Smoothed Boundary Method for Simulating Bulk and Grain Boundary Transport in Complex Polycrystalline Microstructures

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Abstract

Grain boundaries have a major impact on material properties, but explicit consideration of the complex geometries of grain structures in simulations poses a challenge. In this paper, we present a general method for incorporating the effect of grain boundaries based on the Smoothed Boundary Method (SBM). By using multiple domain parameters to define the domains of different grains, this method circumvents time-consuming mesh generation steps that are associated with finite element calculations involving complex microstructures. To validate the approach, we evaluate the accuracy of the SBM against the sharp interface method. The capabilities of this approach were demonstrated through simulations of surface and grain

boundary diffusion, as well as those of electrochemical impedance spectroscopy. This method is applicable to many material systems in which grain boundaries play a crucial role.

1. Introduction

Grain boundaries are ubiquitous in materials because they form during a wide range of processes, including solidification, sintering, and agglomeration. Grain boundaries have a major impact on materials, often resulting in changes in mechanical behavior as well as effective transport properties. This is because material properties of polycrystalline materials arise from the combination of the bulk and grain boundary properties. Atoms on grain boundaries generally lack the periodic structure associated with their lowest energy state and thus interact differently from bulk atoms. For example, bond strength and length can be significantly different, which often leads to diffusivity that is orders of magnitude different from the bulk diffusivity [1].

The challenges with modeling polycrystalline materials stem from the complexity of the grain structures. Thus, many theories consider the effects of grain boundaries using a mean-field approach [1-3]. However, these models cannot capture the effects of detailed microstructures, such as anisotropy or grain size distributions, and thus precise predictions of behavior of polycrystalline materials cannot be obtained.

A typical approach for incorporating grain boundary geometries into simulations is based on the finite element method (FEM) [4-9]. In the FEM, the mesh is generated to conform to grain boundaries, and the surface transport (e.g., diffusion) equation is solved on the mesh. When a complex three-dimensional structure is considered, however, automatically generated mesh lacks sufficient quality required to compute accurate solutions, and manual adjustments must be made. For a system with a large number of grains, the mesh generation process becomes prohibitively

time consuming. Therefore, an advance in the computational approach is required to enable simulations that account for complex grain boundary structures.

In this paper, we focus on transport in polycrystalline materials where grain boundaries enhance diffusion. We present a general method for incorporating the effect of grain boundaries based on the Smoothed Boundary Method (SBM) [10]. In this approach, multiple domain parameters are employed to define the grains in polycrystalline solids. Each domain parameter, indicating a specific grain, has a uniform value of one within the grain, zero outside, and smoothly transitions from one to zero across the grain boundary. The domain parameters can be generated through a fully automated process even for a very complex microstructure [10]. Using these domain parameters, the governing equations for the bulk and boundary diffusion are reformulated and coupled.

We demonstrate the approach for diffusion with a fixed boundary condition and with a cyclic loading condition, which simulates the ionic diffusion in polycrystalline mix conductors under direct current (DC) loading and electrochemical impedance spectroscopy (EIS), respectively. The method is applicable to many material systems in which grain boundaries play a crucial role.

2. Model and Formulation

2.1 Surface Diffusion

We base the formulation of surface diffusion (as well as that of grain boundary diffusion in the next subsection) on Fisher's approach [11]. In his approach, which was originally developed for grain boundary diffusion, concentration evolution is governed by two coupled equations, one for the bulk and the other for grain boundary diffusion. Similarly, we split the rate of change of the

concentration into the bulk and the surface term, each obtained from a conservation law [1, 11]:

$$\frac{\partial C}{\partial t} = \nabla \cdot D_b \nabla C \quad \in \Omega, \quad (1)$$

$$\frac{\partial C}{\partial t} = \nabla_\Gamma \cdot D_s \nabla_\Gamma C - \frac{1}{\lambda_s} [J_n]_{-\lambda_s/2}^{+\lambda_s/2} \quad \in \partial\Omega, \quad (2)$$

where C is the concentration, t is time, D_s and D_b are the surface and bulk diffusivities, respectively, ∇_Γ is the surface gradient, J_n is the inward normal flux at the surface, λ_s is the characteristic thickness of the surface, $[J_n]_{-\lambda_s/2}^{+\lambda_s/2}$ denotes the jump in flux from $-\lambda_s/2$ to $+\lambda_s/2$, and $\partial\Omega$ and Ω denote the surface and bulk domains, respectively. The surface gradient is defined by $\nabla_\Gamma = (\mathbf{I} - \vec{n} \otimes \vec{n}) \nabla$, where $\mathbf{I}$ is the identity tensor, $\vec{n}$ is the inward unit vector of the surface, and $\otimes$ is the Dyadic product. The last term in Eq. (2) accounts for the concentration change due to the flux arriving on the surface from the environment ($J_n|_{-\lambda_s/2}$) and the flux leaving the surface into the bulk ($J_n|_{+\lambda_s/2}$). See Fig. 1(a) for a schematic illustration.

