Physics-based void nucleation model using discrete dislocation dynamics and cluster dynamics models

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Physics-based void nucleation model using discrete dislocation dynamics and cluster dynamics models

by

Millicent Atieno-Orondo Hoback

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Materials Science and Engineering

Program of Study Committee:
Richard LeSar, Major Professor
Peter Collins
Xiong Liming

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2020

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DEDICATION

I am dedicating this thesis to my late grandmother, Sum Atieno, and my late sister, Diana Aoko whose spirits still sustain me. To my parents Michael Orondo and Consolata Anyango, whose prayers and sacrifice have been my fuel.
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ABSTRACT

Focusing on cavity nucleation, continuum damage mechanics models rely on a posteriori calibration of initial site density and loading conditions. However, empirically calibrated parameters are unreliable due to accelerated testing conditions and cannot be transferred to novel materials. To provide a more accurate description of the relationship between temperature, stress, microstructure, and the kinetics of void nucleation, we develop a physically-based nucleation model by coupling discrete dislocation dynamics (DDD) and cluster dynamics (CD) models. First, a continuum statistical approach developed for this study is shown, demonstrating the ability to model vacancies cluster size evolution as a function of time. Second, the implementation of the DDD method in the study of local energetics within a microstructure is presented. DDD has the capability to accurately model complex dislocation networks permitting a high-fidelity account of the local energy landscape arising from defect-defect interactions. Lastly, multiple potential nucleation sites in bulk are examined for nucleation. Our results are consistent with experimental observations indicating that nucleation is highly improbable in bulk.
CHAPTER 1. INTRODUCTION

Material design and development: XMAT Project

Increasing the efficiency of fossil energy power plants is important from both an economic and environmental standpoint. To achieve this, these facilities need to operate at higher temperatures and pressure. However, materials exposed to these conditions face increased creep deformation and oxidation leading to decreased service life. Over the years, studies have indicated that steel alloys enhanced with elements such as nickel, chromium, and molybdenum have higher thermal strength making them excellent candidates for material components i.e. cladding of surfaces in superheaters and exhaust systems \(^1\text{–}^3\).

Traditional methods of design and development of new materials take about 10-20 years, which has led to projects like the Materials Genome Initiative (MGI) being pursued to accelerate this process \(^4\). To achieve this, they propose a co-design process integrating multiscale computational tools and experimental methods in the design process \(^5\). The objective of multiscale models is to describe the physical behavior of materials at different length scales which are then aggregated to accurately model real systems. On the other hand, experimental data obtained in the process is used to validate the models and bridge gaps that may arise from variability in the material length scale. Similarly, “the U.S. Department of Energy Office (DOE) of Fossil Energy’s (FE) Extreme Environmental Materials (XMAT) is harnessing the computational and experimental materials science expertise and capabilities within the DOE national laboratory complex into an integrated, mission-focused team aimed at improving heat-resistant alloys and improving models to predict long-term materials performance in existing and future fossil energy power systems.” Figure 1 illustrates how XMAT is integrating multiscale
modeling methods, empirical data and data analytics to accelerate the design and development of current candidate ferritic materials for use in extreme environments. Vital to the success of XMAT’s program is developing a physics-based cavity nucleation model, as highlighted under task 2 in Figure 1. The work described in this thesis seeks to achieve this goal by using discrete dislocation dynamics (DDD) and cluster dynamics (CD) models to study the relationship between temperature, stress, local microstructure, and kinetics of cavity nucleation. The overall aim of this study to derive a physics-based nucleation rate and the local site density to replace empirical relations in the description of nucleation behavior.

Figure 1: Illustration of XMAT’s implementation of co-design processes across multiple teams integrating multiscale computational tools, experimental methods and data analytics to accelerate design and development of materials. This work is part of subtask 2 as highlighted in red.
Review of cavity nucleation problem

