Atomistic simulations of the effect of helium clusters on grain boundary mobility in iron

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Abstract. A series of molecular dynamics simulations was performed in this work to investigate the kinetic interaction between helium clusters and grain boundaries in iron. Helium cluster formation and size distributions were found to be markedly different in the bulk compared to the region of a stationary boundary. Upon reaching a steady-state cluster distribution, the spatial fluctuation of cluster-enriched boundaries was analyzed to determine the grain boundary mobility using the random walk method. Segregated clusters reduced the boundary mobility, the drag effect of clusters increasing as the bulk solute concentration increases. The drag effect was further rationalized by employing Cahn’s solute drag model using the effective binding energy of He clusters and the grain boundary diffusivity of a single He atom, their magnitudes having been determined from the segregation level and from monitoring the trajectory of a solute atom in the investigated grain boundaries, respectively. The model is found to provide a satisfactory explanation of the simulation results in the zero velocity limit.

1. Introduction
The kinetic interaction between impurities and grain boundaries is conventionally treated within the framework of either solute drag models [1] for mobile solute atoms or particle pinning models [2] for immobile particles. Impurities forming clusters constitute an intermediate case because clusters of a few interacting solutes migrate at a much lower rate than individual atoms. Further, the effect of clusters on grain boundary mobilities has not been extensively explored in spite of its technological importance, e.g. embrittlement in irradiated steel vessels due to He clusters [3] or grain refinement of high-strength low-alloy steels due to Nb clusters [4]. The lack of studies on cluster-boundary interaction may be associated with both the length and time scales of the problem. The atomistic length scale requires experimental and/or simulation techniques with atomic resolution whereas the time scale extends from the order of atomic frequency to that of diffusion.

Atomistic computational tools can provide a valuable insight to tackling such a multi-scale problem. In this work, the interaction between grain boundaries in iron (Fe) and clusters of helium (He) in the limit of a dilute solution will be explored using molecular dynamics simulation. The formation and distribution of He clusters in the bulk matrix and grain boundaries of Fe will first be analyzed. Segregation behaviour of He will be characterized using a classical model to determine the effective binding energy. The mobilities of cluster-enriched grain boundaries in the limit of zero-velocity will then be extracted. This will permit an evaluation of the overall drag effect due to segregated clusters and its dependence on
properties such as solute diffusivity and binding energy. Finally, the simulation results will be assessed against a classical model on solute-grain boundary interaction.

2. Simulation methodology
Simulations were run using LAMMPS [5] with a time step of 1 fs. Visuals were produced using AtomEye [6]. The interaction among Fe atoms, among He atoms and between Fe and He atoms were modelled using the Ackland-04 [7], the Aziz-95 [8] and the Gao-11 [9] EAM potentials, respectively.

Figure 1. (a) A bicrystal cell with planar boundaries separating two grains, their orthogonal axes indicated in Table 1, (b) A magnified two-dimensional view of the bicrystal cell, populated with multiple He atoms (coloured pink) occupying tetrahedral interstitial sites.

The simulation box is a bicrystal cell, see Fig. 1(a), containing two crystals, A and B, of different orientation being separated by planar grain boundaries and having a total number of Fe atoms \(N_{\text{Fe}}\) in excess of 600,000 (see Table 1). Four types of boundaries were simulated, their geometrical features being given in Table 1. Each boundary is identified by their inclination angle measured relative to a symmetric coherent twin boundary, i.e. a grain boundary with \(Y_A/Y_B\) axes of \(\langle 111 \rangle/\langle 11\bar{1} \rangle\) and \(Z_A/Z_B\) axes of \(\langle \bar{T}12 \rangle/\langle 112 \rangle\).

The interaction between grain boundaries and He atoms was studied by introducing He atoms into each bicrystal using two types of configurations. In the first configuration, a He atom was placed in a tetrahedral site at the boundary. The binding energy profile of a single He atom was then obtained from molecular statics simulations, see [10] for details. The grain boundary width \(\delta\) was also extracted by determining the distance within which the binding energy is less than \(-10^{-3}\) eV. Molecular dynamics simulations were then run at 1000 K for 3 ns to track the trajectory of the He atom along the boundary. By computing its mean-squared displacement, \(\langle r^2 \rangle\), as a function of time-interval, \(\tau\), the single-atom boundary diffusivity, \(D_{\text{gb}}\), can be determined via \(\langle r^2 \rangle = 6D\tau\), see [11] for example.