If we assume a closed system, we have $J_n|_{-\lambda_s/2} = 0$, signifying the fact that no mass can leave the system. Flux from the bulk to the surface is described by Fick's First Law:

$J_n|_{+\lambda_s/2} = -D_b \partial C / \partial n$. Equation 2 can then be written as

$$\frac{\partial C}{\partial t} = \nabla_\Gamma \cdot D_s \nabla_\Gamma C - \frac{1}{\lambda_s} \left(-D_b \frac{\partial C}{\partial n} \right) \quad \in \partial\Omega. \quad (3)$$

In order to circumvent the difficulty with solving the boundary-value problem defined by Eqs.

(1) and (3), we apply the Smoothed Boundary Method [10], based on the diffuse interface

approach. We introduce a continuous domain parameter, ψ , to define the domain of the bulk, such that $\psi = 1$ inside Ω , $\psi = 0$ outside Ω , and $0 < \psi < 1$ within the region around $\partial\Omega$ with finite thickness, where ψ changes gradually (thus termed diffuse interface). Multiplying Eq. (1) by ψ and applying the product rule for differentiation, we manipulate Eq. (1) into

$$\psi \frac{\partial C}{\partial t} = \nabla \cdot \psi D_b \nabla C - \nabla \psi \cdot D_b \nabla C = \nabla \cdot \psi D_b \nabla C - |\nabla \psi| D_b \frac{\partial C}{\partial n}. \quad (4)$$

Note that $\nabla \psi \cdot D_b \nabla C = |\nabla \psi| D_b \partial C / \partial n$, where $\nabla \psi / |\nabla \psi| = \vec{n}$ is the definition of the inward unit normal vector, and thus $\partial C / \partial n = \vec{n} \cdot \nabla C = (\nabla \psi / |\nabla \psi|) \cdot \nabla C$. As a result, Eq. (4) becomes

$$\psi \frac{\partial C}{\partial t} = \nabla \cdot \psi D_b \nabla C - |\nabla \psi| \left(\lambda_s \frac{\partial C}{\partial t} - \nabla_\Gamma \cdot \lambda_s D_s \nabla_\Gamma C \right), \quad (5)$$

which accounts for both the bulk and surface diffusion.

2.2 Grain Boundary Diffusion

As mentioned earlier, we apply the approach developed by Fisher [11] in which the bulk and the grain boundary diffusion are described by two coupled partial differential equations. The bulk diffusion is again governed by Eq. (1), but the second equation is replaced by one that describes grain boundary diffusion:

$$\frac{\partial C}{\partial t} = \nabla_{\Gamma_g} \cdot D_g \nabla_{\Gamma_g} C + \frac{2D_b}{\lambda_g} \frac{\partial C}{\partial n_g}, \quad (6)$$

where ∇_{Γ_g} is the surface gradient along grain boundaries, D_g is the grain boundary diffusivity,

λ_g is the width of grain boundaries, and $\partial / \partial n_g$ is the inward normal gradient at grain

boundaries. When the grain boundary is aligned with one of the Cartesian axes, the equation

becomes identical to that of Fisher's model. As in that model, the factor of two in the last term in Eq. (6) arises from the assumption that the normal fluxes on the two sides of a grain boundary are opposite to each other, which ignores the higher-order correction that may become important for highly curved boundaries.

Now we consider a system with two grains that are in contact. We use two domain parameters, ψ_1 and ψ_2 , to define the domains of these grains. Each of the domain parameters is one inside its corresponding grain and zero outside. As before, the domain parameters vary smoothly within the diffuse grain boundaries. The sum of the two domain parameters in the solid region is one: $\psi_1 + \psi_2 = 1 \in \Omega$. See Fig. 1(b) for a schematic illustration.

Following the procedure used to derive Eq. (5), we apply the SBM and combine the grain boundary and bulk diffusion equations to obtain

$$\psi_1 \frac{\partial C}{\partial t} = \nabla \cdot \psi_1 D_b \nabla C - |\nabla \psi_1| \frac{\lambda_g}{2} \left(\frac{\partial C}{\partial t} - \nabla_{\Gamma_1} \cdot D_g \nabla_{\Gamma_1} C \right), \quad (7)$$

$$\psi_2 \frac{\partial C}{\partial t} = \nabla \cdot \psi_2 D_b \nabla C - |\nabla \psi_2| \frac{\lambda_g}{2} \left(\frac{\partial C}{\partial t} - \nabla_{\Gamma_2} \cdot D_g \nabla_{\Gamma_2} C \right), \quad (8)$$

for the system consisting of two grains, where ∇_{Γ_i} is the surface gradient along the i -th grain surface. The sum of Eqs. (7) and (8) provides the governing equation for concentration evolution, accounting for both bulk and grain boundary diffusion:

$$\frac{\partial C}{\partial t} = \nabla \cdot D_b \nabla C - \frac{\lambda_g}{2} \sum_{q=1}^2 |\nabla \psi_q| \left(\frac{\partial C}{\partial t} - \nabla_{\Gamma_q} \cdot D_g \nabla_{\Gamma_q} C \right). \quad (9)$$

This equation can be generalized to systems with an arbitrary number of grains by defining additional grain domain parameters, ψ_q , and extending the summation over all grain indices, q .

