

Supplemental Material to “The Role of Grain Boundaries under Long-Time Radiation”

1 Derivation of Eq. (3)

Here we derive Eq. (3) using matched asymptotic techniques. To this end, we non-dimensionalise by

$$\bar{x} = \frac{x}{L}, \quad \bar{y} = \frac{y}{L}, \quad \bar{t} = \frac{tD}{L^2}, \quad \bar{S} = \frac{SL^2}{D}, \quad (1.1)$$

where a bar is added to a variable to denote its non-dimensional counterpart. Note that at a point close to a GB dislocation at the origin, say, the hydrostatic pressure can be expressed by [14]

$$p = \frac{Gb(1+\nu)}{3\pi(1-\nu)} \cdot \frac{y}{x^2 + y^2} + p_m, \quad (1.2)$$

where G and ν are the shear modulus and Poisson ratio, respectively. Note that in Eq. (1.2), the first term is induced by the almost singular stress field due to the GB dislocation and p_m captures the mean-field hydrostatic pressure due to the external loads and all other dislocations. If we non-dimensionalise p by

$$\bar{p} = p \cdot \frac{3\pi L(1-\nu)}{Gb(1+\nu)}, \quad (1.3)$$

incorporating Eq. (1.2) into (1.3) gives

$$\bar{p} = \frac{\bar{y}}{\bar{x}^2 + \bar{y}^2} + \bar{p}_m. \quad (1.4)$$

Using Eqs. (1.1) and (1.3), Eqs. (1) and (2) become

$$\frac{\partial c}{\partial \bar{t}} = \bar{\nabla} \cdot \bar{\mathbf{J}} + \bar{S} \quad (1.5)$$

and

$$\bar{\mathbf{J}} = - \left(\bar{\nabla} c + \beta \theta \epsilon c \bar{\nabla} \left(\frac{\bar{y}}{\bar{x}^2 + \bar{y}^2} + \bar{p}_m \right) \right), \quad (1.6)$$

where “ $\bar{\nabla}$ ” denotes the spatial gradient with respect (\bar{x}, \bar{y}) and

$$\beta = \frac{G\Delta\Omega(1+\nu)}{3\pi k_B T(1-\nu)}. \quad (1.7)$$

As discussed in the main text, the PD-GB interaction can be investigated at three different length scales, characterised by the Burgers modulus b , the GB dislocation spacing d and a macroscopic length parameter L , respectively. Based on the hierarchic relation $b \ll d \ll L$, two small nondimensional parameters are introduced:

$$\epsilon = \frac{d}{L}, \quad \theta = \frac{b}{d}. \quad (1.8)$$

We consider the asymptotic behaviour of equation system (1.5) - (1.6) in the three regimes identified by Fig. 1 in the main text.

1.1 Isolated regime

In the isolated regime as indicated in the right hand panel of Fig. 1, the natural length should be measured by $(\xi, \eta) = (\frac{\bar{x}}{\theta\epsilon}, \frac{\bar{y}}{\theta\epsilon})$. Then Eqs. (1.5) and (1.6) can be combined to give an equation for $c_{\text{in}}(\xi, \eta)$:

$$(\epsilon\theta)^2 \cdot \frac{\partial c_{\text{in}}}{\partial t} = \nabla_{\text{in}} \cdot \left(\nabla_{\text{in}} c_{\text{in}} + \beta c_{\text{in}} \nabla_{\text{in}} \left(\frac{\eta}{\xi^2 + \eta^2} + (\epsilon\theta)^2 \bar{p}_{\text{m}} \right) \right) + (\epsilon\theta)^2 \bar{S}, \quad (1.9)$$

with

$$c_{\text{in}} = c_{\text{e}} \quad \text{on} \quad \sqrt{\xi^2 + \eta^2} = \frac{r_{\text{c}}}{b} := \frac{1}{\lambda}; \quad (1.10)$$

here “ ∇_{in} ” denotes the spatial gradient with respect to (ξ, η) .