In tertiary creep, accelerated deformation is mainly driven by voids. Thus, understanding physically-based mechanisms underlying void formation and growth is necessary for the design and development of metals with longer service life in high-temperature environments. Significant experimental studies have been performed to highlight the correlation between local microstructures, loading conditions, and external environments to the void evolution process.\(^8\)\(^-\)\(^10\). Concurrently, theoretical studies in this field have been pursued to develop constitutive relations describing the cavitation process. Key to the study of the evolution of the creep-damage problem is Continuum Damage Mechanics (CDM), whose constitutive relations are derived from damage variables and local plasticity to simulate cavity nucleation, growth, coalescence, and rupture in materials.\(^11\)\(^-\)\(^13\). Examples include the Gurson, Tvergaard, and Needleman (GTN) model, which couples damage and mechanical properties using the void volume fraction damage parameter of a material to describe its failure process\(^14\)\(^-\)\(^17\), and the Lemaitre Damage model developed from thermodynamic theory to describe the change in the damage variables.\(^18\),\(^19\). The damage variables at the macroscale stem from functions derived at lower length scales that are based from fracture toughness, stress, strain, and defect density.\(^20\) In the cavitation process, comprehensive studies in void growth and coalescence have been performed, leading to a better understanding of these mechanisms. We note that, despite agreements on the fundamental process of cavity nucleation, there are still uncertainties that need to be resolved. The functions of microscale damage variables for the cavity nucleation process have been challenging to obtain hence the adoption of empirical-based variables. However, to achieve a more accurate
prediction of the nucleation process using simulation tools, mechanistic models, as opposed to empirical, are preferred.

Classical nucleation theory (CNT), initiated by Volmer and Weber and modified by Becker, links thermodynamics and kinetics in the modeling of nucleation rates, from which physical-based models have been derived. The most referred to mechanical-based nucleation model was developed by Raj and Ashby. They proposed that nucleation of cavities is probable in heterogeneous sites with low wetting angles. These conditions, however, suggested threshold stresses needed for nucleation are in the order of $E/100$, which is unattainable in environments where creep has been observed. Mechanisms such as grain boundary sliding and dislocation pile-up have been studied and proposed to be the source of high-stress concentrations. This study will focus on the latter mechanism by incorporating the strain energy contribution of dislocations. In most cases, simple dislocation pileup models have been used to determine the Gibbs free energy for the nucleation of voids. Although these models provide insights into the location of nucleation sites and the size of the cavity that is formed, they fail to capture the complexity of dislocation network interactions and the stochastic nature of the distribution of energy sites within a microstructure. Additionally, while CNT has been successfully used to capture the rate of nucleation of cavity clusters of a specific size per unit time within a specific volume, it fails to account for the evolution of cluster size as a function of time and size.

Discrete dislocation dynamics (DDD), can be used to describe calculate dislocation motion and interactions and to determine the strain energy landscape in two dimensions. The rationale behind using DDD is based on its ability to capture complex dislocation networks and the interactions of the dislocations with other defects, such as dislocation-point defects and
dislocation-planar defects $^{39,40}$. To assess the effect that the strain energy consumed during the formation of a cavity, calculated from the energy landscape in DDD, has on the cavitation process, cluster dynamics (CD)$^{41}$, an alternative approach to modeling the kinetics of void nucleation, has been adopted. CD, a mean-field, rate-theory based evolution model, calculates the rate of vacancy absorption and emission from a cluster and thus captures both simultaneous and independent growth within a representative volume.

In our approach, we use DDD simulations in which local stress are calculated using Fast Fourier transform model (DDD-FFT) to map out the formation energy landscape of nucleation and growth of voids as a function of size within a simulation volume$^{42,43}$. The strain energy distribution within a microstructure is calculated from the local mechanical fields in Fourier space and the stable cavity nucleation rate is determined using cluster dynamics. The data obtained in these simulations are used to develop a statistical distribution model of nucleation sites in bulk.

**Thesis Outline**

In chapter 2, the fundamentals of the cavity nucleation process will be discussed. In the beginning, a similar approach to the Hull-Rimer diffusion model was adopted to derive the rate of vacancy absorption into a vacancy cluster. To study vacancy evolution, the rate of vacancy absorption is decomposed into partial rates and implemented into the cluster dynamics. Given that the thermodynamic component dominates, a review of the thermodynamics of void nucleation will be discussed, incorporating the contribution from dislocation networks. Further, a continuum statistical approach using the Fokker-Planck model is demonstrated.
In chapter 3, implementation and validation of the DDD-FFT calculations used to map the local energies consumed during void formation is presented. A statistical database of consumed strain energy is built.

Finally, in chapter 4, the data collected obtained from both models is presented and analyzed. From the data, it is shown that nucleation is highly improbable in bulk systems indicating a need to study other potential mechanisms that drive nucleation.
CHAPTER 2. THERMODYNAMICS AND KINETICS OF CAVITY NUCLEATION

Summary

The purpose of this chapter is to present the fundamental derivation of the vacancy absorption rate and the free energy of formation widely used in the study of cavitation problems. The vacancy absorption rate provides kinetic and thermodynamic contributions that drive the void evolution problem. The contributions are decomposed into cluster dynamics partial rate equations and the evolution of vacancy cluster size is solved numerically using the Fokker-Planck solution. Moreover, from the vacancy absorption rate, it is evident that the dominant contribution needed to enable the growth of vacancy clusters is from the thermodynamics. The second section establishes whether the strain energy obtained from the local dislocation network provides the additional energy required for void nucleation to occur. An analytical expression of the critical strain energy per unit length required for nucleation given local pressure and surface energy is obtained.