In addition, surface diffusion can be included in the same manner as in the previous section. A general governing equation for systems with Q grains with or without surfaces is thus

$$\begin{aligned} \psi \frac{\partial C}{\partial t} = & \nabla \cdot \psi D_b \nabla C - |\nabla \psi| \left(\lambda_s \frac{\partial C}{\partial t} - \nabla_{\Gamma} \cdot \lambda_s D_s \nabla_{\Gamma} C \right) \\ & - \psi \frac{\lambda_g}{2} \sum_{q=1}^Q |\nabla \psi_q| \left(\frac{\partial C}{\partial t} - \nabla_{\Gamma_q} \cdot D_g \nabla_{\Gamma_q} C \right), \end{aligned} \quad (10)$$

where Q denotes the number of grains within the solid, and the sum of all grain domain parameters, $\psi = \sum_{q=1}^Q \psi_q$, indicates the solid region.

By collecting the time derivative terms and nondimensionalizing the equation, we obtain the final form of the governing equation for concentration evolution, which accounts for bulk, surface, and grain-boundary diffusion:

$$\begin{aligned} & \left(\psi + |\hat{\nabla} \psi| \hat{\lambda}_s + \psi \frac{\hat{\lambda}_g}{2} \sum_{q=1}^Q |\hat{\nabla} \psi_q| \right) \frac{\partial C}{\partial \hat{t}} \\ & = \hat{\nabla} \cdot \psi \hat{\nabla} C + |\hat{\nabla} \psi| \hat{\nabla}_{\Gamma} \cdot \hat{D}'_{\Gamma} \hat{\nabla}_{\Gamma} C + \psi \frac{1}{2} \sum_{q=1}^Q |\hat{\nabla} \psi_q| \hat{\nabla}_{\Gamma_q} \cdot \hat{D}'_g \hat{\nabla}_{\Gamma_q} C \end{aligned}, \quad (11)$$

where the hat ($\hat{\cdot}$) denotes dimensionless quantities, $\hat{\nabla} = l \nabla$, $\hat{t} = t / \tau$, $\hat{\lambda}_s = \lambda_s / l$, $\hat{\lambda}_g = \lambda_g / l$,

$\hat{D}'_s = \hat{\lambda}_s D_s / D_b$, and $\hat{D}'_g = \hat{\lambda}_g D_g / D_b$. Note that Eq. (11) has been nondimensionalized with a length scale l and a time scale $\tau = l^2 / D_b$. For simplicity in expressing equations, the hat will be dropped hereafter.

2.3 Concentration Responding to Sinusoidal Loadings

A mix conductor is a material that can conduct both electrons and ions simultaneously: usually conducting electrons much faster than ions (e.g., solid oxide fuel cell cathode materials and

many Li-ion battery cathode materials). For a mix conductor, the ionic concentration is assumed to be proportional to electrostatic potential [12]. For sinusoidal loading, the time-dependent part of the concentration can be represented by a sinusoidal function with the same frequency as the loading frequency, and thus the ionic concentration responding to an sinusoidal loading (i.e., alternating current) is separated into spatial and time-dependent components:

$$C = \frac{1}{2} [\tilde{C} \exp(i\omega t) + \tilde{C}^* \exp(-i\omega t)], \quad (12)$$

where $\tilde{C} = C_R + iC_I$ (C_R and C_I are the real and imaginary parts of $\tilde{C}$, respectively), $\tilde{C}^*$ is the complex conjugate of $\tilde{C}$, i is the imaginary unit number, and ω is the angular frequency of the load. Substituting Eq. (12) into Eq. (11) and reorganizing terms, we obtain the following two coupled equations:

$$\begin{aligned} \left(\nabla \cdot \psi \nabla + |\nabla \psi| \nabla_{\Gamma} \cdot D'_s \nabla_{\Gamma} + \psi \frac{1}{2} \sum_{q=1}^Q |\nabla \psi_q| \nabla_{\Gamma q} \cdot D'_g \nabla_{\Gamma q} \right) C_R = \\ - \left(\psi + |\nabla \psi| \lambda_s + \psi \frac{\lambda_g}{2} \sum_{q=1}^Q |\nabla \psi_q| \right) \omega' C_I \end{aligned} \quad (13)$$

$$\begin{aligned} \left(\nabla \cdot \psi \nabla + |\nabla \psi| \nabla_{\Gamma} \cdot D'_s \nabla_{\Gamma} + \psi \frac{1}{2} \sum_{q=1}^Q |\nabla \psi_q| \nabla_{\Gamma q} \cdot D'_g \nabla_{\Gamma q} \right) C_I = \\ \left(\psi + |\nabla \psi| \lambda_s + \psi \frac{\lambda_g}{2} \sum_{q=1}^Q |\nabla \psi_q| \right) \omega' C_R \end{aligned} \quad (14)$$

where $\omega' = \omega l^2 / D_b$ is the dimensionless frequency. The left-hand side of each of Eqs. (13) and (14) contains linear differential operators that combine the Laplacians for bulk, surface, and grain boundary diffusion, while the right-hand side has a constant coefficient that is a function of the domain parameters.