Table 1. Geometrical setup of bicrystals and their solute contents. Each bicrystal shares a common \(X_A/X_B\) axis, \(\langle 1\bar{T}0 \rangle\), with a dimension \(L_X\) of 20.2 nm.

| Inclination \(\varphi\) [°] | Orthogonal axes, see Fig. 1(b) | Dimensions [nm] | \(N_{\text{Fe}}\) | \(N_{\text{He}}\) [atoms] |
|---------------------------|---------------------------------|----------------|-----------------|--------------------------|
| 19.5 \(\langle 112 \rangle\) | \(Y_A\) = \(\langle 11\bar{1} \rangle\) | \(Z_A\) = \(\langle 5\bar{5}\bar{2} \rangle\) | \(Y_B\) = \(\langle 115 \rangle\) | \(Z_B\) = \(\langle 1\bar{T}1 \rangle\) | \(L_Y\) = 20.0 | \(L_Z\) = 17.8 | 646000 | 647 | 3256 | 6543 |
| 44.7 \(\langle 118 \rangle\) | \(Y_A\) = \(\langle 11\bar{1} \rangle\) | \(Z_A\) = \(\langle 17\bar{1}4 \rangle\) | \(Y_B\) = \(\langle 2\bar{2}\bar{1}\bar{7} \rangle\) | \(Z_B\) = \(\langle 1\bar{T}2 \rangle\) | \(L_Y\) = 20.9 | \(L_Z\) = 19.7 | 712200 | 709 | 3560 | 7157 |
| 70.5 \(\langle 115 \rangle\) | \(Y_A\) = \(\langle 5\bar{5}\bar{2} \rangle\) | \(Z_A\) = \(\langle 1\bar{T}1 \rangle\) | \(Y_B\) = \(\langle 11\bar{1} \rangle\) | \(Z_B\) = \(\langle 1\bar{T}1 \rangle\) | \(L_Y\) = 22.2 | \(L_Z\) = 16.8 | 642000 | 648 | 3230 | 6485 |
| 90.0 \(\langle 112 \rangle\) | \(Y_A\) = \(\langle 1\bar{T}1 \rangle\) | \(Z_A\) = \(\langle 1\bar{T}1 \rangle\) | \(Y_B\) = \(\langle 1\bar{T}1 \rangle\) | \(Z_B\) = \(\langle 1\bar{T}1 \rangle\) | \(L_Y\) = 21.0 | \(L_Z\) = 17.8 | 642000 | 645 | 3230 | 6485 |
In the second configuration, multiple He atoms were placed randomly in tetrahedral interstitial sites, see Fig. 1(b). Several levels of bulk solute concentration, $C_0$, were initiated, i.e. 0.1 at%, 0.5 at% and 1.0 at%. Table 1 lists the number of He atoms, $N_{He0}$, that correspond to each concentration. Periodic boundary conditions were applied in all directions. Simulations were run at 1000 K under zero-pressure condition for a duration of 20 to 40 ns. Atomic positions were recorded every 1 ns during which time the cluster distribution was analyzed.

To characterize and quantify the size distribution of clusters, this work employs the Ward’s technique [12] implemented via the Lance-Williams algorithm [13]. It is chosen since the number of clusters are not known prior to the analyses. A detailed discussion of this technique is available elsewhere [14]. Clustering is deemed to reach steady state if the distributions from two snapshots taken within a 3 ns interval differ by less than 20%. Additionally, to investigate the effect of grain boundaries on clustering, clusters were classified into boundary and bulk clusters. Clusters are considered to belong to the boundary if 60% of their constituents are within $\delta/2$ from the average boundary position.

After steady state clustering has been achieved in the bulk and boundary portion of the bicrystal, the average position of the boundary, $\overline{h}$, is monitored over time to determine the boundary mobility using the random-walk (RW) technique [15]. A detailed discussion of the technique adapted to compute $\overline{h}$ is available elsewhere [16]. This technique can be applied since the boundary is rough at 1000 K, i.e. it performs a random walk that exhibits diffusive characteristics. The evolution of mean-squared displacement, $\langle \overline{r^2} \rangle$, of the average position of the boundary yields a coefficient that is directly related to the boundary mobility, $M$, via [15]

$$\langle \overline{r^2} \rangle = 2Mk_BT\tau/A$$

where $\tau$ is the time-interval, $A$ is the boundary area, and $k_BT$ is the product of Boltzmann’s constant and absolute temperature.