Noting that $(\epsilon\theta)$ is small, Eq. (1.9) becomes

$$\nabla_{\text{in}} \cdot \left(\nabla_{\text{in}} c_{\text{in}} + \beta c_{\text{in}} \nabla_{\text{in}} \frac{\eta}{\xi^2 + \eta^2} \right) = 0 \quad (1.11)$$

to leading order. Introducing polar coordinates $\varrho = \sqrt{\xi^2 + \eta^2}$ and $\varphi = \tan^{-1}(\eta/\xi)$, as in Ref. [18], the solution to Eq. (1.11) can be expanded in terms of the modified Bessel functions as

$$c_{\text{in}} = (f(\varrho, \varphi) + g(\varrho, \varphi)) \exp \left(\frac{\beta\lambda \sin \varphi}{2\varrho} \right), \quad (1.12)$$

where

$$f(\varrho, \varphi) = \sum_{n=1}^{n=\infty} (\alpha'_n \cos n\varphi + \beta'_n \sin n\varphi) \left(\alpha''_n I_n \left(\frac{\beta}{2\varrho} \right) + \beta''_n K_n \left(\frac{\beta}{2\varrho} \right) \right) \quad (1.13)$$

and

$$g(\varrho, \varphi) = \alpha_0 I_0 \left(\frac{\beta}{2\varrho} \right) + \beta_0 K_0 \left(\frac{\beta}{2\varrho} \right), \quad (1.14)$$

where $\alpha'_n, \alpha''_n, \beta'_n$ and β''_n are as yet undetermined coefficients.

In order to match with the discrete regime, the PD concentration must not grow too quickly as $\varrho \rightarrow \infty$, requiring $\beta''_n = 0$ for $n = 1, 2, \dots$. Thus Eq. (1.12) becomes

$$c_{\text{in}} = \exp\left(\frac{\beta \sin \varphi}{2\varrho}\right) \sum_{n=1}^{n=\infty} (\alpha_n \cos n\varphi + \beta_n \sin n\varphi) I_n\left(\frac{\beta}{2\varrho}\right) + \exp\left(\frac{\beta \sin \varphi}{2\varrho}\right) \left(\alpha_0 I_0\left(\frac{\beta}{2\varrho}\right) + \beta_0 K_0\left(\frac{\beta\lambda}{2\varrho}\right)\right), \quad (1.15)$$

where $\alpha_n = \alpha'_n \alpha''_n$, $\beta_n = \beta'_n \alpha''_n$, β_0 are still undetermined coefficients. Incorporating Eq. (1.15) into the boundary condition (1.10) gives

$$c_e \exp\left(-\frac{\beta \sin \varphi}{2\lambda}\right) = \alpha_0 I_0\left(\frac{\beta\lambda}{2}\right) + \beta_0 K_0\left(\frac{\beta\lambda}{2}\right) + \sum_{n=1}^{\infty} (\alpha_n \cos n\varphi + \beta_n \sin n\varphi) I_n\left(\frac{\beta\lambda}{2}\right). \quad (1.16)$$

The left part of Eq. (1.16) can also be expanded as Fourier's series

$$c_e \exp\left(-\frac{\beta\lambda \sin \varphi}{2}\right) = I_0\left(\frac{\beta\lambda}{2}\right) + 2 \sum_{p=1}^{\infty} (-1)^p I_{2p}\left(\frac{\beta\lambda}{2}\right) \cos 2p\varphi + 2 \sum_{q=1}^{\infty} (-1)^q I_{2q-1}\left(\frac{\beta\lambda}{2}\right) \sin ((2q-1)\varphi). \quad (1.17)$$

A comparison between Eqs. (1.16) and (1.17) gives

$$\alpha_n = \begin{cases} 0, & n = 2k-1 \\ 2(-1)^k c_e, & n = 2k \end{cases} \quad \beta_n = \begin{cases} 2(-1)^k c_e, & n = 2k-1 \\ 0, & n = 2k \end{cases} \quad (1.18)$$

and

$$\alpha_0 I_0(\beta\lambda/2) + \beta_0 K_0(\beta\lambda/2) = c_e I_0(\beta\lambda/2), \quad (1.19)$$

Up to now, there is still one coefficient α_0 (or β_0) undetermined, and it will be calculated through matching with the results from the other regimes.

