Point defect sink efficiency of low-angle tilt grain boundaries

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Abstract

We examine the common assumption that grain boundaries (GBs) are ideal (or perfect) sinks for point defects by comparing and contrasting its implications with an explicit model of a low-angle tilt GB described by an array of edge dislocations which annihilate point defects by climbing. We solve the resultant diffusion equation in the absence and presence of irradiation-induced point defects. The GB sink efficiency depends on the physical parameters describing the boundary geometry (*i.e.*, misorientation), material properties, and/or irradiation conditions (point defect generation and annihilation within the interior of grains). When the constituent dislocation spacing is small (large misorientation), the GB sink efficiency approaches that of the ideal sink. However, for small misorientations, the GB sink efficiency drops rapidly to zero and the ideal sink assumption for the GB fails dramatically. We derive a reduced dimension description of GBs where the influence of GB structure is captured in a single parameter in a Robin boundary condition for the diffusion equation. For the case of a low-angle tilt GB, we explicitly relate this parameter to the GB structure. We discuss the generality of this approach for cases where the low-angle GB model applies and parameterize the model so that it accurately reproduces the results of the two-dimensional dislocation model. The applicability of the approach to more general GBs is discussed as well as the implication of these results for predicting grain size effects under irradiation conditions.

Keywords: Grain boundaries; Point defects; Sink efficiency; Dislocation climb; Irradiation

1. Introduction

Because grain boundaries provide potent sinks for point defects [1], increasing the density of grain boundaries (GBs) provides a promising route to develop materials for radiation environments that produce large numbers of vacancies and interstitials (such as the environment in the current and future nuclear reactors [1, 2]). Point defects can readily combine to form dislocation loops, nucleate voids and create stacking-fault tetrahedra [3, 4, 5, 6], leading to material swelling, radiation hardening, amorphization and embrittlement [7, 8]. Hence, nanocrystalline materials, where the density of GB sinks is very high, are of growing interest for applications in such environments [9, 10, 11].

The grain boundary sink efficiency, defined as the ratio between the fluxes of point defects into a GB to that into an ideal planar sink (where the point defect concentration is fixed at its thermal equilibrium value), is a measure of the efficacy of the grain boundary to absorb point defects. Many experimental studies and atomistic simulations have been performed to understand the factors that determine the GB sink efficiency [12, 13, 10, 14, 15]. For example, Bai *et al.* [16] used accelerated molecular dynamics to investigate the point defect-GB interaction mechanism from picosecond to microsecond time scales. Their simulations revealed that the existence of GBs leads to a vacancy-interstitial recombination mechanism with a lower energy barrier than the bulk equivalent, which implies an efficient route towards self-healing. Uberuaga *et al.* [17] also employed molecular dynamics simulations to address this and concluded that GB sink efficiency evolves in a complex manner as a function of defect mobility during irradiation rather than being a static quantity. However, such fundamental understanding cannot be easily applied to the rational GB engineering of radiation-resistant material design. To make such methods useful for such applications requires the development of a continuum, mechanism-based model that can effectively predict GB sink efficiency.

In most of the extant continuum models that consider the sink effect of grain boundaries, grain boundaries are treated as ideal (*i.e.*, perfect) sinks and/or sources – for theoretical convenience [1]. However, this contradicts many experimental observations, which suggest that some GBs have significantly different sink properties than others [12, 1]. For example, Han *et al.* [13] investigated

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the width of the void-denuded zone around GBs of different character in Cu irradiated with He ions at elevated temperature and concluded that the GB sink efficiency depends on the overall GB character, including both misorientation and inclination. In addition, many experiments show that radiation-induced segregation (RIS) is also strongly influenced by GB character [18, 19] - RIS is the segregation of some alloy components to GBs driven by the flux of radiation-produced defects and is associated with co-diffusion of alloy elements and point defects diffusing toward GBs. Obviously, a model that treats GBs as ideal or perfect point defects sinks is incapable of describing GB sink behavior in a manner consistent with these observations. A useful continuum model for GB sinks must account for this GB-character dependence.