Vacancy absorption rate

Consider a vacancy in different configurations within a grain boundary, as illustrated in Fig. 2. Assuming a dilute system, the formation energy of the vacancy at a \( G_v^a \) and b \( G_v^b \) is

\[
\begin{align*}
G_v^b &= G_{n-1}^f + G_v^f - G_n^f \\
G_v^a &= G_v^f
\end{align*}
\] (1a) (1b)
where $G_v^f$ and $G_n^f$ is the Gibbs free energy of formation of a single vacancy and a cluster of n vacancies respectively. Note that $G_v^b$ is equivalent to the binding energy of vacancy into a cluster of vacancies. The concentration of vacancies at these two configurations is obtained by:

$$\begin{align*}
C_v(a) &= \frac{1}{\Omega} \exp \left( \frac{-G_v^f}{kT} \right) \exp \left( \frac{1}{kT} (G_n^f - G_{n-1}^f) \right) \\
C_v(b) &= \frac{1}{\Omega} \exp \left( \frac{-G_v^f}{kT} \right)
\end{align*}$$

(2a)  \hspace{1cm} \text{(2b)}

where $C_v$ is the concentration of vacancies, $\Omega$ is the atomic volume, $k$ is the Boltzmann constant and $T$ is the temperature of the system. A concentration gradient is built across these two configurations. Hull-Rimer$^{44}$ were the first to propose that cavitation is driven by vacancy diffusion. This model has been modified to account for the combined effects of creep and diffusion in grain boundary cavitation with an initial rough approximation by Speight and Beere$^{45}$ and later a more exact solution by Needleman and Rice$^{44}$. Using this model, the current of vacancies into a cavity is

$$\dot{n}_v = \iiint -D \nabla C_v(l)$$

(3)

Here, $\dot{n}_v$, is the rate of vacancy absorption and/or emission, and $D$ is the diffusion coefficient for the vacancy and $C_v(l)$ is the concentration of vacancies at a distance $l$. Satisfying Fick’s second law by assuming that the system is in steady-state and mass is conserved,

$$\frac{\partial C}{\partial t} = 0 = -D \nabla^2 C_v(l)$$

(4)
Solving the current of vacancies in a grain boundary in cylindrical coordinates at $\theta = 0$ given

the boundary conditions in equation (4),

$$\dot{n}_v = \frac{4\pi \delta D'}{\log b/a} \left( \frac{1}{\Omega} \exp \left( \frac{-G_v^f}{kT} \right) \left[ 1 - \exp \left( \frac{1}{kT} (G_n^f - G_{n-1}^f) \right) \right] \right)$$

in which $\delta$ is the unit thickness of the grain boundary. Considering a large number of vacancies

in a cluster, the term $\left( G_n^f - G_{n-1}^f \right)$ can be simplified to Taylor function of $n$ vacancies,
\[ \dot{n}_v = \frac{4\pi \delta D' \, 1}{\log b/a \, \Omega} \exp \left( -\frac{1}{kT} \right) \left[ 1 - \exp \frac{1}{kT} \left( \frac{\delta G_v}{\delta n} \right)_n \right] \]  

(6)

Assuming The term \( \frac{4\pi \delta D' \, 1}{\log b/a \, \Omega} \) in equation (6) is site-dependent. For simplicity, a generic version of equation (6) has been adopted for the rest of the calculations in this thesis;

\[ \dot{n}_v = \omega \exp \left( -\frac{1}{kT} \right) \left[ 1 - \exp \frac{1}{kT} \left( \frac{\delta G_v}{\delta n} \right)_n \right] \]  

(7)

Kinetic factor

Thermodynamic factor

Examining equation (7), it can be decomposed into kinetic and thermodynamic components of the nucleation rate as highlighted. It is evident that the thermodynamic contribution is the driving force in cavity growth or shrinkage as the kinetic contribution is a constant function dependent on the local microstructure. In the next two sections, the thermodynamics of cavity formation is reviewed and an analytical expression that describes the contribution of strain energy is defined. Further, a CD approach is taken to model the evolution of vacancy clusters using the growth and shrinkage components as the partial rates.