3. Results

3.1. Grain boundary interaction with a single He atom

The interaction between grain boundaries and a single He atom at 0 K is represented by the single-atom binding energy profile, a typical example shown in Fig. 2. The binding energy, represented by the maximum $E_{b0}$ in Table 2, is in a first order approximation 1.35 eV independent of the boundary inclination. The boundary width, $\delta$, determined from the binding energy profile increases with the boundary inclination from 7 to 9 Å, see Table 2.

![Figure 2](image)

**Figure 2.** The profile of binding energy of a He atom to the 44.7°-boundaries at 0 K, the regime of non-zero binding energy being defined as the boundary width, $\delta$.  

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The kinetic behaviour of a He atom is also significantly affected by the grain boundary. At 1000 K and for all investigated boundaries, the He atom at the boundary performed a random walk motion but remained within the boundary width at all times. Table 2 provides the single-atom boundary diffusivity determined from these simulations, $D_{gb}$. The bulk diffusivity $D_{bulk}$ at 1000 K is also presented in this table, and was obtained from performing the same type of random-walk analysis on a simulation where the He atom occupied tetrahedral sites of a single b.c.c. crystal. $D_{gb}$ is 2 to 3 orders of magnitude lower than $D_{bulk}$, i.e. the grain boundary is not a fast diffusion path for interstitial He atoms. This observation is consistent with simulations [17] and experiments [18] for interstitial diffusion of H, C and He in Fe grain boundaries.

### Table 2. Relevant material properties computed in this work.

| Property | Bulk | 19.5° boundary | 44.7° boundary | 70.5° boundary | 90.0° boundary |
|----------|------|----------------|----------------|----------------|----------------|
| $E_b$ [eV] | 0    | 1.31           | 1.34           | 1.34           | 1.38           |
| $\delta$ [Å] | -    | 6.8            | 7.7            | 7.8            | 8.8            |
| $D$ [m$^2$s$^{-1}$] | $1.24 \times 10^{-8}$ | $1.53 \times 10^{-11}$ | $3.10 \times 10^{-11}$ | $1.60 \times 10^{-10}$ | $1.37 \times 10^{-10}$ |
| $E_b^*$ [eV] | 0    | 0.48           | 0.50           | 0.53           | 0.52           |

3.2. Helium clustering and segregation

The behaviour of multiple He atoms in a bicrystal at 1000 K is now presented. He cluster formation occurs within a few ns, as is evident from Fig. 3(a), due to the high diffusivity of He atoms in the Fe matrix. There is, however, a markedly different clustering trend in the bulk and in the boundary, both in terms of their size distribution and their evolution. Figs. 3(b) and (c) illustrate the cluster distribution in the bulk and boundary, respectively, having been obtained from the Ward’s technique applied at different times during the simulation run.

Figure 3. (a) A snapshot of 44.7°-bicrystal containing 0.5 at% He taken at 3 ns, showing only He clusters, coloured according to their size, i.e. the number of atoms, (b) and (c) evolution of cluster size distribution in the bulk and boundary portion of the bicrystal in (a), respectively.

The bulk distribution, see Fig. 3(b), shows a negligible variation over a 36-ns simulation time, suggesting a steady state cluster distribution. Additionally, these bulk clusters are essentially immobile. This implies that, within the same period of time, no bulk clusters migrated to the boundary. Clusters found at the boundary form during the initial transient time (< 3 ns), due to the segregation of single fast-diffusing He atoms to the boundary. Solute segregation takes place rapidly and reaches steady state at approximately the same instance as the bulk clustering does.
In contrast to the bulk cluster distribution, the distribution at the boundary exhibits a notable evolution, see Fig. 3(c). Segregated individual He atoms diffuse along the boundary to form larger clusters, thereby changing the cluster size distribution at the boundary. The slow formation of boundary clusters compared to that of bulk clusters is consistent with the single-atom boundary diffusivity being 2 to 3 orders of magnitude lower than the bulk diffusivity, see Table 2. The single-atom boundary diffusivity can thus be considered as the rate-controlling process of cluster formation at the boundary. While the cluster distribution at the boundary continues to change over time even after 36 ns, the variation becomes increasingly negligible at longer times. The boundary distribution is deemed to have reached steady state at 12 ns, for the 44.7° boundary containing 0.5 at% He, because the distribution captured at that time differs only by 15% with that captured at 15 ns. Similar observations can be made for the other three boundaries studied here.