The GB-character dependence of the sink behavior can be established based on a model for GB structure and the interaction mechanism between elements of this structure and point defects. Low-angle GBs represent a class of GBs for which the structure and its dependence on GB geometry is both simple and well understood. In a low-angle GB, point defect absorption/emission takes place via the climb of the lattice dislocations that compose the GB structure [20]. The first application of this low angle GB/lattice dislocation model to predict GB sink efficiency was that of Siegel *et al.* [10]. They showed that the sink efficiency of a low angle, symmetric tilt GB composed of an array of dislocations can be expressed as $\eta = \left(1 + \frac{p}{2\pi x_\infty} \ln \frac{p}{2\pi x_d}\right)^{-1}$, where p is the dislocation spacing, x_d is the dislocation core radius, and x_∞ is the distance between the GB plane and a plane where the point defect concentration is fixed. (A similar expression [21] was also used to study the GB-character dependence of RIS [22, 19].) However, this equation was derived for a special, unrealistic boundary condition; *i.e.*, where the point defect concentration is fixed at a plane x_∞ away from only one side of the GB. This approach is obviously not applicable to the case of a polycrystal nor to the irradiation case where the appropriate boundary conditions are set by the point defect dynamics within the interiors of the grains.

Recently, we derived a general dislocation climb formulation for arbitrarily curved dislocations in three-dimensions [23]. This new formulation gives an accurate solution to the classical vacancy/interstitial-assisted dislocation climb model, based on a Green's function solution for the point defect distribution. This method has been employed to understand the effect of dislocation climb on GB stability [24]. In this paper, we investigate the defect sink properties of low-angle GBs under both non-irradiation and irradiation conditions, and show the influence of low-angle

tilt GB structure on the sink efficiency. We derive a reduced dimension description of GBs where the influence of GB structure is captured in a single parameter in a Robin boundary condition for the diffusion equation. We also show that by proper parameterization, the simple, non-irradiation problem can serve as an approximation to the irradiation problem.

In our analysis, we focus on the low-angle symmetric tilt GBs in a two-dimensional coordinate system in which this boundary is located at $x = 0$. In the classical dislocation model of GBs [25], a low-angle symmetric tilt GB consists of a regular array of edge dislocations with lattice Burgers vectors, $\mathbf{b} = (b, 0)$. We explicitly assume that the constituent dislocation lines are perpendicular to the x - y plane and locate at $y = jp$ (j is integer). The spacing between the neighboring dislocations p is related to the misorientation angle θ and the magnitude of the Burgers vector by $\theta = b/p$. Under the condition of point defect supersaturation, the constituent dislocations will move within the GB plane by climb.

2. Non-irradiation problem

We first consider the case in which the point defect (vacancy) concentration is governed by the classical (constant diffusivity) diffusion equation within the grains, in the absence of irradiation (*i.e.*, no production/annihilation of point defects within the grains).

2.1. Sink efficiency

In the analysis of this problem, we assume that the constituent dislocations of the low-angle tilt GB act as ideal point defect sinks/sources rather than assuming that the entire GB plane is an ideal sink/source. This process of vacancy absorption/emission coupled with dislocation climb is described by the following model [24]:

$$\frac{\partial c}{\partial t} = D_v \Delta c - bv_{\text{cl}} \delta(\Gamma), \quad (1)$$

where c is the vacancy concentration (mole fraction), $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2$ is the Laplace operator, D_v is the (constant) vacancy diffusivity, Γ represents the positions of the constituent dislocations, $\delta(\Gamma)$ is the Dirac delta function of Γ (with dimensions of length per unit volume), and v_{cl} is the dislocation climb velocity. In what follows, we focus on the steady-state problem, where the concentration is not a function of time:

$$D_v \Delta c = bv_{\text{cl}} \delta(\Gamma). \quad (2)$$

Note that in this analysis, we do not consider the elastic interactions between point defects and the dislocations that comprise the GB structure, although some recent work suggests that in some circumstances this should not be ignored [26].

Since our GB is an array of edge dislocations with line directions perpendicular to the xy -plane, periodically spaced along the y -axis with a period equal to the inter-dislocation spacing p , $\delta(\Gamma) = \sum_{j=-\infty}^{\infty} \delta(x)\delta(y - jp)$. A solution to Eq. (2), periodic in y , is

$$c(x, y) = \frac{bv_{\text{cl}}}{4\pi D_v} \ln \left(2 \cosh \frac{2\pi x}{p} - 2 \cos \frac{2\pi y}{p} \right) + C, \quad (3)$$

where C is a constant. The climb velocity v_{cl} and the constant C are determined by the boundary conditions

$$c(\pm x_d, jp) = c_d \text{ and } c(\pm x_\infty, jp) = c_\infty, \quad (4)$$

where j is an integer, x_d is the dislocation core radius, c_d is the vacancy concentration fixed at the dislocation core, and c_∞ is the vacancy concentration fixed at the distance x_∞ (related to the characteristic length of diffusion) from the GB. (N.B., the boundary condition at $\pm x_\infty$ is assumed to be periodic in y in order to keep the solutions relatively simple, but in the limit that the distance between the GB and the location where this boundary condition is applied relative to the dislocation spacing is large, *i.e.* $x_\infty \gg p$, the second boundary condition in Eq. (4) is equivalent to assuming that the point defect concentration at $\pm x_\infty$ is uniform in y ; see Eq. (9) below.)