1.2 Discrete regime

In the discrete regime as indicated in the centre panel of Fig. 1, the length is naturally measured by $(X, Y) = (\frac{\bar{x}}{\epsilon}, \frac{\bar{y}}{\epsilon})$. In this regime, GB dislocations are represented by an array of point sources at positions $(X = 0, Y = n \in \mathbb{Z})$. The PD concentration is then given by $c_m(X, Y)$ and is periodic in $Y \in [-1/2, 1/2]$. Hence Eq. (1.5) becomes

$$\theta \frac{\partial c_m}{\partial t} - \nabla_m \cdot \left(\nabla_m c_m + \beta \theta c_m \nabla_m \left(\frac{Y}{X^2 + Y^2} \right) + \bar{p}_m \right) - 2\pi Q_1 \delta_0(X) \delta_0(Y) = \theta \bar{S}, \quad (1.20)$$

where ∇_m denotes the spatial gradient with respect to (X, Y) ; δ_0 is the Dirac function; Q_1 is a constant to be determined.

Since θ is small, Eq. (1.20) reads

$$\nabla_{\mathbf{m}}^2 c_{\mathbf{m}} = 2\pi Q_1 \delta_0(X) \delta_0(Y) \quad (1.21)$$

to leading order with periodicity in Y imposed by setting $\frac{\partial c_{\mathbf{m}}}{\partial Y} = 0$ at $Y = \pm 1/2$. The solution to Eq. (1.21) is

$$c_{\mathbf{m}} = Q_0 + Q_1 \left(\ln(2 \cosh(2\pi X) - 2 \cos 2\pi Y)^{1/2} - \ln 2 \right). \quad (1.22)$$

Thus we have another two undetermined constants Q_0 and Q_1 in the discrete regime.

1.3 Matching between different regimes

Asymptotic matching techniques formalise the idea that the expression for c obtained in smaller regimes tending to infinity should be consistent with that obtained in larger regimes tending to 0. To this end, as $\varrho \rightarrow \infty$, Eq. (1.15) gives

$$c_{\text{in}} \sim \beta_0 \ln \varrho \alpha_0 - \beta_0 \gamma + \beta_0 \ln \frac{4}{\lambda \beta} + \mathcal{O}\left(\frac{1}{\varrho}\right), \quad (1.23)$$

where $\gamma \approx 0.5772$ is the Euler-Mascheroni number. Meanwhile, the solution from the discrete regime becomes

$$c_{\mathbf{m}} \sim Q_0 + Q_1 \ln \pi + Q_1 \ln \sqrt{X^2 + Y^2}, \quad (1.24)$$

as $\sqrt{X^2 + Y^2} \rightarrow 0$. A comparison between Eqs. (1.23) and (1.24), noting that $\varrho = \theta \sqrt{X^2 + Y^2}$, gives

$$Q_0 + Q_1 \ln \pi \theta = \alpha_0 - \beta_0 \gamma + \beta_0 \ln \frac{4r_c}{\beta b} \quad \text{and} \quad \beta_0 = Q_1. \quad (1.25)$$