2.4 Numerical Methods

We discretize the partial differential equations obtained in the previous sections using the finite difference method. For the time derivative appearing in Eq. (11), first-order explicit time stepping is applied. For the spatial derivatives, the bulk Laplacian operators, as appearing in Eq. (1), are discretized using the scheme in Ref. [10]. As in Ref. [10], the surface Laplacian operators, as appearing in Eq. (2), contain nine in-axis second derivatives (e.g.,

$\partial(D_s \partial C / \partial x) / \partial x$) and 18 cross-derivatives (e.g., $\partial(D_s \partial C / \partial x) / \partial y$). The in-axis derivatives are discretized using the same scheme as for the bulk Laplacian, for which the inner derivatives are first calculated at half points over each grid spacing. Any quantities inside of outer derivatives are also calculated at the half points by first-order interpolation. The outer derivatives are then calculated at each grid point using the two nearest half-point values. This approach gives a second-order accuracy if the nonderivative quantities inside of the outer derivatives are constant. To ensure accuracy, the cross-derivatives are discretized using a seven-point scheme modified from that in Ref. [13], instead of traditional four-point scheme. The details are provided in the appendix.

The time-independent equations are solved using alternating-direction line-relaxation (ADLR) method [10, 14, 15], which utilizes a tridiagonal matrix solver to obtain the values of

concentration along individual columns in the x , y , and z directions, and iteratively updates the values until reaching numerical equilibrium.

3. Results

3.1 Error Analysis and Verification

Here, we examine the error associated with the diffuse interface approach using the simulation configuration similar to that used for the numerical study by Fisher [11] as well as the analytical investigation by Whipple [16]. A straight horizontal grain boundary is placed in the middle of the computational domain that contains 201×201 grid points. Concentration evolution is simulated by Fisher's model and by the SBM on the same grid system for comparison. Both the two simulations are performed using the finite different method. For the SBM simulation, we define the domains of the two grains by $\psi_1 = \left(1 + \tanh\left(\left(101 - y\right)/\zeta\right)\right)/2$ and $\psi_2 = 1 - \psi_1$, respectively.

The diffuse interface thickness is approximately $3 \Delta x$ by setting $\zeta = 0.6$, where Δx is set to one (i.e., $l = \Delta x$). The grain boundary diffusivity is set to be 100 times that of the bulk, and the characteristic width of the grain boundary is set to be $0.25 \Delta x$. The diffusion times over the computational domain for the bulk and grain boundary diffusion are given by

$t_{db} = L^2/D_b = 40401$ and $t_{dg} = L^2/(D_g \lambda_g) = 404$, respectively, where L is the length of computational domain along the main diffusion direction.

Figure 2 shows the concentration distributions simulated by Fisher's model (which we refer to as the sharp interface method) and the SBM. These snapshots are taken at a dimensionless simulation time equal to 202, which is half of the diffusion time for the given

grain boundary diffusion. As can be observed in Fig. 2, the difference in the solutions is indiscernible.

We examine the differences between the sharp interface result and the SBM result to quantify the error associated with the diffuse interface method. Here, we compute the errors as follows. The error of concentration is characterized by the maximum difference (the infinity norm), as well as the maximum difference divided by the characteristic value of concentration, which is taken as 0.5 (the average value at the steady state). For the error in flux, we instead estimate it by characterizing the error in the magnitude of the concentration gradient. Again, we calculate the maximum value and the maximum value divided by the characteristic value, which is taken as the steady-state value ($= 1/L$). It should be noted that maximum difference is the most stringent measure of accuracy, and significant local differences are expected for the diffuse interface approach. The errors are calculated at different stages of evolution since they are time-dependent quantities. Table 1 lists the errors at four different times defined in terms of the diffusion time over the computational domain: $t_{dg}/4$, $t_{dg}/2$, $t_{db}/4$, and $t_{db}/2$. While the maximum errors in the concentration gradients may appear substantial during early evolution ($\sim 9\%$ at $t_{dg}/4$), they are concentrated in a very small region near the grain boundary diffusion front, and do not affect the concentration evolution significantly (with a maximum error level of less than 2%). In addition, the errors decay in time as the system approaches the steady state. Therefore, the overall evolution of the concentration is maintained in the diffuse interface simulations.