A brief note is in order regarding the second boundary condition in Eq. (4). This boundary condition is not necessarily relevant to any particular physical situation; however, it does admit simple, analytical results. These analytical results can be derived as we do here, but also via a new method we introduce below in the following sub-section 2.2. Below, we compare the results of these two approaches to demonstrate the generality of our new approach (below). However, with appropriate choices of c_∞ and x_∞ , this boundary condition can be used to find a steady-state non-irradiation solution that can be applied to approximate the steady-state irradiation solution - following an approach suggested earlier in the literature (e.g., see [1, 10]). In the irradiation case, the diffusion problem is often divided into two spatial regions, (i) far from the sink where the point defect concentration is (nearly) constant and (ii) a region near the sink where it varies rapidly. The boundary condition $c(\pm x_\infty, jp) = c_\infty$ implies that the two diffusion solutions match at x_∞ at a concentration c_∞ (x_∞ and c_∞ are determined by the radiation strength and the sink strength within the grains). In such applications, it is commonly assumed that in region (ii) the diffusion

to the sink is much greater than the (irradiation) source term and in this region the irradiation problem can be approximated by the non-irradiation problem [1].

The value of c_d depends on the climb component of the Peach-Koehler force on the dislocation f_{cl} such that $c_d = c_0 e^{-f_{cl}\Omega/bk_B T}$, where c_0 is the thermal equilibrium vacancy concentration, Ω is the atomic volume, k_B is the Boltzmann constant, and T is the temperature. Due to the concentration difference $c_\infty - c_d$ ($\neq 0$, either due to supersaturations of vacancies or external loadings), there is a vacancy flux from the interiors of the grains towards the GB that causes the constituent dislocations to climb. Under the boundary conditions in Eq. (4), we obtain the climb velocity

$$v_{cl} = \frac{2\pi D_v}{b} \frac{c_\infty - c_d}{\ln(\sinh \pi \tilde{x}_\infty / \sinh \pi \tilde{x}_d)}, \quad (5)$$

from which we find the vacancy concentration

$$c(x, y) = \frac{c_\infty - c_d}{\ln(\sinh \pi \tilde{x}_\infty / \sinh \pi \tilde{x}_d)} \ln \frac{\sqrt{\sinh^2 \pi \tilde{x} + \sin^2 \pi \tilde{y}}}{\sinh \pi \tilde{x}_\infty} + c_\infty, \quad (6)$$

where $\tilde{X} \equiv X/p$ for any quantity X . The absorption of vacancies in this model for the GB structure (per period p) is the total vacancy current towards each dislocation (per unit length along the dislocation):

$$I_0 = \frac{D_v}{\Omega} \oint_{x^2+y^2=x_d^2} \left(-\frac{\partial c}{\partial n} \right) dl = \frac{2\pi D_v}{\Omega} \frac{c_\infty - c_d}{\ln(\sinh \pi \tilde{x}_\infty / \sinh \pi \tilde{x}_d)}, \quad (7)$$

where $\partial c / \partial n$ is the normal derivative of c on the dislocation core surface in the inward direction.

Since traditional analyses of GB sink behavior assume the GB plane is an ideal sink/source of point defects with no internal structure, the GB can be considered to be the plane $x = 0$ (with uniform properties along the y -axis) such that vacancy diffusion is also uniform along y . For this ideal case, vacancy diffusion in the bulk and absorption/emission by the GB are described by the one-dimensional equation,

$$D_v \frac{d^2 \bar{c}}{dx^2} = 0, \quad (8)$$

with Dirichlet boundary conditions at both the GB and the far-field boundary

$$\bar{c}(0) = c_d \text{ and } \bar{c}(\pm x_\infty) = c_\infty. \quad (9)$$

$\bar{c}(x)$ is the vacancy concentration field averaged over the y -axis, *i.e.*, $\bar{c}(x) = (1/p) \int_{-p/2}^{p/2} c(x, y) dy$.

