Abstract. The Phase-Field Crystal (PFC) model represents the atomic density as a continuous function, whose spatial distribution evolves at diffusional, rather than vibrational time scales. PFC provides a tool to study defect interactions at the atomistic level but over longer time scales than in molecular dynamics (MD). We examine the behavior of the PFC model with the goal of relating the PFC parameters to physical parameters of real systems, derived from MD simulations. For this purpose we model the phenomenon of the shrinking of a spherical grain situated in a matrix. By comparing the rate of shrinking of the central grain using MD and PFC we obtain a relationship between PFC and MD time scales for processes driven by grain boundary diffusion. The morphological changes in the central grain including grain shape and grain rotation are also examined in order to assess the accuracy of the PFC in capturing the evolution path predicted by MD.

1. Introduction
The phase field crystal (PFC) method has evolved in recent years as a novel approach for investigating structural evolution at the diffusional time scale with atomic resolution. [1] The underlying feature of the method involves the representation of the atoms in a crystal as a time averaged atomic density field and evolving the density field by solving an evolution equation that drives the free energy density to a minimum. The approach eliminates the need for tracking unproductive local atomic displacements that result from energy excursions that are small compared to the activation energy required to evolve the system through atomic migration. The free energy functional that represents the three-dimensional atomic density with the required crystal symmetry is derived from the atomic density functional theory. For example, a functional that captures the periodicity of body-centred cubic (BCC) iron has recently been developed as shown in Eqn. 1.

\[ F = \int \left[ \frac{B_4 R^4}{2} \rho \left( \frac{1}{R^2} + V^2 \right) \rho + \frac{B_6 - B_4}{2} \rho^2 + \frac{v}{3} \rho^3 + \frac{w}{4} \rho^4 \right] dV \]  

(1)

where where \( \rho \) is the atomic density. In the appendix of their paper, Jaatinen et al. [2] derive a form of the free energy functional where the cubic term is made to vanish. Setting \( -z = 0 \), \( 4z = 0 \), \( z = 1 \), \( 0z = 0 \), \( =0 \), and \( =z \), and using the values based on data for BCC iron at 1772 K given in (A7)-(A11) of [1], the parameters in Eqn. (1) are obtained as \( B_4 = 20.0417 \text{ eVÅ}^3 \), \( B_6 = 22.0789 \text{ eVÅ}^3 \).
The evolution equation for the free energy is based on the modified phase field crystal approach [3] given by

$$\frac{\partial^2 \rho}{\partial t^2} + \beta \frac{\partial \rho}{\partial t} = \alpha \nabla^2 \left( \frac{\delta F}{\delta \rho} \right)$$  \hspace{2cm} (2)

where $\alpha$ and $\beta$ are phenomenological constants. The ability of the PFC approach to capture topological defects such as dislocations and their evolution during deformation has been demonstrated in the literature [4]. The PFC approach is also known to capture the structure of grain boundaries and the variation of the grain boundary energy as a function of boundary misorientation in accordance with the Read-Shockley equation [5]. However, grain boundary motion under the influence of a driving force demonstrated by PFC has not been compared with conventional atomistic techniques such as molecular dynamics (MD) to ascertain the ability of the PFC to capture the atomistic mechanisms involved. For example, curvature driven grain boundary motion occurs by grain boundary diffusion and the grain boundary velocity is determined by the boundary energy as well as its mobility. Anisotropy in grain boundary energy or the mobility can lead to changes in the grain morphology during grain growth. It is interesting to see if such shape changes can be accurately captured by the PFC method. The objective of the present study is to compare the evolution by shrinking of a spherical grain embedded in a matrix using PFC and MD.

2. Simulations

The kinetics of shrinking and the morphological changes in the central spherical grain were investigated using PFC and MD for three different misorientations of the central grain with respect to the matrix to generate grain boundaries with different energies and mobilities. The orientation of the outer matrix grain was set to the reference state with zero rotation about the $x$, $y$ or $z$ - axis. The following three orientations where chosen for the central grain:

- 15 degree rotation about the $z$ axis, labeled (0 0 15)
- 15 degree rotation about $x$, $y$ and $z$ axes, labeled (15 15 15)
- 45 degree rotation about the $z$ axis, labeled (0 0 45)

