1}{2} \frac{\partial^2}{\partial x_1^2} [\phi(x_1, x_2, t)] g_1^2(x_1, x_2, t) \quad (10)$$

$$= 2x_1 \left(c_1 x_2^{1/3} - c_2 x_1 \right) + \frac{1}{2} (2) g_1^2(x_1, x_2, t) \quad (11)$$

Now, according to (8), we have

$$dY(t) = \left[2x_1 \left(c_1 x_2^{1/3} - c_2 x_1 \right) + \frac{1}{2} (2) g_1^2(x_1, x_2, t) \right] dt + 2x_1 g_1(x_1, x_2, t) dW_1(t) \quad (12)$$

and taking expectation values, we get

$$dE[Y(t)] = dE[x_1^2] = \left(2c_1 E[x_1 x_2^{1/3}] - 2c_2 E[x_1^2] + E[g_1^2(x_1, x_2, t)] \right) dt + 2E[x_1 g_1(x_1, x_2, t)] dW_1(t) \quad (13)$$

Since expectation values of white noise terms vanish, we are left with

$$\dot{m}_{20} = 2c_1 E[x_1 x_2^{1/3}] - 2c_2 m_{20} + E[g_1^2(x_1, x_2, t)] \quad (14)$$

Following the same procedure, we obtain the following five coupled differential equations for the first and second moments of the size distribution:

$$\dot{m}_{10} = c_1 E[x_2^{1/3}] - c_2 m_{10} \quad (15)$$

$$\dot{m}_{01} = c_3 E[x_2^{1/3}] - c_4 E \left[x_2^{1/3} \exp \left(c_5 x_2^{-1/3} - \frac{c_6 x_1}{c_6 x_2 - c_7 x_1} \right) \right] \quad (16)$$

$$\dot{m}_{20} = 2c_1 E[x_1 x_2^{1/3}] - 2c_2 m_{20} + E[g_1^2(x_1, x_2, t)] \quad (17)$$

$$\dot{m}_{02} = 2c_3 E[x_2^{4/3}] - 2c_4 E \left[x_2^{4/3} \exp \left(c_5 x_2^{-1/3} - \frac{c_6 x_1}{c_6 x_2 - c_7 x_1} \right) \right] + E[g_2^2(x_1, x_2, t)] \quad (18)$$

$$\begin{aligned} \dot{m}_{11} = c_1 E[x_2^{4/3}] - c_2 m_{11} + c_3 E[x_1 x_2^{1/3}] - c_4 E \left[x_1 x_2^{1/3} \exp \left(c_5 x_2^{-1/3} - \frac{c_6 x_1}{c_6 x_2 - c_7 x_1} \right) \right] \\ + E[\rho g_1 g_2] \end{aligned} \quad (19)$$

Because of the high degree of nonlinearity in these equations, after the application of Itô's rule, we are left with terms with which ensemble averages can not be easily computed directly. When the probability density function, $p(x_1, x_2, t)$ is known, the expectation value of any function, $r(x_1, x_2, t)$, can be numerically computed as

$$E[r(x_1, x_2, t)] = \int \int_R r(x_1, x_2, t) p(x_1, x_2, t) dx_2 dx_1, \quad (20)$$

where the integrated region, R , may be chosen such that it encompasses the entire distribution within some chosen tolerance. In our simulations we have found this approach to be accurate, as well as efficient enough for our application. However, for significantly heavier computations, a linear approximation of the terms may be desired.

The white noise coefficients, $g_i(x_1, x_2, t)$, represent the magnitudes of the fluctuations about the mean, and in general can be functions of x_1 , x_2 and time. In our case, these terms are taken in two categories: (1) fluctuations in the point defect capture and emission from bubbles (i.e. fluctuations in equations (1) and (2)), and (2) fluctuations stemming from the collision cascades themselves [16, 17, 18]. The first source of stochastic fluctuations in the bubble size arises from time lags in the arrival of single point defects. The second source is a result of the statistical nature of point defect production in collision cascades, and their subsequent diffusion. In reference [17], collision cascade size and shape effects on point defect diffusion during irradiation were determined, where a Kinetic Monte Carlo (KMC) model was used