**Thermodynamics of cavity nucleation**

In classical nucleation theory, the two dominant contributions in the free energy formation of the void are the volume contribution and surface contribution as illustrated in the schematic in figure 2. Note that in the description of Gibbs free energy of cavity formation, the stored elastic contribution has been neglected as it scales with \( \frac{\sigma^2}{2E} \) which is negligible given
that the magnitude of $E$ in comparison to $\sigma$. The free energy due to volume contribution is always negative as work is done on the system and dominates as the cluster size increase. However, at the initial stages of vacancy cluster formation, the interface formed between the matrix and the new phase dominates leading to increased free energy in the system. Thus, the total free energy of the system at a given radius is expressed as:

$$G_n = -\sigma F_v(r^3) + \gamma \eta F_A(r^2)$$

where $r$ is the vacancy cluster radius, $\sigma$ normal stress, $\gamma$ surface area and $F_A$ and $F_V$ are factor of area and volume respectively. Figure 3 illustrates individual contributions as shown in equation 8. Based on equation (8), a stable cluster of vacancies is formed when the derivative of Gibbs free energy of formation is equal to zero, thus the critical radius, $r_{\text{crit}}$, is obtained as shown.

Figure 3: Gibbs free energy of cavity formation
where $\eta$ wetting correction. As highlighted earlier, for nucleation to occur either high energies (up to 2Gpa) or very low wetting angles are needed for the energy barrier to be surpassed. Since neither of these conditions is thermodynamically probable at these sites, we hypothesize that an additional contribution to the free energy from the consumption of dislocation content within these regions is needed as suggested by $^{28,47}$. In the presence of dislocations at the nucleation site, equation (7) is modified into

$$G_n^a = -\sigma F_V(r^3) + \gamma F_A(r^2) - \tau$$

(10)

$\tau$ is the line tension obtained by finding the change in strain energy as a function of cavity size. Assuming a spherical void in bulk, $F_V = \frac{4}{3}\pi$ and $F_A = 4\pi$. Differentiating equation (10), a quadratic function is formed indicating that two zero flux sizes as shown,

$$r_c = \frac{\gamma}{\sigma} \left( 1 \pm \sqrt{1 - \frac{\sigma \tau}{4\pi \gamma^2}} \right)$$

(11)

Here we ignore the stable vacancy cluster (minimum in $G_n^a$) and focus on the critical size for cavity nucleation (maximum in $G_n^a$). Increasing the strain energy contribution $\tau$, reduces the thermodynamic barrier and, in cases that the energy is large enough, the barrier can be eliminated entirely. The critical strain energy contribution ($\tau_{crit}$) equals
In the next chapter, we will show how $\tau$ is obtained from the use of DDD-FFT and equation 12 will be used to determine the critical stresses needed. These parameters will be used in CD calculations to study the conditions needed for nucleation to occur.

**Fokker-Planck distribution model**

Atomistic, cluster dynamics (CD), and kinetic Monte Carlo (KMC) methods are commonly used in the simulation of the evolution of vacancy clusters$^{48-51}$. Among these three methods, CD is the most efficient method for use in this study as it can simulate long term evolution of a realistic microstructure at the least computational cost.

The evolution of the size distribution of vacancy clusters in CD models corresponds to the absorption and emission of a single vacancy from the cluster. In modeling this evolution, CD equations are written as a set of ordinary differential equations that are difficult to solve and may lead to high memory use and computational time. To avoid this issues, the stochastic Fokker-Planck method, is often used, which yields the evolution of the probability distribution of vacancies cluster sizes.$^{52-54}$ A one-dimensional Fokker-Planck solution has been developed for this program to study time evolution ($dt$) of cavity size density distribution as a continuous function using the equation:

$$
\frac{dp_n}{dt} = (r_{n-1}^+ p_{n-1} + r_{n+1}^- p_{n+1} - r_n^+ p_n - r_n^- p_n)
$$

(13)
where $p_n$ is the density of cavities of size $n$ and $r^+$ and $r^-$ are the partial rate of absorption and emission. The first term describes a smaller cavity absorbing $n$ vacancies, the second term shows the desorption of $n$ vacancies from a larger cavity, and the third and fourth terms represent absorption and emission of $n$ vacancies from the parent cluster. The vacancy absorption rate equations in equation 7, is decomposed into partial rates for growth and shrinkage as

$$r^+ = \omega \exp \left( \frac{-G^f_n}{kT} \right)$$  \hspace{1cm} (14a)

$$r^- = \omega \exp \left( \frac{-G^f_n}{kT} \right) \exp \left( \frac{1}{kT} \frac{\delta G^f_C}{\delta n} \right)$$  \hspace{1cm} (14b)

Figure 4: Thermodynamic conditions needed for nucleation to at 973K occur using the FP method, left: 20x surface tension reduction is needed. Right: Requires stress concentration above 2Gpa. Image courtesy of Aaron Kohnert
Table 1: Parameters used in simulation of evolution of size distribution of vacancy clusters

