

Diffuse interface modeling of void growth in irradiated materials.

Mathematical, thermodynamic and atomistic perspectives

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ABSTRACT

We present an assessment of the diffuse interface models of void growth in irradiated materials. Since the void surface is inherently sharp, diffuse interface models for void growth must be constructed in a way to make them consistent with the sharp-interface description of the problem. Therefore, we first present the sharp-interface description of the void growth problem and deduce the equation of motion for the void surface. We also compare two existing phase field models to determine which one corresponds to the sharp-interface analysis. It was shown that a phase field model of type C, which couples Cahn-Hilliard and Allen-Cahn equations, is the most adequate since this type of model can take into account the reaction of point defects at the void surface via an Allen-Cahn equation. Fixing the model parameters in the diffuse interface model is discussed from the points of view of asymptotic matching. Sample results for void growth in a single component metal based on sharp and diffuse interface models are presented. Finally, a perspective on the use of atomistic modeling in both constitutive and nucleation modeling within the phase field approach for void formation in irradiated materials is presented.

1. Introduction

Neutron irradiation affects the performance and lifetime of nuclear reactor components. Such a kind irradiation produces large densities of vacancies and interstitials the diffusion and clustering of which result in the formation of microstructural features such as dislocation loops and voids in irradiated materials [1, 2]. These microstructural features influence the dimensional stability and mechanical properties of materials [3, 4]. Voids are particularly important since their presence leads to swelling [5]. Theoretical models were proposed to investigate void formation and growth in irradiated materials [6-14]. These models fall into three categories. The first includes clustering and nucleation type models [6-8], which are concerned with void nucleation as a result of localized fluctuations in the vacancy concentration. A characteristic feature of these models is the existence of a nucleation barrier that must be overcome in order for void nucleation to take place. The second category includes models for void lattice formation [9-11]. Spinodal instabilities of homogeneous vacancy concentrations, elastic interaction of voids and reaction-diffusion aspects of point defects were suggested as possible ordering mechanisms. The last category includes void growth models based on the chemical reaction rate theory [12-14]. This theory considers the point defect and sink concentrations to be spatially uniform fields influencing the growth of a representative void. A typical rate theory model consists of three equations for the rate of change of vacancy and interstitial concentrations and void radius [1, 2]:

$$\dot{c}_v = P_v - K_{vi}c_v c_i - K_{vs}c_v c_s, \quad (1a)$$

$$\dot{c}_i = P_i - K_{vi}c_v c_i - K_{is}c_i c_s, \quad (1b)$$

$$\dot{R} = [D_v(c_v - c_v^{eq}) - D_i(c_i - c_i^{eq})]\Omega / R. \quad (1c)$$

In the above, c_v and c_i are the average vacancy and interstitial concentrations in the irradiated solid, P_i and P_v are the respective production terms, K_{vi} is a rate constant for vacancy-interstitial recombination, K_{vs} and K_{is} are rate constants for defects reaction with sinks of average concentration c_s , R is the void radius, Ω is the atomic volume, c_v^{eq} and c_i^{eq} are the equilibrium vacancy and interstitial concentrations at the void surface, and D_v and D_i are the diffusion coefficients of vacancies and interstitials, respectively.

It is noted that Eq. (1c) for the void growth rate is practically the same as the rate equation for diffusion-controlled precipitate growth from supersaturated matrix in the classical Lifshitz-Slyozov-Wagner theory [15,16] and the Mullins-Sekerka quasistatic models [17]. This similarity stems from the fact that the rate theory assumes that the point defect concentrations at the void surface take on their thermal equilibrium values and hence the growth process is completely controlled by the diffusion of point defects from the bulk to the void surface. The process of void growth, however, is not necessarily diffusion-controlled and the reaction of point defects at the void surface must be taken into consideration in determining the rate of the growth process [18]. The idea of considering the reaction of defects with voids surface was discussed a while back [19, 20], although this was later discarded. An important part of the current work is to show that, as a thermodynamic requirement, reactions of point defect with the void surface must be considered in the treatment of non-equilibrium void growth. This theoretical proof does not, however, aim to prove that void growth is diffusion- or reaction-controlled in the sense these terms are used in the literature [21], but it is rather a statement that reaction of defects at the void surface must be considered in defining the boundary conditions for the diffusion of defects in the solid around the voids. As explained later, this has important implications as to how diffuse interface (phase field) models for voids growth should be constructed.

Unlike nucleation from a supersaturated state or growth in a uniform species background [21], void nucleation and growth in irradiated materials take place under a highly non-equilibrium condition involving generation, diffusion and reaction of defects. The recent surge in interest in nuclear materials performance modeling has led members of the community to adopt the concepts of phase field approach to model voids in irradiated materials [22-33]. This new modeling direction was in part motivated by the need to resolve the nucleation and growth processes in space and time, and to treat the interaction of defects and the growing features, voids in this case, with other extended defects explicitly. Phase field modeling was thus viewed as a means to resolve all temporal and spatial effects in microstructure growth under irradiation and to handle nucleation and growth concurrently.

The initial phase field modeling of voids nucleation and growth adopted a simple intuition of how defects, especially vacancies, agglomerate to form voids and how they contribute to the subsequent growth of such features. Two modeling approaches emerged. In the first approach, [23-28], the process of void formation and growth was viewed as a spinodal instability in media that are supersaturated with vacancies. As such, a generalized diffusion equation of the Cahn-Hilliard type was adequate to describe void nucleation and growth. In the second approach [29-32], both Cahn-Hilliard and Allen Cahn equations were used. Both approaches made the assumption that the void surface can be modeled as a diffuse interface. Aside from the model construction and the assumptions made therein, and further keeping the accuracy of predictions of these preliminary models aside, both kinds of models seem to capture the spatial and temporal details of void formation and evolution in materials under irradiation. A fundamental question then arises as to how such two seemingly different approaches can capture the same process and whether any of these approaches can be proved to represent the physics of the problem with a

higher fidelity. A second related question is how to properly construct a phase field framework for voids and what are the steps required in this regard. These two fundamental questions are addressed in this communication.