The resultant vacancy concentration in this ideal case is

$$\bar{c}(x) = \frac{c_\infty - c_d}{x_\infty} (|x| - x_\infty) + c_\infty, \quad (10)$$

Figure 1: (a) Sink efficiency η_0 for the GB modeled as an array of dislocations in the absence of irradiation given in Eq. (12). The region with $\eta_0 > 0.9$ is located to the right of the black line, where the GB is close to an ideal sink of point defects. (b) Relative error of the approximate sink efficiency η_0^a in Eq. (13) with respect to η_0 , $err = |\eta_0 - \eta_0^a|/\eta_0$. (c) Sink efficiency η_0 as a function of x_∞ for several fixed values of dislocation spacing p . (d) Relative error err as a function of x_∞ for several dislocation spacings p .

and the total vacancy current into the GB per periodic length p is

$$I_0^i = \frac{D_v}{\Omega} p \left(\left. \frac{d\bar{c}}{dx} \right|_{0+} - \left. \frac{d\bar{c}}{dx} \right|_{0-} \right) = \frac{2D_v}{\Omega} \frac{c_\infty - c_d}{\tilde{x}_\infty}, \quad (11)$$

where the superscript “i” refers to the “ideal” sink case and the subscript “0” implies no irradiation.

We define the **sink efficiency** η as the ratio of the steady-state vacancy currents into the GB from the realistic (with dislocation structure) and ideal (structureless) models [12]. In the present case, the sink efficiency of the tilt GB modeled as an array of dislocations is

$$\eta_0 = \frac{I_0}{I_0^i} = \frac{\pi \tilde{x}_\infty}{\ln(\sinh \pi \tilde{x}_\infty / \sinh \pi \tilde{x}_d)} \quad (12)$$

This sink efficiency η_0 as a function of x_∞/x_d ($= \tilde{x}_\infty/\tilde{x}_d$) and p/x_d ($= \tilde{x}_d^{-1}$) is shown in Fig. 1(a) and (c). These results demonstrate that the sink efficiency depends strongly on the ratio x_∞/p and, hence, on the misorientation angle θ as $(x_\infty/b)\theta$. In the limit that $x_\infty/p \rightarrow \infty$, the sink efficiency

Figure 2: Vacancy concentration in the absence of irradiation for the cases of (a) $x_\infty/x_d = 1000$, $p/x_d = 400$, (b) $x_\infty/x_d = 1000$, $p/x_d = 200$, (c) $x_\infty/x_d = 3000$, $p/x_d = 400$, (d) $x_\infty/x_d = 3000$, $p/x_d = 200$, and (e) $x_\infty/x_d = 7000$, $p/x_d = 200$, corresponding to the points A-E in Fig. 1(a). The top image in each panel shows the vacancy concentration distribution for the GB modeled as a dislocation array, and the bottom image shows the concentration profiles, obtained by averaging this over y , for both the GB modeled as a dislocation array (green), an ideal sink (black), and in terms of the one-dimensional Robin boundary condition (red dashed). The vertical black dashed lines indicate $\pm x_\infty$.

$\eta_0 \rightarrow 1$. In other words, the ideal sink model for the GB provides a reasonable approximation to the real GB sink efficiency provided that the spacing between the constituent dislocations is very small (the low-angle GB assumption breaks down there) or the location where the concentration is fixed is far from the GB. Examination of Fig. 1(a) shows that $\eta_0 > 0.9$ holds approximately when $x_\infty/p > 12.5$. With the constituent dislocation spacing increasing (or the misorientation decreasing), η_0 decreases; *i.e.*, the ideal sink model is a poor approximation for the real GB behavior at small x_∞/p . The deviation of the sink efficiency from the ideal sink case can be large; it is already 10% at $x_\infty = 10b$ for a misorientation angle of 5.7° ($p = 10b$).

The vacancy concentration profiles for the real GB (based on the dislocation model) are shown in

Fig. 2 for five cases (corresponding to points A-E in Fig. 1(a)). Comparison is made between these profiles, averaged over the dislocation spacing, for the real (dislocation) and ideal (perfect sink) GB models. We see that, as expected, a real GB can be treated as an ideal sink for point defects only for the cases of large x_∞/p (see Fig. 2(e)). When x_∞/p is small (*e.g.* Fig. 2(a)), the concentration and flux near the GB plane shows strong deviation from the ideal sink behavior (consistent with the results for η_0 in Fig. 1(a)). We note that the average point defect concentration at $x = 0$, $\bar{c}(0)$, is exactly c_d (very close to zero) in the ideal case under all conditions, but is significantly different from zero for most of the dislocation GBs shown in Fig. 2.