<table>
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<tr>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
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<tr>
<td>Atomic Volume</td>
<td>1.2 x 10^{-29}</td>
<td>m³</td>
</tr>
<tr>
<td>Surface energy of Iron</td>
<td>2.0</td>
<td>J/m^2</td>
</tr>
<tr>
<td>Vacancy migration energy</td>
<td>0.57</td>
<td>eV</td>
</tr>
<tr>
<td>Vacancy formation energy</td>
<td>1.67</td>
<td>eV</td>
</tr>
<tr>
<td>Vacancy formation entropy</td>
<td>1</td>
<td>k</td>
</tr>
<tr>
<td>Generation lifetime</td>
<td>1 x 10^{-5}</td>
<td>Hz</td>
</tr>
<tr>
<td>Fokker-Planck width parameter</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>Grain radius</td>
<td>1 x 10^{-5}</td>
<td>m</td>
</tr>
<tr>
<td>Discrete – continuous transition size</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>1.381 x 10^{-23}</td>
<td>J</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.29</td>
<td></td>
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Figure 4, shows a preliminary analysis of the thermodynamics conditions needed for void nucleation in bulk using the FP method and is consistent with results obtained by Raj, as discussed in the previous section. The parameters used for all calculations using the FP method are indicated in table 1. Once the strain energy contribution from the dislocation network, the nucleation kinetics is assessed using the FP method.
CHAPTER 3. ENERGY MAPPING USING DDD-FFT MODEL

Summary

In this section, the basic formulation of the DDD-FFT model, which will be used to accurately quantify the magnitude of consumed line tension energy during the formation of a cavity, is discussed.

Overview of DDD-FFT model

Discrete dislocations dynamics model is a force-driven model of dislocation motion and interactions at the mesoscale. The general procedure of DDD entails representing dislocation networks by nodes connected by segments, which in our implementation are straight. During each timestep, Peach-Koehler force acting on each node is computed by summing the contributions from both long-range and short-range stress fields, which arise from external loading, other dislocations, and other types of defects present in the microstructure, e.g. voids. Assuming over-damped dynamics, the motion for dislocations is solved, which results in an update on the new nodal positions. The most computationally expensive part of the calculations is the determination of the local mechanical fields arising from the dislocation network. To increase the efficiency, in our case DDD simulation employs Fast Fourier transforms in the computation of the mechanical fields.

Validation of FFT-Solver

There are two numerical issues that have to be resolved when using the DDD-FFT method. First, the FFT must be carried out on a discrete grid and the resolution of that grid (i.e.
grid spacing) must be chosen to have a converged solution. In addition, instabilities in the FFT (Gibbs oscillations) arise where there are singularities in the elastic constants, as would be found at the interface of the bulk material and a cavity. To lessen the effects of the bulk/bulk cavity interface, we set the elastic constants within the cavity to a finite value that is large enough to lessen instabilities yet small enough to have little effect on the calculated stress.

Consider a three-dimensional two-phase material system composed of a linear isotropic matrix and spherical void in a unit cell as shown in Figure 5(a). Within the simulation domain, the local mechanical state can be solved using the fundamental boundary value problem

\[
\sigma^{\text{tot}}(\vec{r}) = C(\vec{r}) : (\varepsilon(\vec{r}) - \varepsilon^p(\vec{r}))
\]

\[
\sigma_{ij} = 0
\]

\[
\sigma_{ij} n_j = 0
\]

where \(C(\vec{r})\), \(\sigma^{\text{tot}}(\vec{r})\), \(\varepsilon(\vec{r})\), \(\varepsilon^p(\vec{r})\), and \(n_j\) are the stiffness fourth order tensor, total stress, total strain, plastic strain at a material point, \(r\), and the normal vector respectively. The local stress fields can be computed either using a closed-form solution based on Eshelby’s analysis\(^{58-61}\) or DDD-FFT. The 2D maps illustrating the local stress distribution are shown in figure 5 (b and c). As expected, there is a slight variation in the plots due to discretization in the FFT solver.