Motivated by the above questions, we discuss void growth modeling within the phase field framework here. The discussion focuses on three issues. First is the fact that, being inherently sharp interface microstructure features in solids, voids do not naturally fit into the phase field framework. As such, phase field modeling of void evolution in irradiated solids is a matter of a mathematical choice. As discussed in section 2, the diffuse interface formalism of inherently sharp interface problems has been a successful tradition in modeling microstructure and morphological evolution problems [34-36]. Therefore, this formalism can in principle be used to model void evolution. The second issue is that, having elected to pursue this problem within the framework of diffuse interface modeling, what modeling steps are required to ensure consistency of the void growth model? By consistency here, we mean both thermodynamic consistency and consistency with the sharp-interface formalism itself. The third issue has to do with requiring the phase field models to handle void nucleation concurrently with growth and coarsening. As is well known to experts in this modeling area, the phase field approach is a continuum mesoscale modeling apparatus that discards the discrete atomistic nature of the material and it treats interfacial dynamics in terms of capillary quantities such as surface and interface energies. While the capillary nature of voids is well acknowledged in the classical nucleation theory [21], nucleation models such as cluster dynamics is inherently based on the atomic nature of defect clusters as they are based on single-defect transitions among different cluster sizes [37]. The discrete nature of transitions from one cluster size to another is also an essential feature of simulation models such as Monte Carlo [38].

In order to address the first issue above, a quick review of phase field approach is presented in section 2, focusing on diffuse interface representations of inherently-sharp interface problems and the analyses required to ensure consistency of these models with the corresponding sharp interface formulations. In section 3 and 4, we present thermodynamically based sharp and diffuse interface formulations of the void growth problem and briefly discuss the analysis required to match these formulations. In section 5, we discuss the modeling of gradient free energy terms and nucleation mechanism within the phase field framework, along with the role of atomistic simulations in guiding such a modeling and providing the needed lower scale input. We conclude with some remarks summarizing the contributions made here.

2. Phase field formalism of sharp interface problems

Phase field modeling has been widely used in predicting microstructural evolution in materials [34-36]. The main feature of this approach is the treatment of the interfaces between phases as diffuse, while the material properties of interest, which are represented by phase fields or order parameters, are assumed to change rapidly but smoothly across the interfaces. The position of the interface is implicitly given by a constant phase field level, which obviates the necessity of explicitly tracking the interface. Based on this powerful concept, phase field methods enabled the simulation of complex evolution problems such as the solidification [39], solid-state transformations [40], grain growth [41-43], crack propagation [44], dislocation dynamics [45], sintering [46-48], electromigration [49, 50] and vesicle membranes [51]. Historical developments of the diffuse interface concepts can be traced back to the works of Van der Waals on gas condensation [52], Landau on phase transitions [53] (where the concept of order parameter or phase field was first introduced), Landau and Ginzburg [54] on superconducting states [54], and Cahn and Hilliard on the thermodynamics of heterogeneous

systems [55]. In all of these and in subsequent works, order parameters may represent conserved quantities such as mass and energy density or non-conserved quantities such as polarization, long-range order and grain orientation. In analogy to the stochastic models of dynamic critical phenomena [56], phase field models are often classified into models of type A, B and C. Models of type A describe systems with non-conserved order parameters which evolve according to time-dependent Ginzburg-Landau (or Allen-Cahn) equations [57]. Models of type B describe systems with conserved order parameters governed by Cahn-Hilliard equations [58]. Models of type C describe systems with both conserved and non-conserved order parameters, which are described by coupled Cahn-Hilliard and Allen-Cahn equations [43, 46].

When interfaces are inherently diffuse, such as with magnetic domain walls and in ordered-disordered systems, phase field formulations offer a natural mathematical description of the physical or chemical phenomenon. In such situations, the sharp-interface descriptions, if desired for any reason, must be constrained to capture the physics of the diffuse interfaces. On the other hand, the sharp interface approach is the natural formalism to describe interfaces that are atomically sharp such as free surfaces, void or bubble surface in irradiated solids, or grain boundaries. Diffuse interface formalisms of the latter situations must be consistent with the corresponding sharp interface models. This consistency can be ensured by requiring the kinetic equations of the phase field models to reduce to their sharp interface counterparts when the diffuse-interface width approaches zero. This is usually accomplished by using a formal asymptotic analysis based on singular perturbation theory [59-63]. Typical of such analysis is the expansion of phase fields in terms of a small parameter, which represents the diffuse-interface width, far from the interface (outer expansion) and within the interface (inner expansion). Matching conditions are then applied to guarantee a smooth transition between the outer solution

and the inner solution. In this context, the Allen-Cahn equation was shown to describe surface motion driven by mean curvature [60]. Also, in addition to its ability to capture the kinetics of the early stage of phase transition by spinodal decomposition [58], the Cahn-Hilliard equation was shown to represent the growth and coarsening kinetics that mark the intermediate and late stages of phase transition [64]. The formal asymptotic analysis was first given by Pego [61] who showed that Cahn-Hilliard equation recovers the quasi-static Mullins-Sekerka models (or the classical and modified Stefan-type models) as limiting cases. In a different context, Cahn-Hilliard equation was utilized to depict surface motion by surface diffusion (by the laplacian of the mean curvature) [62]. Such a limiting case of the Cahn-Hilliard equation is obtained by requiring the diffusional mobility to vanish in the bulk phases [62].

The problems of curvature driven motion and morphological surface evolution by surface diffusion are invoked here because they are examples of diffuse interface formulations of inherently-sharp interface situations. It will be shown in the next section that the sharp interface formalism of voids combines aspects of both problems. As such, constructing the corresponding diffuse interface model will involve aspects of both formalisms.