The PD concentration from the discrete regime should also be matched with that from the continuum regime. As $X \rightarrow \pm\infty$, Eq. (1.22) gives

$$c_{\mathbf{m}} \sim \pm Q_1 \pi X - Q_1 \ln 2 + Q_0. \quad (1.26)$$

At the continuum regime, we have the expansion in the vicinity of the GB (locally expressed by $\bar{x} = 0$)

$$c \sim c|_{\bar{x}=0} + \left. \frac{\partial c}{\partial \bar{x}} \right|_{\bar{x}=0} \cdot \bar{x} + \mathcal{O}(\bar{x}^2). \quad (1.27)$$

Matching between Eqs. (1.26) and (1.27) gives

$$c(0) = -Q_1 \ln 2 + Q_0 \quad \text{and} \quad \left[\frac{\partial c}{\partial \bar{x}} \right]_{\bar{x}=0-}^{\bar{x}=0+} = \frac{2\pi Q_1}{\epsilon}. \quad (1.28)$$

Combining Eqs. (1.19), (1.25) and (1.28), we obtain

$$\left[\frac{\partial c}{\partial \bar{x}} \right]_{\bar{x}=0-}^{\bar{x}=0+} = \frac{2\pi}{\epsilon} \frac{c|_{\Gamma} - c_e}{\ln \frac{2}{\pi\theta} - h}, \quad (1.29)$$

with h a material parameter given by

$$h = \ln \left(\frac{\beta b}{r_c} \right) + \frac{K_0(\beta b/(2r_c))}{I_0(\beta b/(2r_c))} + 0.5772. \quad (1.30)$$

Redimensionalising Eq. (1.29) gives Eq. (3) in the main text.

Note that Eq. (3) can be generalised to the case with multiple species of straight GBDs which are mutually parallel (as shown in the case of Fig. 4(a) in the maintext). In that scenario, the magnitude of the “Burgers vector” is calculated by a weighted average of all dislocations:

$$b = \left| \frac{\sum_{i=1}^M |\rho^i| \mathbf{b}^i}{\sum_{i=1}^M |\rho^i|} \right| \quad (1.31)$$

and the effective dislocation spacing is given by

$$d = \frac{1}{\sum_{i=1}^M |\rho^i|}, \quad (1.32)$$

where M is the number of GB species. Thus the misorientation angle θ can be expressed by

$$\theta = \frac{b}{d} = \left| \sum_{i=1}^M |\rho^i| \mathbf{b}^i \right|. \quad (1.33)$$

2 Derivation of Eq. (5)

Now we will derive the explicit formula estimating PD concentration in polycrystalline. Here we refer to the laminar polycrystalline specimen illustrated by Fig. 2. Given the the assumption that PDs are simply generated by irradiation from the left side of the specimen ($x < 0$), we have in each layered grain:

$$\frac{d^2 c}{dx^2} = 0 \quad (2.1)$$

showing that the PD concentration $c(x)$ is piecewisely linear in x . The connection of c across GBs should be formulated by Eq. (3) in the main text. If we use c_i to denote the concentration fraction at the i -th GB, then the following recursive relation should hold:

$$\begin{pmatrix} c_i - c_e \\ k_i \end{pmatrix} = \begin{pmatrix} 1 & -l \\ -\omega_0 & 1 + \omega_0 l \end{pmatrix} \begin{pmatrix} c_{i-1} - c_e \\ k_{i-1} \end{pmatrix}, \quad (2.2)$$

for $i = 1, \dots, n$, where $k_i = -\left. \frac{dc}{dx} \right|_i$ measures the negative slope of c in the i -th grain. Noted that the matrix appearing in Eq. (2.2) can be decomposed by

$$\begin{pmatrix} 1 & -l \\ -\omega_0 & 1 + \omega_0 l \end{pmatrix} = P \Lambda P^{-1}, \quad (2.3)$$

where

$$P = \begin{pmatrix} 1 & 1 \\ \frac{(\omega_0 l) - \sqrt{4(\omega_0 l) + (\omega_0 l)^2}}{2l} & \frac{(\omega_0 l) + \sqrt{4(\omega_0 l) + (\omega_0 l)^2}}{2l} \end{pmatrix} \quad (2.4)$$

and

$$\Lambda = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \quad (2.5)$$

with $0 < \lambda_1 < 1 < \lambda_2$. The two eigenvalues of Λ are given by

$$\lambda_{1,2} = \frac{2 + (\omega_0 l) \mp \sqrt{4(\omega_0 l) + (\omega_0 l)^2}}{2}. \quad (2.6)$$