As noted above, we want to avoid oscillations caused by the use of an elastic tensor of zero within the cavity. Considering these limitations, the maximum allowable mechanical contrast is obtained analytically by using Eshelby solution to calculate the magnitude of the local stress field of using different void stiffness modulus taking the configuration with vacuum as the base. The stress fields across the y-axis are plotted in Figure 6 (left).
In this study, the contrast ratio selected for the rest of the calculations was taken as 100 (Table 2). This value is within the optimal range of the contrast ratio for stable solutions from FFT and yield good agreements with the results with zero Young’s modulus. Note that in this study Gibbs oscillations are attenuated by using a filtered discrete operator.$^{62}$

Figure 5: Schematic of the model and 2D maps of the stress fields calculated using FFT solver. a) Illustration of an isotropic iron matrix with a void inclusion /phi. b) The stress field distribution calculated using Eshelby’s inhomogeneity closed-form solution. c) Stress fields around an inclusion using FFT solver. The transition is not as smooth as that obtained using closed-form solution as expected due to Gibbs oscillations.
Lastly, the variation in the computation of the local stress fields using DDD-FFT and the closed-form solution is performed and values plotted are as shown in Figure 6 (right). From the illustration, the minimum allowable cavity radius is 10nm which corresponds to a grid size of 5nm. Experimentally, cavities of radii ranging between 10 nm – 100 nm have been observed, which correlates well with the range of 10 nm – 70 nm selected for this study, all of which being within the desired FFT resolution. To achieve higher accuracy, a higher FFT resolution (smaller grid sizes) than the minimum allowable value, i.e., 2 nm - has been employed by reduction of simulation volume.

Figure 6: Plots of stress fields along the Y-axis computed analytically and using FFT-Solver. **Left:** Comparison of the local stress field by varying the elastic stiffness of void as shown on the legend. The minimum allowable contrast ratio is 100. **Right:** Comparison of the local stress fields varying the radius of the cavity to determine the resolution of FFT solver to adopt.
Table 2: Elastic Constants (GPa) of BCC Iron Matrix and Voids used in simulations. The values for voids have been approximated to reduce computation time and singularity error.

<table>
<thead>
<tr>
<th></th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Matrix</td>
<td>233.1</td>
<td>135.4</td>
<td>117.8</td>
</tr>
<tr>
<td>Cavity</td>
<td>0.2331</td>
<td>0.1354</td>
<td>0.1178</td>
</tr>
</tbody>
</table>

**Generation of dislocation microstructure**

Multiple periodic dislocation microstructures were generated in the bcc α-Fe matrix cubic domain of sizes $[512 \times 512 \times 512]$ nm and $[256 \times 256 \times 256]$ with dislocation densities ranging from $1 \times 10^{13}$ m$^{-2}$ to $3 \times 10^{15}$ m$^{-2}$. Examples of dislocation microstructures generated from DDD-FFT are shown in Figure 7. For each case, randomly created elliptic dislocation loops are placed in a simulation volume with periodic boundary conditions and initially discretized with 64 Fourier points in each direction. High strain rates ranging ($10^5$ - $10^6$ s$^{-1}$) are applied for a few hundred timesteps to multiply the dislocation density. To achieve equilibrated network of dislocations, relaxation of the generated microstructure is needed. Initially a zero-strain rate ($\dot{\varepsilon} = 0$) loading condition is applied to relax the microstructure given as,

$$
\delta \tilde{\varepsilon} = \dot{\varepsilon} \delta t = 0 \\
\delta \tilde{\sigma} = \mathcal{C} : (\delta \tilde{\varepsilon} - \delta \tilde{\varepsilon}^p) = \mathcal{C} : -\delta \tilde{\varepsilon}^p
$$

(14)
In equation 14, the system equilibrates in the given loading condition by reduction in its volume. However, since placement of a cavity also results to volume change, it is critical to ensure the loading conditions applied during relaxation do not significantly change the volume of the iron matrix. To verify this, a comparison is made using a stress rate $\dot{\sigma} = 0$

$$\delta \dot{\sigma} = \dot{\sigma} \delta t = 0$$

$$0 = C : (\delta \ddot{e} - \delta \ddot{\bar{e}})$$

(15)

In this condition, the system equilibrates by change in elastic strain which has no effect on the systems volume hence we can use this model to assess the magnitude of energy loss due to change in volume during the relaxation process. Assessing the results obtained from these two approaches, we see that the variation in total energy of the system as a result of applied strain or stress rate control was infinitesimal (an average percentage change of $10^{-7}$ between energy calculations due to applied zero strain rate and stress rate during relaxation). Thus, either of the methods can be used. For this study, a zero-stress rate is adopted for all microstructure simulations.

After 70,000 timesteps, the FFT resolution was increased, for further relaxation of the microstructure using a voxel size of 128 in all directions. The local strain energy at each grid point $k$ is obtained by

$$\partial E_{el}^k = \frac{1}{2} \sum_i \sum_j \sigma_{ij} \varepsilon_{ij} \partial V^k$$

(16)
where $E_{el}^k$ is the total elastic strain energy at grid point $k$, $V^k$ is the volume of grid point $k$, $\sigma_{ij}$ is the stress field, and $\varepsilon_{ij}^e$ is the elastic strain field at grid point $k$.