In the last decade, the phase field approach was used to tackle radiation effects problems [22-33]. Traditional forms of Cahn-Hilliard and/or Allen-Cahn equations were used, with some modifications accounting for the irradiation driver and defect reactions [22-33]. As mentioned in the introduction, there are two different types of phase field models in literature for the case of voids/bubbles. The first type utilizes a phase field model B with point defect concentrations as the conserved order parameters [23-28]. The void region in such models is represented as a region with high concentration of vacancies. The second type is a phase field model of type C with point defects concentrations as conserved parameters plus a non-conserved order parameter

distinguishing between the void as a phase and the matrix as the second phase [29-32]. The latter model was first motivated by the need to uniquely define the void surface since point defects energies and mobilities usually differ near the surface from their bulk values. The void surface position is uniquely identified by high gradients in the non-conserved order parameter since under irradiation gradients of the conserved order parameters (the point defects concentration) are present everywhere. Furthermore, a stronger argument about the generality of the phase field model C can be based on the asymptotic behavior of the phase field equations mentioned earlier. As mentioned above, Pego [61] showed that Cahn-Hilliard equation converges to the quasi-static Mullins-Sekerka problem [17]. Hence void/bubble growth based on phase field model B recovers the diffusion-controlled growth given by equation (1). Nonetheless, as discussed earlier, point defect reactions at the void surface must be taken into account in determining the overall rate of the growth process. Therefore, phase field model C seemed a logical choice for such a general case since the coupling between the conserved and non-conserved fields could be constructed in such a way that both bulk and surface diffusion and reactions are accurately captured. In the next section we show based on formal thermodynamic arguments that model C is more appropriate for void growth under irradiation.

3. Sharp-interface modeling of void growth

We remark here that the problem of void growth is often cast in the form of Eqs. (1a)-(1c) in most classical literature [1,2]. This classical form implies that it is accepted that void growth is diffusion controlled. A limited set of publications has, however, addressed the question of whether void growth is surface (reaction-rate) controlled [19, 20] but the literature does not appear to have a firm conclusion in this regard. Our formalism of the void growth problem brings up the need to consider surface reactions of defects based upon a thermodynamic

reasoning, without necessarily judging whether the void growth is diffusion limited or reaction-rate limited. The main idea is summarized here and the details will appear elsewhere [18].

We consider the mass and energy balance in a single component solid with a void ensemble, as shown in Fig. 1, with point defects being produced by, say, neutron bombardment. Point defects then diffuse, recombine, disappear at sinks and reach the surface of the voids. The evolution of a void surface is a result of absorption of vacancies and interstitials from the matrix. Here we consider voids to take on any shape and thus the void surface velocity is a local quantity. Considering mass balance at a point on the void surface, it can be shown that the local velocity, v , on the void surface is given by:

$$v = \frac{J_i \cdot n - J_v \cdot n - \nabla_s \cdot J_s}{1 + c_i - c_v}, \quad (2)$$

where J_i and J_v are the interstitial and vacancy fluxes, respectively, J_s is the atomic flux along the surface, n is the unit outward normal to the void surface (pointing from the matrix into the void) and ∇_s is the surface del operator. Containing the limiting values of the bulk defect concentrations near the void surface, the denominator in Eq. (2) corrects for the fact that the motion of the surface consumes or builds a defective matrix. The point defect fluxes in the matrix are part of the defect mass balance, which is written in the form:

$$\dot{c}_v = -\nabla \cdot J_v - K_{vi}c_v c_i - K_{vs}c_v c_s + P_v, \quad (3a)$$

$$\dot{c}_i = -\nabla \cdot J_i - K_{vi}c_v c_i - K_{is}c_i c_s + P_i. \quad (3b)$$

Aside from the flux divergence terms, which are added here to indicate the spatial dependence of the defect concentrations and fluxes, all quantities in Eq. (3) have the same definitions as in Eqs. (1).

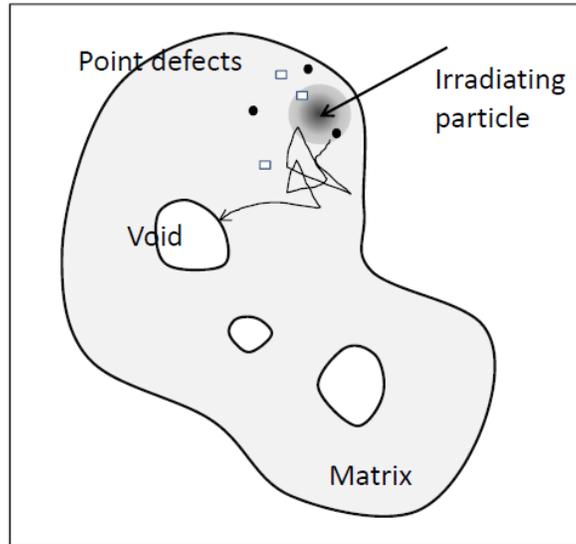


Fig. 1. A schematic of a system of voids in a solid under irradiation. The defect density and flux are assumed to be non-uniform and the surface velocity varies along the surface of each void.