The initial, two-grain geometry was created in PFC by appropriately seeding the orientations of the inner and the outer grains based using an analytical one-mode approximation for the density field outlined by Wu and Karma [5]. The input to the MD simulations was obtained by using the peak positions of the three-dimensional density profiles as the atom positions. However, the density of the PFC peaks near the grain boundary regions is lower than in the grain interior although the overall density in PFC is conserved globally. Therefore, if we assume that the probability of existence of an atom is 1.0 for peaks in the interior locations of the grain, the corresponding probability is lower at the peak positions in the grain boundary regions indicated by PFC. Therefore, in order to use the PFC data as input to MD, it is necessary to devise a method that eliminates some of the PFC peaks near the grain boundary. Here, we propose three different approaches for creating bicrystals where the outer matrix grain is always in the (0 0 0) orientation and the inner grain with a spherical morphology is

\[ R = 0.335 \, \text{Å} \], \( v = 0 \) and \( w = 8.4582 \, \text{eVÅ}^3\text{Å}^{-9} \).
come” method, where the outer and the inner crystals are formed directly from the liquid using the seeding approach of Wu and Karma [6]. The number of density peaks in the bicrystal is carefully monitored as the system evolves and the simulation is terminated when the number of peaks equals \( N_{000} \). The assumption here is that the most probable atoms positions in the bicrystal especially in the grain boundary regions will first develop as PFC density peaks. The third approach involves the creation of the bicrystal geometry using PFC as in the second approach and allowing the simulation to continue until the number of PFC peaks in the system approaches the maximum value. This value is typically higher than \( N_{000} \). The atom positions are then picked from the PFC peaks in the descending order of the peak intensity until the number of atoms becomes \( N_{000} \).

The atomic representation of the bicrystal obtained from PFC was further evolved in MD using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code developed at the Sandia National Laboratory [7]. The simulations were carried out for BCC iron using the embedded atom potential developed by Mendelev et al. [8].

The initial atom positions from PFC were scaled to the lattice constant of BCC iron at 0K. Initially, a minimization run was performed to move the atoms in the grain boundary and interior locations to local energy minima. The next step involved an expansion of the simulation cell to a size corresponding to 873K using a linear thermal expansion coefficient of 11.8 \( \times 10^{-6} \)/K while simultaneously providing a kinetic energy corresponding to 100K, followed by a minimization run. The final step involved an NVT ensemble run at 873K using a time step of 0.001 ps. The MD simulations were continued until the central grain completely disappeared due to curvature driven forces. The PFC simulations were also continued until the disappearance of the central grain. A system size of 360 x 360 x 360 was used in PFC to generate the bicrystal geometry that resulted in an MD domain size of 36 x 36 x 36 BCC unit cells of Fe. PFC simulations were based on a finite difference solution of Eqn. 2 based on an explicit technique with a time step of 0.005.

### 3. Results and Discussion

The variation of the total energy per site with PFC time is shown in Fig. 1 for three different grain boundary types. Since the excess energy is proportional to the grain boundary surface area, and since the grain boundary area decreases linearly with time for curvature-driven grain shrinkage, a linear reduction in energy with PFC time is expected. The shrinkage curve for the \((15\ 15\ 15)\) boundary is closest to the linear behavior, while for the \((0\ 0\ 45)\) boundary the shrinkage curve is slightly convex. The shrinkage curve for the \((0\ 0\ 15)\) boundary appears to deviate slightly from the linear behavior.

![Fig 1. Variation of total energy with simulation time during PFC. The total energy decreases as the central grain shrinks.](image)

---

IUPAP C20 Conference on Computational Physics (CCP 2011) IOP Publishing

Journal of Physics: Conference Series 402 (2012) 012043
doi:10.1088/1742-6596/402/1/012043

---
The temporal evolution of the bicrystals is shown in Fig. 2 as contours of the density field at the mid-section perpendicular to the z-axis. Careful observation of the bicrystals indicated a small rotation of the (0 0 15) grain at the initial stages of shrinkage, with a probable change in the boundary energy and mobility that could account for the small deviation from the linear behavior shown in Fig 1. No such rotation was seen for the (15 15 15) grain that showed a linear shrinkage. The (0 0 45) grain also did not show any rotation. However, the boundary appeared to develop facets at various stages of the shrinkage process that probably resulted in energy and mobility changes. It appears that as the grain size becomes smaller, the number of facets increased, indicating that the average boundary mobility increased with decreasing grain size that results in the convex shrinkage curve shown in Fig 1. The (15 15 15) grain also showed a shape change in the $xy$ plane from an initial circular to an elliptical geometry as the grain shrinks. No significant shape change was seen for (0015) and (0045) grains.

Fig 2. Two-dimensional section perpendicular to the z-axis showing the temporal evolution during PFC simulation of the (0 0 15) (top), (15 15 15) (middle) and (0 0 45) (bottom) grain situated at the center of a (0 0 0) outer grain.