In the limits $x_\infty/p = \tilde{x}_\infty \rightarrow \infty$ and $\tilde{x}_d \ll 1$, we can approximate the sink efficiency as η_0^a :

$$\eta_0^a = \left(1 + \frac{1}{\pi\tilde{x}_\infty} \ln \frac{1}{2\pi\tilde{x}_d}\right)^{-1}. \quad (13)$$

This approximation is good for nearly any value of x_∞/p . The relative error of η_0^a with respect to its exact value η_0 is shown in Figs. 1(b) and (d). It can be seen that the relative error is well controlled (below 0.1% error) when $x_\infty/p \geq 1$ and is accurate even for $x_\infty/p = 0.2$, where the relative error is only $\approx 10\%$. Even when $x_\infty/p < 0.2$, η_0^a is still a reasonable approximation because both are very small (less than 0.2), *i.e.*, both fall in the $\eta \rightarrow 0$ regime. As $x_\infty/p \rightarrow 0$, the exact asymptotic behavior of the sink efficiency is $\eta_0 \approx \pi\tilde{x}_\infty/\ln(\tilde{x}_\infty/\tilde{x}_d)$. The simple expression η_0^a enables a direct comparison with the sink efficiency of the corresponding irradiation problem, which will be presented in Section 3.

Finally, we remark that in the periodic dislocation model, we chose boundary conditions for Eq. (3) as shown in Eq. (4). This specific choice of boundary conditions was made here, where there is no irradiation, in order to compare the solutions for the non-irradiation and radiation problem in the next section and to enable a simple approximation there. In Ref. [10], the authors solved for the sink efficiency of the same type of periodic dislocation model for a GB by analogy with the solutions to the Laplace equation in electrostatics. However, in their analysis, they set $\bar{c}(x_\infty) = c_\infty$ and no boundary condition is applied at finite x on the other side of the GB (*i.e.*, $x < 0$). The sink efficiency they report is very similar to that given above (Eq. 13) but with a slightly different higher order asymptotic behavior.

2.2. Equivalent Robin boundary condition

We have shown that the GB point defect sink efficiency depends on the dislocation structure. For continuum simulations of point defect diffusion and absorption/emission by GBs, it is desirable to capture the effects of GB structure in the form of a simple boundary condition at the GBs, especially one informed by the GB structure parameters (*e.g.* p and x_d) and independent of the external boundary conditions (*e.g.* x_∞ and c_∞). In this section, we demonstrate that this can be achieved using a Robin boundary condition at the GB [27] (*i.e.*, a linear combination of the function and its normal derivative at the boundary).

Focusing on the one-dimensional diffusion equation Eq. (8), we replace the first boundary condition in Eq. (9) by

$$-\alpha \frac{\partial \bar{c}}{\partial n} = \bar{c}(0) - c_d, \quad (14)$$

where α is a parameter to be determined. This is the general form of the Robin boundary condition, where $\partial/\partial n$ is the derivative in the outer normal direction of the domain. For our case, Eq. (8), the Robin boundary condition is simply $\alpha(d\bar{c}/dx)|_{x=0^\pm} = \pm[\bar{c}(0) - c_d]$. The solution is

$$\bar{c}(x) = \frac{c_\infty - c_d}{x_\infty + \alpha}(|x| - x_\infty) + c_\infty. \quad (15)$$

Thus the vacancy current into the GB I_0^R and sink efficiency η_0^R for the Robin boundary condition are

$$I_0^R = \frac{2pD_v}{\Omega} \frac{c_\infty - c_d}{x_\infty + \alpha}, \quad (16)$$

$$\eta_0^R = \frac{I_0^R}{I_0^I} = \frac{1}{1 + \alpha/x_\infty}. \quad (17)$$

We determine the parameter α by setting $\eta_0^R = \eta_0$. Inserting Eqs. (13) and (17), we find

$$\alpha = \frac{p}{\pi} \ln \frac{p}{2\pi x_d}. \quad (18)$$

Note that in this formula, α depends only on the GB structure through its parameters p and x_d . The relatively simple form of the Robin boundary condition and its single GB structure parameter makes it convenient to use in analytical or numerical studies of point defect diffusion in the presence of a GB for any external condition. Interestingly, we see that α increases (decreases) monotonically with the inter-dislocation spacing p (misorientation θ). This implies that the vacancy concentration at the GB $\bar{c}(0)$ (Eq. (15)) increases monotonically with increasing p , as clearly seen in Fig. 2.