Eqs. (2) and (3) imply that it is possible to solve for the local defect concentration everywhere in the matrix, with the void surface being a moving (internal) boundary. In order to accomplish this task, the velocity of the surface and all energy and mass fluxes must be fixed. Considering such quantities as generalized velocities, the second law of thermodynamics can be used to provide the appropriate constraints for all of them (surface velocity, diffusive defect fluxes, energy flux, and the atomic flux along the void surface). Ignoring defect reaction at sinks other than voids, which will have no consequence on the results below, the system can be viewed as a thermodynamic system in which point defects diffuse in the bulk and react with each other, atoms diffuse along the void surface and the void surface moves as a result of surface mass diffusion and absorption of point defects coming from the bulk. The following statement of the second law is then used: *In the thermodynamic system just described, the entropy production is non-negative as the system relaxes towards lower free energy states.* A mathematical

implementation of this statement results in two sets of inequalities [18]. In the bulk, the following inequalities hold:

$$-\frac{\nabla T}{T} \cdot J_e \geq 0, \quad (4a)$$

$$-\left[\nabla \mu_i - \mu_i \frac{\nabla T}{T} \right] \cdot J_i \geq 0, \quad (4b)$$

$$-\left[\nabla \mu_v - \mu_v \frac{\nabla T}{T} \right] \cdot J_v \geq 0, \quad (4c)$$

$$(\mu_v + \mu_i) \dot{\xi} \geq 0. \quad (4d)$$

In the above, T is the absolute temperature and J_e is the heat flux, μ_i and μ_v are the chemical potentials of interstitials and vacancies, respectively, and $\dot{\xi}$ is the rate of recombination of vacancies and interstitials. In addition, the following inequalities hold on the void surface, which is treated here as a singular surface:

$$-\frac{\nabla_s T}{T} \cdot J_{es} \geq 0, \quad (5a)$$

$$-\left[\mu_i - \frac{f + \Omega \kappa \gamma}{1 + c_i - c_v} \right] J_i \cdot n \geq 0, \quad (5b)$$

$$-\left[\mu_v + \frac{f + \Omega \kappa \gamma}{1 + c_i - c_v} \right] J_v \cdot n \geq 0, \quad (5c)$$

$$-\nabla_s \left[\frac{f + \Omega \kappa \gamma}{1 + c_i - c_v} \right] \cdot J_s \geq 0. \quad (5d)$$

In these inequalities, J_{es} is the surface energy flux, f is the free energy density of the defective matrix, Ω is the atomic volume, κ is the void surface curvature, γ is the void surface energy

and J_s is the atomic surface flux along the void surface. Eqs. 4(a)-4(d) are classical results in the sense that they connect the driving forces for the heat and defect (mass) diffusion in the system, as well as the reaction rate, to the corresponding thermodynamic forces driving those processes. Once the free energy of the system is defined in terms of defect concentrations and the chemical potentials are derived, constitutive expressions of all fluxes and reaction rates can be found via an Onsager-type procedure assuming, for example, a linear response regime [65]. Eqs. (5a) and (5d) are also classical and can be found in the relevant literature on morphological surface evolution with a sharp interface character [66]. What is new here for the case of voids are Eqs. (5b) and (5c). These equations state that the normal fluxes of defects into the surface are associated with thermodynamic forces given by the expressions between brackets. As a result, these normal fluxes must be expressed in terms of such forces. We postulate here that the process of defect interaction with the surface must be considered in details to accomplish this task, and for this we invoke the transition state theory concepts [18]. Omitting details, it is found that the normal fluxes of point defects into the surface, which must match the reaction rates of point defects at the surface, are given by:

$$J_i \cdot n = \delta c_i \nu_i \exp(-\Delta g_i / kT) \{1 - \exp[-(\mu_i - \Delta E) / kT]\}, \quad (6a)$$

$$J_v \cdot n = \delta c_v \nu_v \exp(-\Delta g_v / kT) \{1 - \exp[-(\mu_v + \Delta E) / kT]\}, \quad (6b)$$

where δ is a length scale on the order of the lattice parameter, ν_i and ν_v are the attempt frequencies of interstitials and vacancies as these species jump from the bulk into the surface, Δg_i and Δg_v are the corresponding activation barriers, and ΔE is given by

$$\Delta E = \frac{f + \Omega \kappa \gamma}{1 + c_i - c_v}. \quad (7)$$

In the above c_i and c_v are the limiting values of bulk concentrations of defects at void surface, and the free energy density, f , is expressed in the dilute defect concentration limit by

$$f(c_i, c_v) = E_i c_i + E_v c_v + kT [c_i \ln c_i + c_v \ln c_v + (1 - c_i - c_v) \ln(1 - c_i - c_v)], \quad (8)$$

with E_i and E_v being the formation energies of interstitial and vacancy, respectively, and k the Boltzmann constant.

The governing equations for the void growth problem in a sharp-interface framework are summarized as follows:

- Eqs. (3a) and (3b) for the defect diffusion, reactions and production,
- Eq. (2) for the surface motion, and
- Eqs. (6a) and (6b) for the equivalence of the normal defect fluxes into the surface with reaction rates serving as boundary conditions.

We note here that if surface mass diffusion is to be considered, an additional mass diffusion equation must be solved on the surface in conjunction with the reaction-diffusion equations (3a) and (3b) for defects and the boundary conditions (6). For this surface diffusion, the atomic flux is given by:

$$J_s = -M_s \nabla_s \left(\frac{f + \Omega \kappa \gamma}{1 + c_i - c_v} \right), \quad (9)$$

where M_s is the atomic mobility on the void surface. In a phase field (diffuse interface) framework, the diffusion equations (3a) and (3b) can be generalized to Cahn-Hilliard equations by including gradient terms. While the Cahn-Hilliard equations are generalized equations that govern diffusional processes, the velocity of the surface in the above is governed by the reaction

of defects at the surface, a consequence of the inequalities (5b) and (5c). As such, in the diffuse interface representation of the same problem, an Allen-Cahn type equation must be considered. With this in mind, we discuss in the following section a thermodynamically consistent phase field approach that corresponds to this physical condition at the surface.