to study different cascade structures, including sub-cascades in high energy collisions. The significant influence of collision cascades on the strength of point defect fluctuations was clearly shown [17]. In his simulations of collision cascade fluctuations, Marwick [18] has concluded that the RMS fluctuations in defect concentration are comparable to, or larger than, the mean concentration for all the irradiation conditions studied. For interstitials the fluctuations were found to be much larger than the mean. For the first category, we use the terms on the right hand side of equations (1) and (2). Since interstitial and vacancy absorption by bubbles leads to a spreading of the size distribution surface, all terms have a positive contribution. For the second category, we define two parameters, G_{He}^{casc} and G_V^{casc} , to represent fluctuations per unit time in the absorption of point defects due to the effects of the varying collision cascade atmospheres. Thus, our white noise coefficients take the form

$$g_1^2(x_1, x_2, t) = \frac{1}{2}c_1\bar{m}_{01}^{1/3} + \frac{1}{2}c_2\bar{m}_{10} + G_{He}^{casc}, \quad (21)$$

$$g_2^2(x_1, x_2, t) = \frac{1}{2}c_2\bar{m}_{10}^{1/3} + \frac{1}{2}c_4\bar{m}_{10}^{1/3} \exp(c_5\bar{m}_{01}^{-1/3} - \frac{c_6\bar{m}_{10}}{c_6\bar{m}_{01} - c_7\bar{m}_{10}}) + G_V^{casc}, \quad (22)$$

where the $\bar{m}_{ij}$ terms represent moments from the previous timestep. Now that all terms are properly accounted for, we may proceed to the solution.

3. Results

The task is to solve the rate equations for the moments of the distribution, (15)-(19), coupled with the reduced-set of rate equations. The rate-theory model is parametrized to represent a tungsten plasma-facing component operating under continuous irradiation. Solution of the stochastic differential equations for the moments requires the variables, c_1 - c_7 to be known. When an operating temperature for the simulation is chosen, all c_i 's are known except for c_1 and c_3 , which depend on time through the concentrations C_g , C_v , and C_i . Therefore, small concentrations are initially chosen for the species. To begin the simulation, initial values for the first moments, variances, and covariance of the distribution were also chosen and an initial (approximate) distribution was constructed. A grid of 40 by 40 points was used for its construction, and for the calculations involving integration over the distribution. As the means of the distribution changed in time, a remeshing of the grid was performed. To do this, at each timestep the rectangular grid was reconstructed, with its center at (m_{10}, m_{01}) and with half-lengths of $3\sigma_1$ and $3\sigma_2$ in the x_1 and x_2 directions, respectively, where σ_i is the computed standard deviation in the i^{th} direction. Several tests showed this indeed covered over 99% of the distribution as the distribution moved in He-V space. For very small bubble sizes (small m_{01}) with low helium content, a truncation of the distribution was made if at any time the tail of the distribution crossed into negative space, leading to incorrect values for the moments.

The results of an example simulation run at 1800 K is shown in figure 1, showing the evolution of the distribution in the first 200 seconds of irradiation time. Projections of the vacancy and helium profiles of the distribution are seen in blue and red, respectively, and the mean bubble radius and mean pressure ratio, are plotted in the inset plot on the left and right ordinate axes, respectively. Here, the mean pressure ratio represents the current pressure of the mean bubble (located at (m_{10}, m_{01}) in the size distribution) divided by the equilibrium pressure, P_{eq} , of a void containing the same number of vacancies, where $P_{eq} = 2\gamma/R$ and the pressure is computed according to (3). A listing of the parameters used can be found in table 1. The initial distribution was chosen to have a mean located at (60,140) with small standard deviations and a covariance factor of $\rho = 0.5$. The chosen damage rate is 3×10^{-3} dpa/s with a helium production rate of 5 appm/dpa. A homogeneous density of dislocation sinks is chosen

in the reduced rate equations, corresponding to a dislocation density of $3 \times 10^{10} \text{cm}^{-2}$.