Figure 4. (a) Average segregation for different boundaries as a function of \(C_0\), error bars being the standard deviation, (b) the effective binding energy according to the Langmuir-McLean model, Eq. (2).

The segregation level at the boundaries is quantified by normalizing the number of segregated He atoms, i.e. the area under the graphs in Fig. 3(c), with the total number of boundary sites, i.e. the number of tetrahedral sites available in a perfectly planar grain boundary. The segregation level was computed in intervals of 3 ns to obtain the average segregation level. Fig. 4(a) shows the segregation level \(C_{gb}\) as a function of bulk content \(C_0\). The minor variation in \(C_{gb}\) with inclination angle \(\phi\) indicates that the sink strength of these four boundaries is similar. Furthermore, the effective binding energy of these boundaries, \(E_{b0}^*\), can be estimated from \(C_{gb}\) using the Langmuir-McLean model [19], i.e.

\[
E_{b0}^*/k_B T = \ln \left( \frac{C_0(1 - C_{gb})}{((1 - C_0)C_{gb})} \right)
\]

and is plotted as a function of \(C_0\) in Fig. 4(b). The effective binding energy varies moderately with \(C_0\), indicating that the model assumption of non-interacting solute atoms [19] is a simplification for the Fe-He system. The magnitude of this variation is about 5% (or \(0.3k_B T\)) for all boundaries. The model is thus considered a reasonable first approximation for \(E_{b0}^*\), which is taken as the average of the values obtained from three different \(C_0\), see Table 2.

These binding energies, \(E_{b0}^*\), are about three times smaller than the single-atom binding energies, \(E_{b0}\), see Table 2. The single-atom binding energy \(E_{b0}\) has been obtained from 0 K simulations and would lead to saturated segregation, i.e. \(C_{gb} = 1\), at 1000 K, overestimating the actual segregation in Fig. 4(a). \(E_{b0}^*\) can thus be considered a more representative parameter than \(E_{b0}\) to describe the interaction between grain boundaries and He clusters.
3.3. Mobilities of cluster-enriched grain boundaries

Upon clusters reaching a steady-state distribution at the boundary, simulations were run for another 20 to 30 ns, during which the boundary position, \( h \), was recorded every 0.1 ns. Fig. 5(a) shows an example of the distribution of boundary displacement \( \Delta h(\tau = 0.2 \text{ ns}) \) for the pure and cluster-enriched (\( C_0 = 0.5 \text{ at\%} \)) 44.7\(^\circ\)-boundaries. Both distributions are Gaussian, their width indicating the extent of boundary fluctuation. The average mean-squared displacement (MSD) at different \( \tau \) for the pure and enriched boundaries are plotted in Fig. 5(b) and (c), respectively. The boundary mobility is obtained from the slope of linear regression of the MSD via Eq. (1).

![Figure 5](image)

**Figure 5.** (a) Distribution of boundary displacements at an interval \( \tau \) of 0.2 ns, for the pure and cluster-enriched (\( C_0 = 0.5 \text{ at\%} \)) 44.7\(^\circ\)-boundaries; the mean-square displacement as a function of \( \tau \) of (b) the pure boundary, and (c) the cluster-enriched boundary.

The same procedure was repeated for different boundaries and solute contents to compute the mobilities of these boundaries, see Fig. 6(a). These mobilities are labelled as an effective quantity, \( M_{\text{eff}} \), because they arise from the intrinsic mobility of the boundary, \( M_{\text{pure}} \), and the contribution of cluster segregation, \( M_{\text{clus}} \). The presence of clusters reduces the mobility by about 3 to 4 orders of magnitude as well as the effect of \( \varphi \) on the mobilities.