To illustrate the utility of the sharp interface void growth formalism outlined above we give two sample numerical results for a copper crystal. The model parameters for copper are: are $E_v = 1$ eV and $E_i = 2.2$ eV, $E_v^m = 0.8$ eV, $E_i^m = 0.24$ eV, and $\gamma = 0.11$ eV/Å². The pre-exponential factors for vacancy and interstitial diffusivities are 2500 and 200 nm²/ns, respectively. In Fig. 2 we show the evolution of the radius of a void from an initial value of 30 nm at 1000 K as a function of supersaturation of defects. The theory reproduces the expected behavior of the void radius. Basically, the radius grows under vacancy supersaturation and shrinks when interstitials are dominant. In Fig. 3, we show the effect of the defect reaction barrier Δg at the surface on the growth rate in the presence of vacancies with a supersaturation ratio of $S_v = 100$ and interstitial concentration initially set at its thermal equilibrium value. As such, in this particular example, vacancies dominate the void evolution process. Data for the barrier Δg is not available yet as this barrier was only defined as part of the theoretical analysis leading to Eqs. (6). It is thus treated as a parameter that we represent here in terms of the respective bulk migration barrier. It is clear from Fig. 3 that the growth rate is diminished significantly as the surface reaction barrier of is increased. This is of course an intuitive result for the simple case considered in this example. The value of this reaction boundary condition will become important, though, in the more complex situations involving non-uniform defect fluxes into the surface.

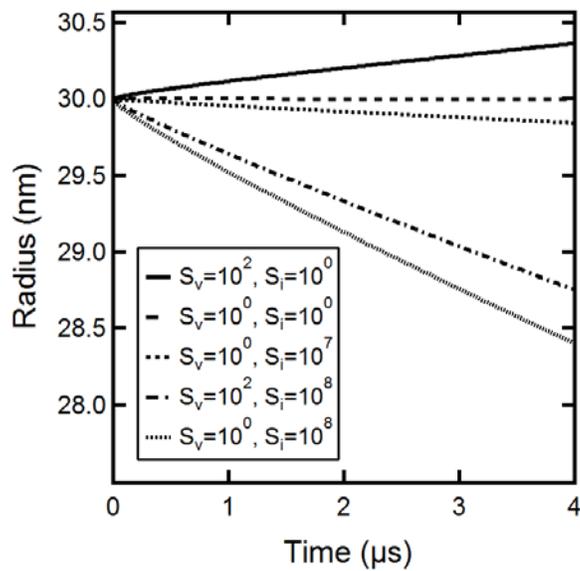


Fig. 2. Evolution of the radius of a void from an initial value of 30 nm at different levels of vacancy (S_v) and interstitial (S_i) supersaturation in copper at 1000K.

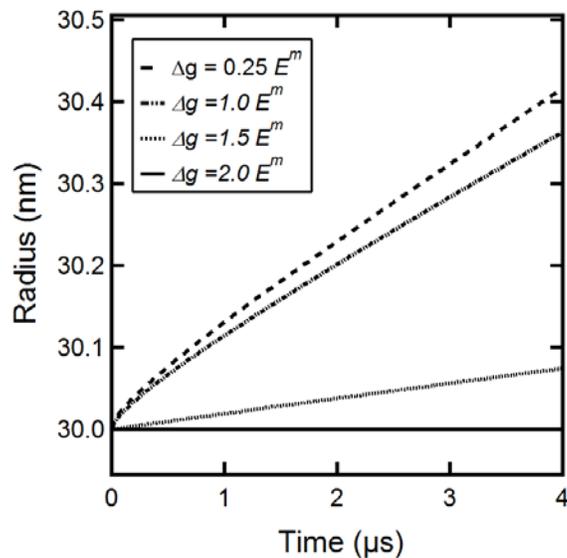


Fig. 3. Evolution of the radius of a void from an initial value of 30 nm at vacancy concentration supersaturation ratio $S_v = 100$ as a function of the defect-surface reaction barrier, Δg , expressed in terms of the lattice migration barriers of defects in copper, E^m .

4. Diffuse-interface modeling of void growth

The conservation principles of non-equilibrium thermodynamics can be used to derive the phase field model for void growth in irradiated solids. Starting from global balance laws of mass and energy, Rokkam [67] derived generalized Cahn-Hilliard equations for point defects under irradiation. These equations are equivalent to the mass conservation laws (3a) and (3b) but with point defect fluxes obtained from a chemical potential that accounts for gradient effects as is customary in phase field modeling. It is important to note that the gradient effects can also be incorporated into Eqs. (3a) and (3b) without changing the fact that these equations are a part of a sharp interface mathematical description of the void growth problem.

Rokkam's treatment [67] leads to the local form of the mass balance laws in the form (3a) and (3b) for the kinetics of vacancies and interstitials with the fluxes given by

$$J_v = -M_v \nabla \frac{\delta F}{\delta c_v}, \quad (10a)$$

$$J_i = -M_i \nabla \frac{\delta F}{\delta c_i}. \quad (10b)$$

Here, M_v and M_i are the mobilities of vacancies and interstitials, respectively, and F is the free energy functional of the system. The defect mobility varies smoothly across the interface from their solid values to zero inside the void. The variational derivatives $\delta F / \delta c_v$ and $\delta F / \delta c_i$ are the chemical potentials, μ_v and μ_i , of vacancies and interstitials, respectively. The free energy functional itself is expressed in the form:

$$F = \int_{\Omega} \hat{f}(c_v, c_i, \eta) \, d\Omega, \quad (11)$$

with η being the non-conserved order parameter invoked to describe the multi-phase nature of the system (voids plus matrix) and $\hat{f}(c_v, c_i, \eta)$ is a free energy density function that includes homogeneous and gradient terms. This free energy density is expressed in the form:

$$\hat{f}(c_i, c_v, \eta) = N_o \left[(1-h(\eta))(f(c_i, c_v) - f^{eq}(c_i, c_v)) + h(\eta)f^{void} + \psi(c_i, c_v, \eta) + \kappa_i |\nabla c_i|^2 + \kappa_v |\nabla c_v|^2 + \kappa_\eta |\nabla \eta|^2 \right]. \quad (12)$$