In the very early stages of irradiation, we observe a rapid spreading of the distribution in the vacancy direction which continues to grow, stabilizing after about 100 seconds of irradiation. This rapid dispersion stems from the increased effect of the stochastic fluctuations when bubble sizes are very small. The stabilization begins to occur as the average bubble size increases. In these early times, from the nucleation regime until the average bubble reaches roughly 3 nm, the bubbles are observed to be highly pressurized ($P/P_{eq} \gg 1$). Due to the large difference in mobilities, when bubble concentrations and sizes are small, helium interstitials can more effectively find their way to bubbles than vacancies, leading to these large pressures. However, as the internal helium interstitial population decreases due to bubble capture, the vacancy capture rates become large enough to keep the pressures low. The steady state bubble pressures are strongly controlled by the helium generation rate, H , and the re-solution parameter, b , which can be tuned to replicate specific experimental data.

In the helium direction, the observed dispersion is also present, though not quite as significant, due primarily to the relatively low chosen helium production rate. A relatively stable period follows, where the dimensions of the distribution surface (governed by the second moments) remained approximately constant as the mean moved through the He-V phase space. After a short time, when the mean bubble sizes become larger, the width of the distribution in the vacancy direction begins to shrink. Physically, this signifies a tendency toward a more uniform bubble size distribution over time, which is observed experimentally from TEM micrographs [1, 2]. Physically, this can be explained by the coalescence of bubbles leading to a smaller spectrum of bubble sizes. In the post-nucleation regime, stochastic events will lead to a broad distribution in bubble sizes. Figure 2 shows the time evolution of the moments of the distribution (i.e. equations (15)-(19)) during the simulation.

The primary motivation for the present work is to introduce the methodology of the stochastic description of the size distribution evolution. Thus, the simulations conducted here were chosen to illustrate the core model. It is also important, however, to discuss how the model naturally lends itself to being extended to include full spatial resolution of the irradiated sample. Such an extension would be particularly useful for the identification of changes in the bubble distribution near highly-strained regions (near large precipitates, external stresses, etc.) which could help identify, among other things, regions at serious risk for the formation of a porous microstructure and/or micro-cracks. To accomplish this, a finite element model could be developed and the reduced set of rate equations modified to include spatially-dependent flux terms. Since the cluster size distribution varies from point to point in the material, one or several points in the material to probe the physics and obtain the size distribution would be chosen. The reduced set would be divided into two groups: mobile and immobile. For the mobile species, it is natural to choose vacancies, self-interstitials and helium interstitials, which carry the lowest migration barriers. Rate equations for all other species may remain spatially invariant due to their increased solubility in the matrix. To modify the rate equations for the mobile species, two additional diffusional flux terms must be added to the rate equations. The first term is the Brownian flux, $D_\alpha \nabla^2 C_\alpha$, and the second term is the flux due to drift forces, $\frac{D_\alpha}{kT} \nabla \cdot [C_\alpha \nabla E_{int}^\alpha]$, resulting from internal stress gradients. Here, α denotes the defect species (e.g. $\alpha = \text{V, SIA, He}$), D_α is its diffusion coefficient and E_{int}^α is the interaction energy of the defect. Under the influence of stress fields, the interaction energy of a species α , can be expressed as

$$E_{int}^\alpha = -\sigma_{ij} V_{ij}^\alpha, \quad (23)$$

where the formation volume tensor, V_{ij}^α , for cubic materials can be calculated in terms of the

dipole tensor, P_{ij} , as

$$V_{ij}^{\alpha} = \frac{P_{ij}c_{11} - (\text{tr}\mathbf{P} - 2P_{ij})c_{12}}{3\kappa(c_{11} - c_{12})}\delta_{ij} + \frac{1}{2c_{44}}P_{ij}(1 - \delta_{ij}), \quad (24)$$

where the material is defined by elastic constants c_{11}, c_{12}, c_{44} , and the bulk modulus $\kappa = \frac{1}{3}(c_{11} + 2c_{12})$. In a previous paper, we outlined a methodology by which the dipole tensor, and thus the formation volume tensor, for various point defects may be obtained through a matching procedure with atomistic calculations [19]. Diffusional drift terms for bubbles may also be added to include the effects stress [20] and temperature gradients [21] on bubble diffusion.