3.2 Simulations of Grain Boundary Diffusion

To demonstrate the capability of our approach, we generate a complex grain structure using

Dream3D [17] for the input geometry. The microstructure generated by Dream3D is represented by a $400 \times 400 \times 400$ 3D array, as shown in Fig. 3(a). The grain sizes follow a truncated normal distribution with a mean size (in diameter) of 40 grid spacings (Δx , which is again set to unity), with upper and lower bounds of 31 and 50 Δx , respectively, resulting in 1880 grains in the computational domain. In Dream3D, each voxel is assigned an integer value that indicates the grain that occupies the voxel. The SBM requires continuous domain parameters. Therefore, we employ a polycrystalline phase field model (Allen-Cahn-type equation) [18] with 1880 order parameters to smooth the discrete voxel values to generate continuous domain parameters, ψ_q . The thickness of the diffuse grain boundaries is set to approximately 3 Δx . For computational efficiency, grains that are not in contact can be reassigned to the same domain parameter. As a consequence, the number of domain parameters required to describe the 1880 grains is reduced to 12. This drastically curtails the memory requirement for computation. The grain structure described by domain parameters is shown in Fig. 3(b).

For the boundary conditions, constant values of one and zero are imposed on the left ($y=0$) and right ($y=400$) boundaries, respectively, while no-flux boundary conditions are imposed on the remaining four faces. We simulate enhanced grain boundary diffusion by setting the grain boundary diffusivities to be several orders of magnitude larger than the bulk diffusivity.

Figure 4 shows the snapshots of concentration at three different simulation times during the early evolution. Figures 4(a) and (b) are for $D'_g=100$ and $D'_g=10000$, respectively. As shown in Figs. 4(a)-i through iii, concentration gradually increases along the grain boundaries from the left boundary toward the right boundary, which reflects the effect of grain boundary diffusion. With high grain boundary diffusivity ($D'_g=10000$), diffusion along the complex grain

boundary network is more evident (See Figs. 4(b)-i through iii). The simulation results clearly exhibit coupled bulk and grain boundary diffusion where transport occurs primarily via the grain boundary network. The magnified views of the concentration near the top computational-domain boundaries in Figs. 4(a)-iii and 4(b)-iii are provided in Fig. 5, which clearly show enhanced diffusion along grain boundaries at early times.

Figure 6 shows the snapshots of concentration for $D'_g = 100$ at three intermediate evolution times much longer than those in Fig 4(a). In contrast to the early evolution, the concentration within the grains greatly increases, showing a substantial “diffusant leakage” [1] from the grain boundaries into the bulk of grains, as described in Ref. [1]. The concentration becomes more uniform over the grain boundaries and the bulk of grains, and the grain boundaries are no longer clearly visible by $t = 500$ (Fig 6(b)), indicating the coupled bulk and boundary diffusion where transport occurs primarily via the bulk of the grains.

Coupled bulk and boundary diffusion is typically classified into three regimes [1, 19]: the A regime, in which the transport is dominated in the bulk; the B regime, in which the transport is dominated by the grain boundary network; and the C regime, in which diffusion only occurs in the grain boundaries. Three dimensionless parameters [1, 2, 20-22] are usually employed to characterize these regimes: $\alpha = \lambda_g / (2\sqrt{D_b t})$, $\beta = (D_g / D_b - 1)\lambda_g / (2\sqrt{D_b t})$, and $\Lambda = d / (2\sqrt{D_b t})$, where β describes the temporal decay of enhanced grain boundary diffusion, α distinguishes the B and C regimes, and Λ distinguishes the A and B regimes. The original criterion derived by Harrison [19] for the A regime requires $\Lambda < 1/300$, which is only valid for D_g / D_b ratios larger than 10^6 [1]. For D_g / D_b ratios lower than 10^6 , the threshold between regimes A and B is not clearly defined [1, 23]. Therefore, we examine the diffusion regimes using the Λ parameter

against the criterion acquired by Monte Carlo simulations [23, 24] where D_g / D_b are $10^2 \sim 10^4$. According to Refs. [23, 24], the B regime occurs when $\Lambda > 2$ [23] or 3 [25, 26] and $\alpha < 0.1$ [22] for β values larger than 10. The parameters corresponding to the early stages ($t = 5 \sim 15$; Fig 4) and late times ($t = 250 \sim 1500$; Fig 6) are provided in Table 2, which shows the α values are below 0.1 for the cases of $D'_g = 100$ (Fig 4(a)) and $D'_g = 10000$ (Fig 4(b)) at early stages, while the corresponding β and Λ values are above 10 and 3, respectively, for both cases. Thus, these results are clearly in the B regime and far away from the C regime. Conversely, at later times (corresponding to Fig 6), the β and Λ values are in the range of $0.5 < \Lambda < 1.3$ and $1.3 < \beta < 3.2$, respectively; therefore, the kinetics is classified as the transition between the A and B regimes (the AB regime) [23]. However, because the β values are small, the kinetics are very close to the A regime.