In the above, N_o is the lattice site density, $h(\eta)$ is an interpolation function, $f(c_i, c_v)$ is the free energy of the matrix phase with defects and $f^{eq}(c_i, c_v)$ is its equilibrium value, $f^{void} = 0$ is the void free energy density, $\psi(c_i, c_v, \eta)$ is a Landau energy term, and the last three terms are the usual gradient terms. The Landau energy term is chosen to ensure bistability of the two-phase (matrix/void) system. With the defect fluxes given by Eqs. (10a) and (10b), which account for the gradient effects, Eqs. (3a) and (3b) now serve as the Cahn-Hilliard equations for the vacancies and interstitials in the heterogeneous system. The associated Allen-Cahn equation for the non-conserved order parameter falls out of the principle of non-negative entropy production and it takes on the form

$$\dot{\eta} = -L \frac{\delta F}{\delta \eta}, \quad (13)$$

with L being the Allen-Cahn mobility. This equation comes as a constitutive law for the non-conserved order parameter evolution. A comparison between the governing equations in the sharp and diffuse interface models shows that they are equal: two diffusion equations in both models and an equation governing the interface motion. The latter comes out to be an expression of the velocity in terms of reactions in the sharp interface model and an Allen-Cahn equation in the diffuse interface model. This equality makes the matching step possible.

Without a formal matching with the sharp interface counterpart, the just outlined diffuse interface model has a set of undefined parameters: amplitude of the Landau energy, $\psi(c_i, c_v, \eta)$, gradient coefficients and the Allen-Cahn mobility. This matching step is currently underway. However, with a double well construction of the Landau energy term and a set of model parameters chosen or assumed to represent copper, see [67] for details, the phase field model discussed above has been tested for void nucleation and growth under random defect generation conditions. The model produced virtually all dynamical aspects of defect behavior, void nucleation and growth. The nucleation process is assisted by the fluctuations of the generation process. These fluctuations were found to be more important than the thermal fluctuations assumed in conventional phase field models [34].

Fig. 4 shows the behavior of a void radius under various levels of vacancy and interstitial concentrations in copper at 1160K. The model is solved in a non-dimensional form in which the following model parameters are used: $\kappa_i = \kappa_v = \kappa_\eta = 10$, amplitude of the Landau energy is 0.4, defect diffusivities, $D_v = 1$, $D_i = 20$, Cahn Hilliard mobility $L = 1$; see [67] for the non-dimensionalization procedure. Like the sharp interface counterpart, the phase field model predicts that the void grows at high vacancy supersaturation and shrinks when interstitials are dominant in the matrix. We also noticed that it is possible for a void to completely disappear if interstitials are abundant in the surrounding matrix. Figs. 5 and 6 illustrate the void nucleation and growth under random defect generation by sustained irradiation at 1160K. In both figures, the top, middle and bottom rows are profiles of the vacancy, interstitial and non-conserved order parameter, respectively. The interstitial concentration in the void is typically zero. Fig. 5 shows void nucleation and growth in the bulk while Fig. 6 shows the same for a slab configuration. We notice that while in Fig. 5 the nucleation of voids is more or less homogeneous, the behavior in

Fig. 6 reflects a strong effect of the boundary. Because interstitials migrate faster to the boundary, they sweep vacancies in a boundary layer leaving behind more vacancies in the interior to nucleate first at a distance from the boundary and then into the bulk. Such a boundary effect is common in irradiation experiments. The rapid migration of interstitials to the surface is also associated with boundary motion and physical expansion of the domain (swelling) due to the deposition of interstitials on the outer boundary. The boundary layer or denuded layer effect is also observed when grain boundaries are present and are assumed to act as point defect sinks. Fig. 7 shows a typical test for nucleation and growth in polycrystalline solid under irradiation. The results clearly show nucleation at a distance from grain boundaries. It also shows that void nucleation may not occur at all in small grains because defects readily migrate to the grain boundary and become less available for nucleation within the grain interior. Based on Figs. 4 through 7, it is clear that the phase field model presented here produces many features of void evolution that have been observed in irradiation experiments.

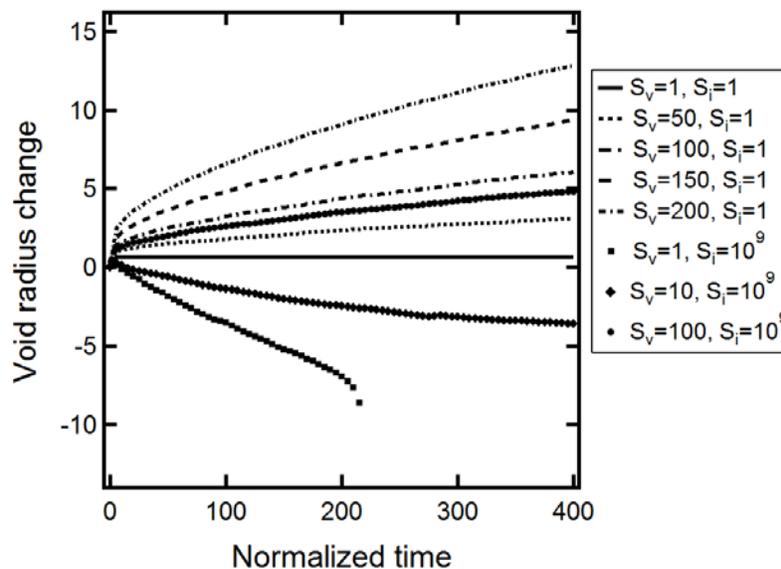


Fig. 4. Void growth and shrinkage as a function of vacancy and interstitial supersaturation.

We remark here that, real space and time units have not been used in Figs. 4 through 7. Such units can only be used when all phase field model parameters are fixed, and this requires kinetic quantities such as the Allen-Cahn mobility and the Landau energy amplitude fixed instead of assumed. Like those presented in [24-32], the phase field results presented here, are considered qualitative. A formal matching with the sharp interface theory makes it possible to obtain quantitative predictions by fixing the model parameters. This matching can only be done for the phase field models of the type reported here and in [29-32, 67] because these models are consistent with the sharp interface model. The matching in this case will be based on the asymptotic analysis of model C similar to that carried out in [69-70]; see also section 2.