To reduce the computational cost, the total strain energy in the simulation is calculated via sub voxel quadrature integration of the total stresses including short-range corrections. To ensure that the microstructure is equilibrated, fluctuations in total energy are tracked until the energy is converged, as shown in Figure 8.

**Determination of consumed strain energy**

Once the dislocation network has equilibrated within a microstructure, a systematic procedure based on an energy-based criterion is used to determine potential nucleation sites.

1. Define a 10 nm search radius and find all the grid points within the volume defined by a sphere of that radius at each grid point in the microstructure
2. Sum all the strain energy values within each bound sphere for every grid point.

Figure 7: Examples of three types of periodic dislocation microstructures in bulk. The dislocation densities are $5.95 \times 10^{13} \text{ m}^2$ (left), $1.66 \times 10^{14} \text{ m}^2$ (center) and $2.27 \times 10^{14} \text{ m}^2$ (right)
Figure 8: Plot illustrating the change in the total energy at different timesteps of two dislocation microstructures of densities 2.93x10^{14} m^{-2} (blue) and 1.41x10^{14} m^{-2} (yellow). In these two-dislocation microstructures, the relaxation process takes 5000 timesteps.

Figure 9: Illustration of calculated potential nucleation sites within a microstructure with 2.27x10^{14} m^{-2} dislocation density. To determine the nucleation site, the sum of local energies of neighboring sites bound by a radius of 10nm is performed on all sites.
3. Loop over all grid points and determine the top 10 points with the highest energy that also has a dislocation junction within its bound volume. Using energy as the determinant ensures that both the principal and shear stress contributions are incorporated in the selection of the most suitable site. The point that satisfies these two conditions is selected as a site. Fig 9, illustrates this condition.

Each microstructure is replicated depending on the number of sites obtained above, with a maximum of 10 potential sites selected per microstructure. A cavity having a radius of 10nm is placed and grown to 70nm as illustrated here:

![Diagram](Place cavity (Grow by 10nm) ➔ Calculate change in energy ➔ Relax (250 timesteps) ➔ Place cavity (Grow by 10nm))

Figure 10: Cavity growth process

Given that the volume changes with cavity growth, a volume correction factor is incorporated in estimation of cavity formation energy, $E_n^f$ of cavity size,
\[ E_n^f = E_{el}^{\text{tot}(\text{in})} - \frac{V_{\text{tot}(\text{in})}}{V_{\text{tot}(\text{in}-n)}} \times E_{el}^{\text{tot}(\text{in}-n)} \]  

(17)

where \( E_{el}^{\text{tot}(\text{in})}, E_{el}^{\text{tot}(\text{in}-n)} \) is the total energy of the microstructure before and after placement of the cavity of size \( n \). Similarly, \( V_{\text{tot}(\text{in})}, V_{\text{tot}(\text{in}-n)} \) is the simulation volume before and after placement of the cavity of size \( n \). The value obtained from equation (17) corresponds to the Gibbs free energy of cavity formation in the bulk, similar to a modified version of equation (10) excluding the surface energy contribution.

\[ E_n^f = -\sigma F_v (r^3) - \tau r \]  

(18)

The first term is the work done in the formation of the cavity, the second term represents the strain energy consumed by the cavity during its formation. The value \( \tau \) obtained in the DDD-FFT framework comprises of contributions from three factors; line tension consumed, interaction energy among consumed dislocation, and the strain energy of the remaining dislocations. At zero strain rate, the work done is eliminated, reducing equation (18) to

\[ E_n^f = \tau r \]  

(19)

\( \tau \) can easily be obtained by differentiating equation 19 as a function of the cavity radius \( r \). For simplicity, the values solved for equation 19 are plotted against the cavity radius and the slope of the line becomes \( \tau \). This is a coarse estimate as it will be shown later that the plot of \( E_n^f \) values against \( r \), rarely follows a linear trend.
CHAPTER 4. RESULTS AND DISCUSSION

Summary

An analysis is performed on the data collected from the energy landscape generated from the DDD-FFT framework and the nucleation rate parameters from the Fokker-Planck method. In the first subsection, we demonstrate that the DDD-FFT method can adequately describe the energy landscape arising from dislocations by capturing line tension and interaction contributions to the energy. The correlation between initial dislocation density and the consumed strain energy is also assessed. In most cases, higher dislocation densities result in the formation of complex dislocation microstructures leading to increased strain energy consumed during the formation of a cavity.