Figure 3 shows the shrinkage curves obtained from MD simulations for the three different grain boundary types. Three sets of curves are shown in Fig 5 for each of the approaches described earlier for obtaining the initial atom positions from PFC. Red curves correspond to the baseline approach, the green curves correspond to the “first-come” approach, and the blue curves correspond to the sorting approach. The initial portion of the curve in which the energy increases with time is due to the increase in the thermal energy associated with heating the system to 873K. It is possible that some evolution occurred during the heating period. The shrinkage portion of the curves appears to contain many of the features exhibited by the PFC simulations. These include the almost linear behavior for
the (15 15 15) boundary, a convex shrinkage behavior for the (0 0 45) boundary and smaller deviation from the linear behavior for the (0015) boundary. The shrinkage kinetics for the (0 0 45) boundary is significantly lower than for the other boundaries, which is the same behavior exhibited for the PFC as shown in Fig 1. The baseline approach results in the highest and the sorting approach the lowest energies for the initial bicrystal geometry. The baseline approach in which the initial single crystals are grown separately and then put together mechanically had the highest pressure during the MD runs as shown in Fig. 4. In the baseline approach, even though the total number of peaks in the bicrystal was equal to N000, there was probably an overcrowding of the atom positions near the grain boundary that did not relax completely during the 873K run.

The “first-come” approach gives an initial energy that is between those of the baseline and the sorting approaches. The baseline approach shows a lower shrinkage kinetics for the (15 15 15) boundary
compared to the (0 0 15) boundary which is not shown by either of the other two approaches, as well as by PFC. Based on these findings, it appears that the “first-come” or the sorting approach is probably better than the baseline approach for mapping atom positions from PFC for MD.

Figure 5 shows the temporal evolution of the grain structures obtained by the MD for the sorting approach. The atom positions shown in Fig. 5 were obtained by a minimization step carried out after the 873K NVT run for the times shown. The atoms are colored based on the potential energy of the atoms to obtain a good contrast for the grain boundary atoms. The behavior of the (0 0 15) bicrystal is very similar to that in the PFC simulations in that there is no significant faceting or shape change during shrinking. However, the (15 15 15) boundary becomes more elliptical during shrinking which is also captured by the PFC simulations. The (0 0 45) bicrystal shows evidence for faceting, which is again captured by PFC simulations. Therefore, it is safe to conclude that the PFC does capture both the relative shrinkage kinetics and the shape changes associated with changes in the grain boundary energy and mobility during shrinking of specific boundary types.

The time step in PFC simulations is a dimensionless quantity. The velocity of the grain boundary during shrinking is controlled by the phenomenological constants $\alpha$ and $\beta$ in Eqn. 2. However, by comparing the number of time steps in PFC required to fully shrink the grain with the MD time steps we can get an estimate for the time step used in PFC. In the PFC simulations, a time step of 0.005 was used. From Fig. 1, the number of PFC time steps to shrink the (0 0 15), (15 15 15),
and the (0 0 45) bicrystals were 4000, 2800 and 6000 respectively. The corresponding simulation times from the MD simulations shown in Figs. 3 and 4 are 19000 fs, 14000 fs and 87000 fs, respectively. Therefore, the equivalent time steps in the PFC simulation were 4.75 fs, 3.95 fs and 14.5 fs respectively.

4. Summary
The shrinking of a spherical grain situated in a matrix was simulated using PFC. Three different methods were developed for generating equivalent atomic positions for MD from the peak density positions obtained using PFC. The shrinking of the central grain with three different orientations was studied using PFC and MD using the different mapping procedures. PFC was able to capture the relative shrinking kinetics and the shape changes during shrinking of the central grain shown by MD. The relative speed up of PFC over MD for these grain boundary diffusion driven problems is orders of magnitude lower than for bulk diffusion driven evolution problems. Of the three methods used for mapping atom positions from PFC to MD, the method based on the sorting of PFC intensities and the method based on considering the earliest forming peaks appeared to provide reasonable comparisons between PFC and MD.

5. Acknowledgements
Research funded by the Energy Frontier Research Center (EFRC) project, Center for Defect Physics, Basic Energy Sciences, DOE at ORNL under contract DE-AC05-00OR22725. Computational resources were provided by the National Center for Computational Sciences at ORNL, which is supported by the Office of Science of the Department of Energy under Contract DE-AC05-00OR22725.

References
[1] Elder K et al 2007 Physical Review B 75 064107
[2] Jaatinen A et al 2009 Physical Review E 80 031602
[3] Stefanovic P et al 2006 Physical Review Letters 96 225504
[4] Chan PY et al 2010 Physical Review Letters 105 015502
[5] Provatas N et al 2007 JOM 59 83
[6] Wu KA and Karma A 2007 Physical Review B 76 184107
[7] lammps.sandia.gov
[8] Mendelev MI et al 2003 Philosophical Magazine A 83 3977