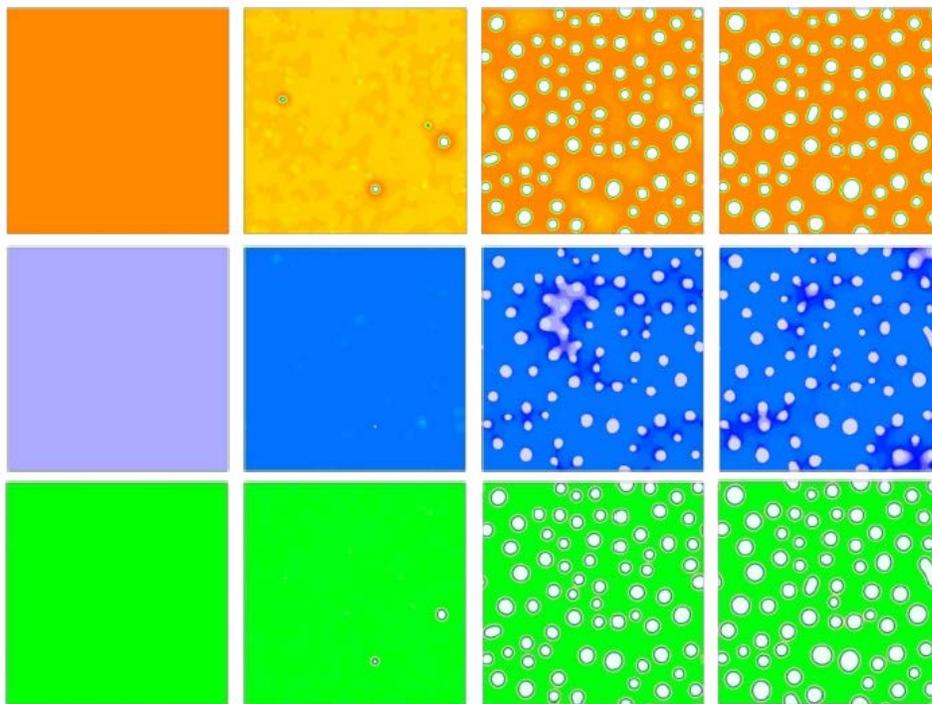


Fig. 5. Void nucleation and growth under random defect generation by irradiation. The top, middle and bottom rows are profiles of the vacancy, interstitial and non-conserved order parameter, respectively. Time increases from left to right.

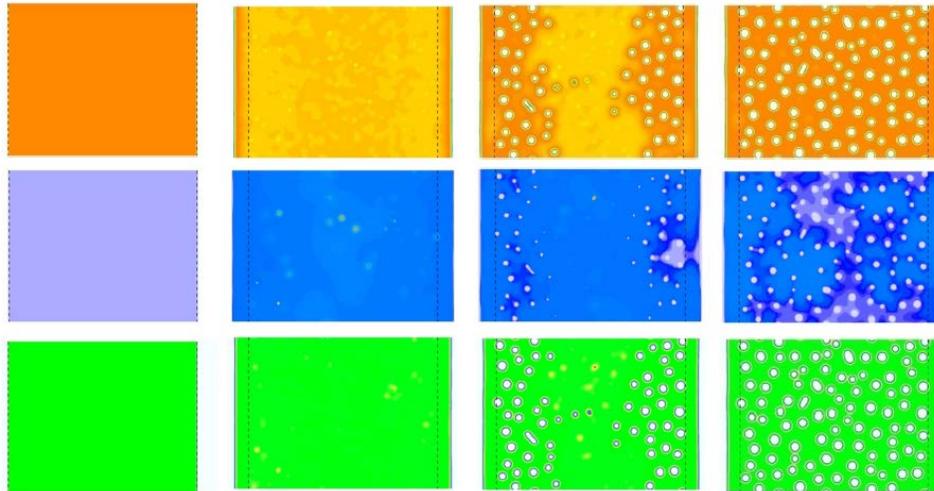


Fig. 6. Void nucleation and growth under random defect generation by irradiation in a slab. The top, middle and bottom rows are profiles of the vacancy, interstitial and non-conserved order parameter, respectively. The domain size change is obvious. Time increases from left to right.

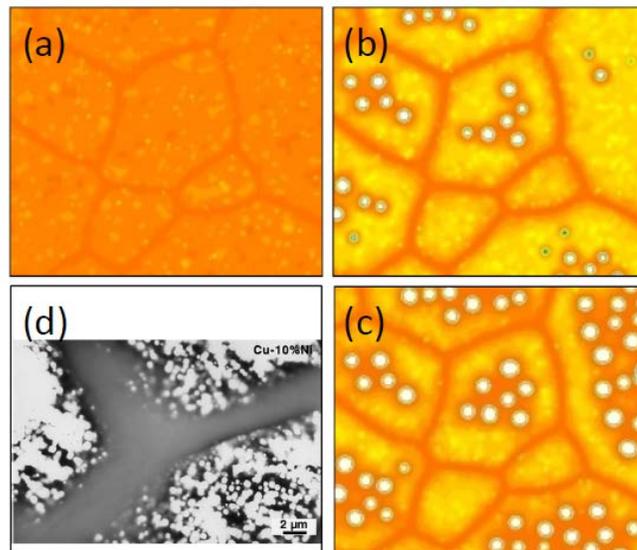


Fig. 7. Void nucleation and growth in a polycrystalline solid under irradiation. The grain boundaries are treated as defect sinks and, as a result, a denuded zone is formed around the grain boundary. Time increases from (a) to (b) to (c). (d) Depleted zone formation near grain boundary in Cu-Ni alloy [68].