The steady-state solutions can be obtained either by evolving the time-dependent evolution equation to the steady state, or alternatively solving the governing equation with $\partial C / \partial t = 0$ using a relaxation algorithm such as the ADLR. The latter approach is more efficient and thus should be used when only the steady-state solution is of interest. Steady-state concentration distributions calculated using the ADLR method are presented in Fig. 7. The net flux across the computational domain boundary consists of the bulk and grain boundary fluxes:

$$J_{net} = J_b + J_g = -\nabla C - \frac{1}{2} D'_g \sum_{q=1}^Q \left| \nabla \psi_q \right| \nabla_{\Gamma_g} C \quad (15)$$

which can be used to compute the effective diffusivity of the polycrystalline solid at the steady state

$$D_{eff} = -J_{net} \frac{L}{\Delta C}, \quad (16)$$

where ΔC is the concentration difference across the computational domain. The effective diffusivities for the cases of $D'_g = 100$ and $D'_g = 10000$ are calculated to be 5.9 and 526.4, respectively, based on the simulation results. These values are about 20% smaller than 7.4 and 641, respectively, predicted by the Hart equation [27], $D_{eff}^{Hart} = D_g \varepsilon + D_b (1 - \varepsilon)$. Here, $\varepsilon = \lambda_g A_g / \Omega = 0.016$ is the volume fraction of grain boundaries for the polycrystalline microstructure in the simulations, where the total volume Ω is $400^3 \Delta x^3$ and the total area of grain boundaries ($A_g = 1.02 \times 10^6 \Delta x^2$) is calculated by summing the areas of triangular patches generated using Matlab® of the isosurfaces at $\psi_g = 0.5$. This discrepancy arises because the grain boundaries in the simulations are tortuous, different from the grain boundaries that were assumed to be flat and aligned in the main diffusion direction in the derivation of the Hart equation.

3.3 Simulation of Electrochemical Impedance Spectroscopy

For the EIS calculation, we generate a microstructure of a polycrystalline particle that has a radius of $117 \Delta x$ and contains 418 grains. The grain size (in diameter) has a truncated normal distribution with a lower cutoff of $30 \Delta x$, upper cutoff of $45 \Delta x$, and a mean diameter of $36 \Delta x$. This virtual polycrystalline particle is truncated at the two ends in the y -axis, so that the two flat truncated surfaces can be assumed to be in direct contact with electron-blocking electrodes. The resulting computational domain has $256 \times 200 \times 256$ grid points. See Fig. 8 for the microstructure of the generated simulation configuration. The boundary conditions for C_R are +0.5 and -0.5 at the planes of $y = 0$ and $200 \Delta x$, respectively, while C_I is set to zero at both of these planes. Assuming diffusion on a free surface is faster than through the grain boundaries, the surface and

grain boundary diffusivities are set to $D'_s = 500$ and $D'_g = 100$, respectively.

Figure 9 shows the distribution of C_R and C_I at three representative loading frequencies. At low frequencies, C_R varies gradually from +0.5 to -0.5 between the two electrodes, which can be seen in Fig 9(a)-i. The effect of enhanced surface and grain boundary diffusion is negligible in comparison with the overall concentration change across the particle. In contrast, enhanced grain boundary diffusion can be clearly observed in the imaginary part, which is shown in Fig 9(a)-ii. The value of C_I in grains near the $y=0$ plane is lower than that at the grain boundaries, while the opposite occurs near the $y=200$ plane. As the loading frequency increases (Fig 9(b)), C_R in the middle of the particle begins to flatten, causing the large gradients to occur near the loading boundaries. Consequently, the gradient of C_I in the middle of the particle decreases, and the minimum and maximum of C_I shift toward the loading boundaries. As a result, significant concentration variations only appear in the narrow regions close to the electrodes. The thickness of these narrow regions can be viewed as an effective diffusion length over the cycle duration associated with the loading frequency. As the frequency increases, the diffusion length associated with the frequency decreases. At high frequencies (Fig 9(c)), sharp concentration gradients are confined along the particle surface and grain boundaries, indicating that only the surface and grain boundaries have diffusivities high enough to respond to the fast change driven by the oscillating load.

The net fluxes through the particle are comprised of real and imaginary parts:

$\tilde{J}_{net} = J_R + iJ_I$, where J_R and J_I are the net fluxes calculated using C_R and C_I , as in Eq. (15). At each frequency, the impedance, $\tilde{Z}$, of the particle is evaluated by

$$\tilde{Z} = \frac{\Delta\tilde{C}}{\tilde{J}_{net}}, \quad (17)$$

where $\Delta\tilde{C} = C_R|_{y=200} - C_R|_{y=0}$. The results are plotted in Fig 9(d). For the polycrystalline particle examined in this work, the EIS curve in the low-frequency region exhibits a well-defined semicircle, characteristic of a single time constant (e.g., for a circuit with a capacitor and resistor connected in a transmission line) [28]. At higher frequencies, the curve extends linearly toward the origin. Here, we did not simulate the very high frequency regime since it requires finer grid spacings in order to numerically resolve the resulting large concentration gradients.