Repeatedly applying Eq. (2.2) and using (2.3) links c_n , the concentration fraction at the n -th GB, with c_0 , the PD concentration generated by irradiation:

$$\begin{pmatrix} c_0 - c_e \\ k_0 \end{pmatrix} = P \Lambda^{-n} P^{-1} \begin{pmatrix} c_n - c_e \\ k_n \end{pmatrix}. \quad (2.7)$$

Practically, the PD flux is supposed to vanish at the far end of the specimen, which gives $k_n = 0$. Thus Eq. (2.7) is reduced to

$$\frac{c_0 - c_e}{c_n - c_e} = \lambda_1^{-n} \cdot \frac{\sqrt{4(\omega_0 l) + (\omega_0 l)^2} + \omega_0 l}{2\sqrt{4(\omega_0 l) + (\omega_0 l)^2}} + \lambda_2^{-n} \cdot \frac{\sqrt{4(\omega_0 l) + (\omega_0 l)^2} - \omega_0 l}{2\sqrt{4(\omega_0 l) + (\omega_0 l)^2}}. \quad (2.8)$$

It is observed that the inter-relation between c_n and c_0 is fully controlled by the non-dimensional parameter $\omega_0 l$. According to Eq. (4) in the main text, a misorientation angle of $\theta \approx 2.5^\circ$ roughly returns $\omega_0 \sim 1 \text{ nm}^{-1}$. Thus, for a grain whose size is greater than 10nm, this parameter already exceeds 10. Hence it is practically reasonable consider the behaviour of Eq. (2.8) in a regime characterised by large $\omega_0 l$. In this scenario, the second term on the right side of Eq. (2.8) vanishes, and we reach

$$\frac{c_n}{c_0} = \left(\frac{1}{\omega_0 l} \right)^n. \quad (2.9)$$

Here we set the equilibrium PD concentration $c_e = 0$ for simplicity. Literally, the number of grains n should be given by L/l , where L is the specimen size. However, for the applicability of our model to three dimensions, we introduce an adjusting parameter k , such that $n = L/kl$. Finally, since the locations where the defect density is measured in experiments are not specified by Ref. [30], we let the average PD concentration fraction equal c_n , i.e., $c_n = c_a$. Combine all these factors with Eq. (2.9) we have

$$\frac{c_n}{c_0} = \left(\frac{1}{\omega_0 l} \right)^{\frac{L}{kl}}, \quad (2.10)$$

which is Eq. (3) in the main text.

3 Derivation of Eq. (8)

As discussed in the main text, the PD absorption rate by a GB can be calculated by means of the PD flux difference across the GB. As from Eq. (3), the PD absorption rate (number per second) $\dot{\phi}$ due to a GB of area A satisfies

$$\dot{\phi} = \frac{D\omega_0 AN}{b} \cdot (c - c_e), \quad (3.1)$$

where N is recalled to be the number of atoms per volume in perfect lattices and b is given by Eq. (1.31). On the other hand, the PD absorption also induces the climb motion of GB dislocations. For a straight dislocation segment of length l_0 , its climb speed is related with its PD absorption rate by [6]

$$\dot{\phi}_i = b^i v_c^i l_0 N. \quad (3.2)$$

Thus the overall PD absorption rate due to a GB of area A is calculated by

$$\dot{\phi} = NA \sum_{i=1}^M \rho^i b^i v_c^i. \quad (3.3)$$

Equating Eq. (3.1) with (3.3) gives Eq. (8).