5. A perspective on atomistic modeling requirements

Phase field modeling is inherently connected to atomistic modeling. An explicit aspect of this connection is reflected in a number of recent attempts to develop phase field models that make predictions at the atomic or lattice scale in crystal. Indeed, such models are known as *phase field crystal* models [71]. The fundamental input to such models is interatomic force data. On the other hand, an attempt to make a direct connection between phase field simulations and atomistic models in the case of solidification was also made relatively recently [72]; the authors were successful in propagating the order parameters in time and space by both molecular dynamics and phase field models and one to one correspondence was ensured, which gave insight as to how phase field model can be constructed to be consistent with the behavior of the underlying atomic system. The above aspects of connection between phase field and atomic scale modeling will not be discussed here. Rather, we focus here on the possible use of atomistic models to help the development of phase field models for void nucleation and growth in irradiated solids. A straightforward task is the use of molecular dynamics to fix model parameters such as defect energies, bulk migration and surface reaction barriers, etc. Calculating such energetic quantities by molecular dynamics is systematic. Two important areas of atomistic modeling that are relatively more complex than the defect or surface energetics are the constitutive or thermodynamic modeling of the heterogeneous solid and the nucleation process.

Gradient terms in the free energy represent the nonlocal aspects of interactions within the solid. For a thermodynamically uniform, or a homogeneous, phase, no such effects exist. When gradients of state variables are present, the assumption of local thermodynamic equilibrium (meaning that the constitutive laws of the solid can be cast point-wise in terms of the local state variable at each point as if the solid is under equilibrium) is no longer adequate, and non-local

effects must be included. The representation of the non-local effects in terms of the lowest order gradients provides a simple approximation of the non-local effects. For most systems, however, it is a hard problem to fix the energy of the system in terms of gradients of state variables or order parameters. In the context of irradiation induced defects, fixing the gradient terms amounts to including the pair interactions between defects over a small neighborhood of the individual defects. A formal statistical averaging over such small neighborhoods makes it possible to provide operational forms for both the gradient terms and higher order terms in the homogeneous free energy expression (8) but the constants in these forms will depend on the crystal bonding model. Molecular statics experiments can be designed to compute the parameters and hence fix the gradient coefficients and non-linear concentration-dependent terms. Some theoretical background for such atomistic experiments can be found in the work of Imada [9].

A closely related problem is the coupling between conserved and non-conserved order parameters in the Landau energy term, $\psi(c_i, c_v, \eta)$. This coupling is a feature of the diffuse interface model and it arises as a mathematical necessity in the case of void growth. The presence of this term corrects the interpolated phase energy (first two terms in Eq. (12)). A molecular simulation is possible to tackle this term but that requires large scale simulations near the melting point where the void-matrix interface may indeed be diffuse. In such experiments, a void may be created in a single crystal then the temperature of the atomic system is raised to a value reasonably close to the melting point. Some of the vacancies will escape from the void to saturate the solid around it but the remaining void will likely have a diffuse interface because the temperature is close to the melting point. A smoothing procedure for the defect concentration can be used to establish a concentration field and a non-conserved order parameter field. The local energy density can also be computed then mapped onto a suitable form of the Landau term from

the spatial mapping of the order parameters themselves. Such simulations are obviously unconventional and may require some trials before they are successful.

Finally, atomistic simulations can be used to tackle the problem of nucleation at the lattice level for the purpose of building suitable nucleation criteria in the diffuse interface model. A robust phase field model must be able to resolve the stable nuclei. Setting aside any potential numerical difficulty, this model requirement can be achieved by properly calibrating the model to detect and introduce nuclei when thermodynamically and kinetically possible. A Monte Carlo (MC) approach can be used to model the nucleation process at the lattice level. In particular, a Lattice Monte Carlo (LMC) approach can be effective in analyzing the thermodynamics of nucleation and clustering, while a Lattice Kinetic Monte Carlo (LKMC) approach can be used to analyze the statistical fluctuations leading to stable nuclei. Both approaches can be tied to Cluster Dynamics (CD) models [37], which provide a detailed picture of the subcritical cluster population in the system. Both MC and CD approaches require parameterization from atomistic models, which can be provided by molecular dynamics or molecular statics. A perceived advantage of molecular simulations is the accurate determination of the critical cluster size and its sensitivity to the cluster shape. Molecular dynamics can also be used to delineate the size range over which the capillary approximation is valid in modeling the thermodynamics of nuclei.

6. Concluding remarks

In this communication we discussed three issues of phase field modeling of void growth in irradiated solid. The first issue is the sharp interface character of voids and how that is factored into phase field modeling; the second is the construction of proper sharp and diffuse interface models for void growth and the consistency issues for the diffuse interface models; the third is

the atomistic modeling needs in the areas of defect energetics and kinetics, thermodynamic modeling of heterogeneous system and nucleation. It has been shown that an accurate sharp interface model of void growth must account for the defect reactions at the void surface. As a part of the theoretical and thermodynamic arguments leading to this finding, a set of kinetic barriers for the defect-surface reaction were defined. The effect of these barriers on void growth was shown to be important. It was also shown that a phase field model of type C, which includes both Cahn-Hilliard and Allen-Cahn equations, is most adequate for a diffuse interface description of voids. This finding was supported by the fact that, while the Cahn-Hilliard equations describe the diffusion and reactions of defects in the bulk, Allen-Cahn equation captures the physics of reactions of defects at the surface. The void surface motion, therefore, is not tied to the dynamics of defect concentration gradients but rather to change from the disordered nature of vacancies in the matrix to the void phase where vacancies are perfectly ordered on the lattice. Finally, three key areas of connection between phase field modeling and diffuse interface modeling are discussed, the usual defect energetics and kinetic modeling, and two new topics related to the constitutive modeling of the heterogeneous systems and nucleation. We speculate that the atomistic modeling of the gradient and Landau energy terms, which is a necessity in building diffuse interface void growth models, will provide novel and challenging topics for atomic scale simulations.

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