Energy landscape

Numerous calculations were performed with multiple sites for many microstructures and the change in cavity formation strain energy per unit size was determined. The average of all the cavity formation energies due to the dislocation network is plotted as a function of the size of cavities. The plot follows a non-linear trendline as illustrated in figure 10(left). The line tension energy scales as $1/r$, which yields with a linear relationship. The non-linear variation in the trendline of the plot, indicates that the contributions of the interaction energies from consumed dislocations and the strain energy of the remaining dislocations over the volume consumed, cannot be ignored requiring, the use of DDD method. This inference is supplemented by watching a video of the relaxation process of dislocation network upon placement of a cavity, which is shown Appendix 1. From the video, it is evident that there is further relaxation of
dislocation microstructure when a cavity is placed, since the local configuration of equilibrated dislocation networks is altered. Note that, to ensure accuracy of our model, the dislocation segments in the pseudo-vacuum region representing a cavity has minimal interactions with segments in the matrix. Additionally, the total energy within the pseudo-vacuum region is calculated independently and has been excluded in the computation of consumed strain energy.

**Figure 11:** Cavity formation energies calculated from 523 probable sites of nucleation. **Left:** Average cavity formation energies per unit size. The energies obtained follow a cubic trend indicating there is an extra contribution from the complex dislocation interaction. **Right:** Plot highlighting the correlation of the consumed strain energy per unit size as a function of the initial dislocation density of the microstructure.

**Effect of dislocation density**

Experimental evidence supports the view that nucleation of cavities occurs in regions with high dislocation density, such as near grain boundaries. In principle, an increase in dislocation density results in an increased magnitude of local stress concentration. A scatter plot of consumed strain energy per unit size, $\tau$ for all sites against initial dislocation density, confirms this, as shown in Figure 11 (right). However, there are cases, i.e., within initial
dislocation densities ranging 4.1-4.4 \times 10^{14} \text{ m}^2, where a noticeable variance in the magnitude of \( \tau \) is observed. To establish the cause of this variance, first, a correlation between the average value of \( \tau \) and the total energy of each microstructure is determined. Comparing the two parameters against initial dislocation density as shown in Figure 11 (a and b), it is evident that \( \tau \) is directly proportional to the total initial energy of the microstructure. With this, the two cases are studied by assessing the relationship between the local dislocation configuration, the initial total energy, and initial dislocation density, as illustrated in section c of figure 11. The difference in the total energy of the two microstructures largely correlates to the local microstructure variables (i.e. junction, the character of segments (screw, edge and mixed, and the number of connections). Despite special considerations highlighted above, most complex microstructures are formed at higher dislocation density.

**Statistical distribution of critical pressure**

From our simulations, we assume each of the \( \tau \) values calculated for each site is assumed to be critical. With this, we use equation 12 to determine the critical stress for each site assuming that the selected material is 100% pure. The statistical distribution of all critical pressures calculated from 523 sites is plotted required Figure 12. From the plot, the lowest critical pressure obtained has a magnitude of 1.5 GPa. Realistically, from these results the nucleation of voids under these conditions is still thermodynamically improbable even in cases where the density of dislocation network is high. This outcome is not surprising and matches the lack of evidence for bulk nucleation.
Figure 12: A comparison on the cause of variance in consumed strain energy as a function of its size. a) A plot of average $\tau$ versus initial dislocation density. b) A plot of total energy versus initial dislocation density. Plots in a and b have a similar trend suggesting that $\tau$ is directly proportional to total energy of the microstructure. c) Comparison of two cases where higher dislocation density does not necessarily result in higher total energy.
Figure 13: Critical pressure distribution function
CHAPTER 5. CONCLUSION

In this study, a novel approach has been presented to model a physical-based void nucleation model. In summary,

- A Fokker-Planck based expression has been derived for continuum statistical modeling of the evolution of vacancy clusters. With this, the conditions needed for nucleation to occur can be examined.

- Detailed description of the DDD-FFT method to mapping of the local energy landscape in a dislocation microstructure is presented. This method accurately represents complex networks leading to a high-fidelity calculation of line energy contribution.

- In most cases, higher dislocation densities lead to complex network configurations leading to higher local energies. However, this is dependent on the actual network configurations as few cases where the initial dislocation density results in higher consumed line tension and interaction energies.

- The probability for nucleation due to local stress concentration arising from static dislocation network in the bulk of a pure metal is highly improbable which correlates with experimental observation in existing studies. However, this presents an opportunity to further these studies by using our approach to assess other mechanisms that could potentially generate the additional stress build-up needed for nucleation to occur.
REFERENCES


APPENDIX. MICROSTRUCTURE RELAXATION UPON PLACEMENT OF CAVITY

Figure A1: Microstructure relaxation animation