![Figure 6](image)

**Figure 6.** (a) Effective mobility of pure and enriched grain boundaries, (b) Cluster drag contribution, \( M_{\text{clus}}^{-1} \) in Eq. (3), as a function of bulk solute content.
The effective mobility can be further decoupled into its intrinsic and extrinsic component following, for example, Cahn [1], i.e.

\[ M^{-1}_{\text{eff}} = M^{-1}_{\text{pure}} + M^{-1}_{\text{clust}} \]  

(3)

The cluster drag, i.e. the inverse of cluster contribution to the boundary mobility, is plotted in Fig. 6(b) as a function of \( C_0 \). Within the range of solute content investigated here, the cluster drag appears to show a linear increase with increasing \( C_0 \), which is consistent with Cahn’s solute drag model [1]. This linear relationship, i.e. \( M^{-1}_{\text{clust}} = \alpha C_0 \), is represented by the dashed lines in Fig. 6(b) where \( \alpha \) denotes the drag coefficient.

4. Discussion

To further analyze the cluster drag coefficient \( \alpha \) in Fig. 6(b), the solute drag model of Cahn [1] is adopted. The model postulates that, in the limit of low velocity, the drag coefficient, \( \alpha \), can be obtained from

\[ \alpha = 4N_v k_B T \int_{-\delta/2}^{+\delta/2} \frac{\sinh^2 \left[ E_b(z) / 2k_B T \right]}{D(z)} \, dz \]  

(4)

where \( N_v \) is the bulk atomic concentration \( (8.4 \times 10^{28} \text{ m}^{-3}) \), \( E_b(z) \) and \( D(z) \) are the profile of binding energy and solute diffusivity along the boundary normal \( z \), respectively.

![Figure 7. Assumed profile of (a) binding energy and (b) diffusivity to estimate \( \alpha \) from Eq. 4.](image)

The parameters \( D(z) \) and \( E_b(z) \) specified in Cahn’s model correspond to properties that represent the interaction between the grain boundary and a single solute atom. In order to adapt this model for the drag effect of He clusters, the effective binding energy of clusters was employed, instead of the single-atom binding energy, to obtain an enrichment level consistent with the simulation results. The single-atom grain boundary diffusivity was also implemented because the kinetics of this process controls the size distribution of clusters at the boundary. Both parameters were integrated into an assumed triangular profile, see Figs. 7(a) and (b), to obtain a closed-form solution of the drag coefficient \( \alpha \) via Eq. 4.

| Table 3. Cluster drag coefficients \( \alpha \) obtained from simulations and the Cahn’s model. |
|---------------------------------------------------------------|
| \( \alpha \) \([\times 10^{11} \text{ m}^{-4} \text{ s}^{-1}]\) | 19.5° boundary | 44.7° boundary | 70.5° boundary | 90.0° boundary |
| Simulations [Fig. 6(b)] | 5.1 | 4.2 | 2.9 | 2.3 |
| Cahn’s model [Eq. 4] | 4.1 | 2.4 | 1.8 | 1.1 |

Table 3 compares the drag coefficients estimated from Eq. 4 with those extracted from molecular dynamics simulations, shown in Fig. 6(b). Both drag coefficients are in the same order of magnitude. The drag coefficient obtained from Cahn’s model is smaller by a factor of 0.5 to 0.8, but the trends with boundary inclination are similar in both cases. Given the simplifications employed in the continuum model analysis, this is a rather reasonable agreement.
5. Conclusions and Outlook
The effect of solute clusters on grain boundary mobility in the zero velocity limit for dilute solutions in the Fe-He system has been investigated via atomistic simulations. The cluster drag effect observed from simulations can, in a first order approximation, be rationalized using Cahn’s solute drag model.

Properties obtained from these simulations have been shown to provide valuable insight in analyzing the cluster-boundary interaction. The single-atom boundary diffusivity has been identified as the rate-controlling process in cluster formation at the boundary. The cluster drag effect presented in this work is, however, only applicable in the zero velocity limit. From a practical perspective, it is of interest to investigate the case of a migrating boundary. This topic is the focus of a further study where He clusters interact with a capillarity driven migrating boundary. In such a situation, cluster formation at the boundary may never reach steady state. As a consequence, the cluster drag effect of a driven boundary may not be consistent with predictions from the classical solute drag model.

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