4. Conclusions

A novel approach was developed to estimate the time evolution of the full size distribution of bubbles in helium-vacancy phase space. Due to the complex and inherently stochastic nature of the irradiation environment (collision cascades, point defect physics, etc.), a method based on a stochastic differential equations formulation was developed. Expanding on a previously developed rate-theory approach, additional rate equations for the first and second order moments of the distribution were derived via Itô calculus. Solution of these coupled equations enabled a reconstruction of the distribution, under the assumption that it could adequately be modeled as a bivariate Gaussian. The numerical procedure was outlined, detailing the derivations and implementation of the method. The method is very general, and can be easily extended to a description of the size distribution as a function of space and time in any irradiated material. Homogeneous terms in the rate equations allow for pre-defined microstructure attributes (dislocation/sink densities, etc.), while spatially dependent terms can account for the effects of internal heterogeneous stress distributions on clustering characteristics. The large degree of parametrization allows for enhanced flexibility and accuracy, particularly when experimental data is available.

The results illustrate the impact of the stochastic coefficient terms on the evolution of the distribution in time. Specifically, stochastic fluctuations are found to have a greater impact on the width of the distribution when the average bubble sizes are smaller. Bubble pressures may also become exceedingly large when the average sizes are small, due to the much higher mobility, and thus capture rate, of helium interstitials. As the average bubble sizes grow in time, the distribution ceases to spread and instead begins to shrink, showing a tendency toward a more uniform distribution of bubbles. These phenomena depend on the chosen displacement damage and helium generation rate, since bubble pressure plays a key role in the stability of bubbles against point defect emission. Extension of this work could include the development of additional stochastic contributions to provide even greater resolution of the physics at play. This includes consideration of the contributions of bubble coalescence, for example, which may be particularly important when bubble concentrations are high, and sizes become large. Path integral approaches should also be explored if the distribution is known to significantly stray from a Gaussian description.

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	Description	Value	Units	Ref.
K	Displacement damage rate	3×10^{-3}	dpa/s	[12]
E_i^m	Interstitial migration energy	0.102	eV	[22]
E_g^m	Helium migration energy	0.07	eV	[23]
E_v^m	Vacancy migration energy	1.66	eV	[24]
E_{vg}^b	Substitutional binding energy	4.58	eV	[23]
E_v^f	Vacancy formation energy	3.11	eV	[24]
E_{v2g}^b	He to He ₂ V binding energy	3.14	eV	[12]
E_{2g}^b	He to He ₂ binding energy	0.79	eV	[12]
E_i^f	Interstitial formation energy	9.82	eV	[24]
ρ_N	Dislocation density	3×10^{10}	cm ⁻²	-
Z_i	Interstitial bias factor	1.178	-	[25]
Z_v	Vacancy bias factor	1.0	-	[25]
H	Helium to dpa ratio	5×10^{-6}	dpa ⁻¹	[12]
a	Lattice parameter	0.3146	nm	[26]
ν_i	Interstitial vibration frequency	5×10^{13}	s ⁻¹	[12]
ν_g	Helium vibration frequency	5×10^{13}	s ⁻¹	[12]
ν_v	Vacancy vibration frequency	5×10^{12}	s ⁻¹	[12]
b	Re-solution parameter	1.0	s ⁻¹	[27]
B	van der Waal's coefficient	1.75×10^{-23}	cm ³	[28]

Table 1: Simulation and tungsten material parameters used in the rate-theory calculations.

Figure 1: Evolution of the helium-vacancy size distribution spanning the first 200 seconds of irradiation time. The distribution is normalized by an arbitrary value (3×10^{-7}), for plotting purposes. Projections of the vacancy and helium profiles of the distribution are seen in blue and red, respectively, and the mean bubble radius and mean pressure ratio, are plotted in the inset plot on the left and right ordinate axes, respectively.

Figure 2: Log-scale plot of the moments of the size distribution versus time spanning the first 200 seconds of irradiation. The first order and second order moments are shown in the left and right plots, respectively.