SELF-DIFFUSION IN NANOCRYSTALLINE METALS: MODELING THE CONTRIBUTIONS OF TRIPLE JUNCTIONS AND GRAIN BOUNDARIES

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Abstract

This study presents an analytical model for quantifying grain boundary (GB) and triple junction (TJ) contributions to self-diffusion in nanocrystalline metals. Using the tetradecahedral grain model and Maxwell–Garnett effective medium approximation, we derive closed-form expressions that relate the effective diffusion coefficient D_{eff} to the fraction of intercrystalline atoms g_i. The derived formulas allow direct calculation of GB diffusion coefficients D_{gb} and TJ fractions g_{ij} without requiring prior knowledge of grain size d or boundary width δ. The model eliminates the need for explicit geometric parameters in diffusion analysis and provides a practical framework for interpreting atomistic simulation data. The approach demonstrates how microstructure-dependent diffusion can be extracted from bulk measurements or computational results.

Keywords: self-diffusion; grain boundaries; triple junctions; nanocrystalline materials; effective medium theory; microstructure-property relationships.

1 Introduction

Self-diffusion in polycrystalline metals occurs predominantly through microstructural defects such as grain boundaries (GBs), dislocations, and free surfaces [1, 2, 3]. In nanocrystalline materials, where the volume fraction of interfaces is substantial, grain boundary diffusion becomes the dominant transport mechanism, significantly influencing material properties including creep, sintering, and phase stability [4].

The diffusion coefficient in polycrystals varies by several orders of magnitude depending on grain size, boundary structure, and impurity content [3]. Conventional models require precise knowledge of grain size d and boundary width δ, parameters that are often difficult to determine experimentally or in simulations. Furthermore, triple junctions (TJs)—line defects where three grain boundaries meet—constitute additional fast diffusion pathways whose contribution is frequently overlooked in standard analyses [5].

In this work, we present a microstructure-informed model based on the tetradecahedral grain representation [5] and the Maxwell–Garnett effective medium theory [6]. The

model enables extraction of grain boundary diffusion parameters solely from the measured fraction of intercrystalline atoms g_i, bypassing the need for explicit microstructural dimensions. This approach is particularly valuable for analyzing molecular dynamics (MD) simulation data, where g_i is readily accessible but d and δ may be ambiguous.

2 Theoretical Framework

2.1 Effective Diffusion in Polycrystals

The effective self-diffusion coefficient D_{eff} in a nanocrystalline material can be computed from mean square displacement (MSD) data using the Einstein relation for three-dimensional diffusion:

$$D_{\text{eff}} = \frac{\langle r^2 \rangle}{6t}, \tag{1}$$

where $\langle r^2 \rangle$ is the ensemble-averaged MSD over time t:

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} \left[(x_i - x_{i0})^2 + (y_i - y_{i0})^2 + (z_i - z_{i0})^2 \right]. \tag{2}$$

For a two-phase system comprising grain interiors (diffusivity D_l) and grain boundaries (diffusivity D_{gb}), the Maxwell–Garnett mixing rule gives:

$$D_{\text{eff}}(d) = D_{\text{gb}} \frac{2gD_{\text{gb}} + (3-2g)D_l}{(3-g)D_{\text{gb}} + gD_l}, \tag{3}$$

where g is the volume fraction of the GB phase. Under the typical condition $D_{\text{gb}} \gg D_l$ [7], Equation (3) simplifies to:

$$D_{\text{eff}}(d) \approx \frac{2g}{3-g} D_{\text{gb}}. \tag{4}$$

For cubic grains with boundary width δ and grain size d, $g = 3\delta/d$, leading to:

$$D_{\text{eff}}(d) \approx \frac{2\delta}{d-\delta} D_{\text{gb}}, \tag{5}$$

or equivalently,

$$D_{\text{gb}} = \frac{D_{\text{eff}}(d-\delta)}{2\delta}. \tag{6}$$

2.2 Tetradecahedral Grain Model

Following Palumbo et al. [5], we represent grains as tetradecahedra. The volume fractions of atoms associated with different microstructural features are:

$$g_i = 1 - \left(\frac{d-\delta}{d} \right)^3, \tag{7}$$

$$g_{\text{gb}} = \frac{3\delta(d-\delta)^2}{d^3}, \tag{8}$$

$$g_{ij} = g_i - g_{\text{gb}}, \tag{9}$$

where g_i is the total fraction of intercrystalline atoms (GB + TJ), g_{gb} is the fraction of grain boundary atoms, and g_{ij} is the fraction of triple junction atoms.