4. Discussion & Conclusions

In this paper, we have presented the model for surface and grain boundary diffusion and derived the Smoothed Boundary Method formulation of the governing equations. Our method takes advantage of the diffuse interface approach, where the computational mesh is not required to conform to the shapes of the objects being represented. This eliminates potentially time-consuming mesh generation steps that are associated with finite element calculations when it is applied to complex microstructures. The accuracy of the method was tested for straight grain boundaries that are aligned with the diffusion direction. The results show excellent agreement with the sharp interface model. Simulations of surface and grain boundary diffusion, as well as simulations of electrochemical impedance spectroscopy, are performed to demonstrate the capabilities of this approach. The resulting effective diffusivities and impedance spectra provides an insight into how grain boundary structures affect experimentally measurable properties of materials.

The approach can be applied to a number of technologically important problems in which bulk, interfacial, and surface transport play a role. The simulation can be combined with experiments to determine fundamental material properties, such as transport coefficients, that are difficult to measure directly. The model, when parameterized and validated, can then be used to examine how different microstructures enhance or degrade a material's performance. The interfacial and grain boundary diffusion models can also be incorporated into electrochemical simulations such as those we have developed previously [29-33] to examine the role of interfacial/grain boundary Li and electron transport in electrochemical performance. Furthermore, transport properties of an electrolyte in a solid-electrolyte battery are highly dependent on the grain boundary diffusivity [34]. There are also a myriad of applications beyond batteries; for example, diffusion of Cu from the back-contact material (e.g., Zn-Te:Cu) into polycrystalline Cd-Te photovoltaic cells is known to be detrimental to efficiency [35]. The approach presented in this paper opens a new avenue for gaining a fundamental understanding of these systems and offers new opportunities in the pursuit of optimized material performance.

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Appendix

The seven-point stencil for the cross derivative is provided below.

$$\frac{\partial}{\partial x} \left(m \frac{\partial C}{\partial y} \right) = \begin{cases} \frac{1}{2} \left[\frac{m_{i+1/2,j+1/2}}{\Delta x} \left(\frac{C_{i+1,j+1} - C_{i+1,j}}{\Delta y} - \frac{C_{i,j+1} - C_{i,j}}{\Delta y} \right) + \frac{m_{i-1/2,j-1/2}}{\Delta x} \left(\frac{C_{i,j} - C_{i,j-1}}{\Delta y} - \frac{C_{i-1,j} - C_{i-1,j-1}}{\Delta y} \right) \right] & \text{for } n_x \cdot n_y < 0 \\ \frac{1}{2} \left[\frac{m_{i-1/2,j+1/2}}{\Delta x} \left(\frac{C_{i,j+1} - C_{i,j}}{\Delta y} - \frac{C_{i-1,j+1} - C_{i-1,j}}{\Delta y} \right) + \frac{m_{i+1/2,j-1/2}}{\Delta x} \left(\frac{C_{i+1,j} - C_{i+1,j-1}}{\Delta y} - \frac{C_{i,j} - C_{i,j-1}}{\Delta y} \right) \right] & \text{for } n_x \cdot n_y > 0 \end{cases} \quad (18)$$

where $m_{i+1/2,j+1/2}$ is linearly interpolated from the values at the four grid points enclosing the location of mid-point, and n_x and n_y are the x and y components, respectively, of the unit normal vector of the surface or grain boundary. The cross derivatives for the x - z and y - z planes are calculated in a similar manner. If the normal unit vector happens to align along the grid axes, then $n_x \cdot n_y = 0$, and the traditional four-point cross derivative is used, which is given below:

$$\frac{\partial}{\partial x} \left(m \frac{\partial C}{\partial y} \right) = \frac{1}{\Delta x} \left(m_{i+1,j} \frac{C_{i+1,j+1} - C_{i+1,j-1}}{\Delta y} - m_{i-1,j} \frac{C_{i-1,j+1} - C_{i-1,j-1}}{\Delta y} \right). \quad (19)$$

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Table

Table 1. The differences and errors of concentration and the magnitude of the concentration gradient determined by comparing the sharp and diffuse interface methods for the simulation configuration with a straight grain boundary and $D'_g = 100$. Here C_{SI} and C_{SBM} are the concentrations from the sharp and diffuse interface methods, respectively, C_{char} is the characteristic concentration, ∇C_{SI} and ∇C_{SBM} are the concentration gradients from the sharp and diffuse interface methods, respectively, and ∇C_{char} is the characteristic concentration gradient.