Introducing the dimensionless parameter $\phi = \delta/d$, Equations (7)–(9) become:

$$g_i = 3\phi - 3\phi^2 + \phi^3, \tag{10}$$
$$g_{\mathrm{gb}} = 3\phi - 6\phi^2 + 3\phi^3, \tag{11}$$
$$g_{ij} = 3\phi^2 - 2\phi^3. \tag{12}$$

2.3 Inversion of Microstructural Relations

Equation (10) can be rearranged as:

$$\phi^3 - 3\phi^2 + 3\phi - g_i = 0. \tag{13}$$

Substituting $\phi = y + 1$ yields:

$$y^3 - (1 - g_i) = 0, \tag{14}$$

which has a unique real solution:

$$\phi = 1 - (1 - g_i)^{1/3}. \tag{15}$$

This one-to-one mapping allows ϕ to be determined directly from g_i, without requiring separate knowledge of d and δ.

Substituting Equation (15) into (12) and (11) gives explicit expressions for TJ and GB fractions in terms of g_i alone:

$$g_{ij} = 3 - 2g_i - 3(1 - g_i)^{2/3}, \tag{16}$$
$$g_{\mathrm{gb}} = 3(1 - g_i)^{2/3} - 3 + 3g_i. \tag{17}$$

2.4 Diffusion Coefficient Relations

Using Equations (4) and (17), and noting that $g = g_{\mathrm{gb}}$ for the GB phase, we obtain:

$$D_{\mathrm{eff}} \approx \frac{2g_{\mathrm{gb}}}{3 - g_{\mathrm{gb}}} D_{\mathrm{gb}}. \tag{18}$$

Substituting Equation (17) yields the final relations:

$$D_{\mathrm{eff}} \approx \frac{2(1 - g_i)^{2/3} - 2 + 2g_i}{2 - (1 - g_i)^{2/3} - g_i} D_{\mathrm{gb}}, \tag{19}$$
$$D_{\mathrm{gb}} = \frac{2 - (1 - g_i)^{2/3} - g_i}{2(1 - g_i)^{2/3} - 2 + 2g_i} D_{\mathrm{eff}}. \tag{20}$$

3 Results and Discussion

Equations (16), (17), and (20) constitute the main results of this work. They enable determination of microstructurally resolved diffusion parameters directly from the measurable quantity g_i.

For typical nanocrystalline metals where g_i ranges from 0.1 to 0.5, triple junctions account for 1–15% of all atoms according to Equation (16), a non-negligible fraction that can significantly influence effective diffusion.

The significance of Equation (20) lies in its ability to extract the grain boundary diffusion coefficient D_{gb} from the effective diffusion coefficient D_{eff} without requiring grain size or boundary width. This is particularly advantageous for analyzing atomistic simulation data, where g_i can be computed precisely from atomic coordinates, but d and δ are often model-dependent.

Previous studies have highlighted the strong dependence of GB diffusion on boundary structure and purity [3]. Our model provides a consistent framework to deconvolute the contributions of general grain boundaries and triple junctions, which may exhibit different activation energies and pre-exponential factors [2, 5].

The assumption $D_{\text{gb}} \gg D_l$ is well justified for most metals at moderate temperatures, where GB diffusion coefficients exceed lattice diffusion by several orders of magnitude. However, at very high temperatures approaching the melting point, the approximation may become less accurate, and the full Maxwell–Garnett expression (Equation 3) should be used.

4 Conclusion

We have derived a set of analytical relations that quantify the contributions of grain boundaries and triple junctions to effective self-diffusion in nanocrystalline metals. The model requires only the fraction of intercrystalline atoms g_i—a readily obtainable quantity from atomistic simulations—to compute:

- The volume fractions of grain boundary and triple junction atoms,
- The grain boundary diffusion coefficient D_{gb} from the effective diffusion coefficient D_{eff}.

This approach eliminates the need for explicit knowledge of grain size d and boundary width δ, simplifying the analysis of diffusion in microstructurally complex materials. The derived formulas provide a practical tool for interpreting molecular dynamics simulation data and experimental measurements where microstructural dimensions are uncertain.

Future work will focus on validating the model against large-scale MD simulations of nanocrystalline nickel and other FCC metals, and extending the formulation to include temperature-dependent boundary widths and anisotropic diffusion tensors.

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