Simulation time	$101 \left(\frac{1}{4} t_{Dg} \right)$	$202 \left(\frac{1}{2} t_{Dg} \right)$	$10100 \left(\frac{1}{4} t_{Db} \right)$	$20200 \left(\frac{1}{2} t_{Db} \right)$
Max $ C_{SBM} - C_{SI} $	0.0082	0.0052	1.24×10^{-4}	1.03×10^{-5}
Max $\frac{ C_{SBM} - C_{SI} }{C_{char}}$	1.64 %	1.04 %	0.025 %	0.002 %
Max $\ \nabla C_{SBM} - \nabla C_{SI}\ $	4.37×10^{-4}	2.33×10^{-4}	1.94×10^{-6}	1.60×10^{-7}
Max $\frac{\ \nabla C_{SBM} - \nabla C_{SI}\ }{ \nabla C_{char} }$	8.79 %	4.69 %	3.89×10^{-2} %	3.22×10^{-5} %

Table 2. The values of the dimensionless parameters, α , β , and Λ , for the early and later stages of diffusion are provided in this table for characterizing the kinetic regimes. According to these values, the early stages of diffusion ($t = 5 \sim 15$; Figs 4(a) and 4(b)) are classified as the B regime, and the later stages ($t = 250 \sim 1500$; Fig 6) are classified as the transitional AB regime.

$D'_g = 100$	α	β	Λ	$D'_g = 10000$	α	β	Λ
$t = 5$ Fig 4(a)-i	5.59×10^{-2}	22.30	8.94	$t = 5$ Fig 4(b)-i	5.59×10^{-2}	2236.01	8.94
$t = 10$ Fig 4(a)-ii	3.95×10^{-2}	15.77	6.32	$t = 10$ Fig 4(b)-ii	3.95×10^{-2}	1581.10	6.32
$t = 15$ Fig 4(a)-iii	3.23×10^{-2}	12.88	5.16	$t = 15$ Fig 4(b)-iii	3.23×10^{-2}	1290.96	5.16
$t = 250$ Fig 6(a)	7.91×10^{-3}	3.15	1.26				
$t = 500$ Fig 6(b)	5.59×10^{-3}	2.23	0.89				
$t = 1500$ Fig 6(c)	3.23×10^{-3}	1.29	0.52				

Figures

Figure 1. Schematic illustration for (a) fluxes normal to a solid surface; (b) continuous domain parameters describing two grains. Subfigures (i) and (ii) show ψ_1 and ψ_2 for Grains 1 and 2, respectively. The grain boundary is defined by the intermediate values of the domain parameters.

Figure 2. Simulated concentration distributions calculated using (a) Fisher's model and (b) the SBM at a dimensionless simulation time of 202, with a horizontal straight grain boundary in the middle of the computational domain. The grain boundary diffusivity is set to be 100 times that of the bulk. The governing equations of the two methods are solved using the same grid system.

Figure 3. (a) The polycrystalline microstructure generated by Dream3D, which contains 1880 grains. (b) The microstructure described by 12 domain parameters, which is used for the SBM simulations. The color shows the value of $\sum_{q=1}^Q \psi_q^3$.

Figure 4. Concentration distributions for the grain boundary diffusion simulation for (a) $D'_g = 100$ and (b) $D'_g = 10000$. The subfigures (i) through (iii) are taken at dimensionless simulation times equal to 5, 10, and 15, respectively. Grain boundary diffusion with $D'_g = 10000$ is much more pronounced than the case with $D'_g = 100$.

Figure 5. Magnified views near the top face of the computational domain: (a) for Fig. 4(a)- iii; (b) for Fig. 4(b)-iii. Enhanced diffusion along the grain boundary network can be clearly observed.

Figure 6. Concentration distribution at intermediate evolution times for the grain boundary diffusion simulation with $D'_g = 100$. (a) through (c) are taken at dimensionless simulation times equal to 250, 500 and 1500, respectively. Concentration difference between the bulk and grain boundaries becomes less distinct at this diffusion regime.

Figure 7. Steady-state concentration distributions for the grain boundary diffusion simulations with (a) $D'_g = 100$ and (b) $D'_g = 10000$. The concentration changes nearly linearly from one to zero across the computational domain. However, the concentration gradients are not completely uniform due to the microstructure. Additionally, a slight difference between the two results is visible, which reflects the difference in the two grain boundary diffusivities.

Figure 8. (a) Microstructure of polycrystalline particle generated using Dream3D and smoothed using the polycrystalline phase field model. The particle contains 418 grains. (b) The configuration used in the EIS simulation. The particle is truncated at the contact regions to the virtual electrode (shown in brown).

Figure 9 Concentration distributions under sinusoidal loading taken at three representative frequencies. (a) through (c) for dimensionless frequencies ω' equal to 7.1×10^{-5} , 1.08×10^{-2} , and 2.24, respectively. Subfigures (i) and (ii) are the real and imaginary parts, respectively, of the concentration. As the loading frequency increases, the regions with large concentration gradients move toward the loading boundaries. (d) Simulated Nyquist plot for the polycrystalline particle. Each blue circular marker indicates the impedance corresponding to a loading

frequency. As the frequency increases, the marker moves from right to left. The red, green, and magenta markers correspond to (a), (b) and (c), respectively.