When α is given by Eq. (18), the vacancy diffusion equation with the Robin boundary condition (Eq. (14)) at the GB will give the same sink efficiency as the dislocation model of the GB. In other words, the Robin boundary condition incorporates the effect of the dislocation structure of the GB. When $\alpha \rightarrow 0$, the sink efficiency $\eta_0^R \rightarrow 1$ (see Eq. 17), meaning that the GB is an ideal sink of the point defects. In this case, the Robin boundary condition in Eq. (14) reduces to $\bar{c} = c_d$ at the GB (which is the first boundary condition in Eq. (9)), and the problem is reduced to the ideal sink model. For non-zero α , the Robin boundary condition describes the role of the imperfect point defect sink/source of the GB. When $\alpha \rightarrow \infty$, the Robin boundary condition becomes $\partial \bar{c} / \partial n = 0$ and the sink efficiency $\eta_0^R \rightarrow 0$.

Vacancy concentration profiles determined using the GB Robin boundary condition and those obtained using the dislocation model of the GB are shown in Fig. 2. It can be seen that the concentration profiles of these two models always coincide with each other, suggesting that the Robin boundary condition is able to describe the sink behavior of the GB with a dislocation structure to high accuracy.

3. Irradiation Problem

In this section, we consider GB sink behaviors under irradiation conditions. Combining vacancy diffusion under irradiation conditions [1, 28, 29, 11] and the dislocation-based sink model of the GB, we have the following irradiation problem [28, 11, 30]:

$$D_v \Delta c = b v_{cl} \delta(\Gamma) + D_v k^2 c - K, \quad (19)$$

where K is the production rate of vacancies due to irradiation and k^2 is the total sink strength within the grain. The total sink strength within the grain accounts for effects such as vacancy absorption at dislocations within the grain and the formation and growth of vacancy clusters (divacancies, trivacancies, ...) and voids. **A term representing the recombination of vacancies and interstitials could be explicitly included in Eq. (19), but we do not do so here; this is a reasonable approximation for cases where the dislocation density within the grains is high or for high-temperature irradiation, where recombination contributes relatively little [1]. As suggested in the literature for those cases where recombination cannot be neglected (e.g., see [11]), it is possible to modify the value of the parameter k^2 to account for this effect.**

As in the dislocation model for the GB in the absence of irradiation, this problem is periodic in y with the period of the dislocation spacing p . The general form of the solution to Eq. (19) is

$$c(x, y) = -\frac{bv_{\text{cl}}}{2\pi D_v} \sum_{m=-\infty}^{\infty} K_0(k\sqrt{x^2 + (y - mp)^2}) + \frac{K}{D_v k^2}, \quad (20)$$

where $K_0(\cdot)$ is the modified Bessel function of the second kind of order 0. The dislocation climb velocity (determined by the dislocation core boundary condition $c(\pm x_d, jp) = c_d$) and the corresponding vacancy concentration are:

$$v_{\text{cl}} = \frac{2\pi D_v}{b} \frac{\zeta_{\infty} - c_d}{\sum_{m=-\infty}^{\infty} K_0(\sqrt{\tilde{x}_d^2 + m^2/\tilde{\chi}_{\infty}})}, \quad (21)$$

$$c(x, y) = (c_d - \zeta_{\infty}) \frac{\sum_{m=-\infty}^{\infty} K_0(\sqrt{\tilde{x}^2 + (\tilde{y} - m)^2/\tilde{\chi}_{\infty}})}{\sum_{m=-\infty}^{\infty} K_0(\sqrt{\tilde{x}_d^2 + m^2/\tilde{\chi}_{\infty}})} + \zeta_{\infty}, \quad (22)$$

where $\zeta_{\infty} \equiv K/D_v k^2$ represents the concentration in the grain interiors ($x \rightarrow \pm\infty$) and $\chi_{\infty} \equiv k^{-1}$ is the mean free path of a vacancy before being trapped by defects within the grain (and $\tilde{\chi}_{\infty} = \chi_{\infty}/p$).

The total vacancy current into each dislocation (across the dislocation core surface) in this radiation case I_r is

$$I_r \approx \frac{2\pi D_v}{\Omega} (\zeta_{\infty} - c_d) \frac{\tilde{x}_d}{\tilde{\chi}_{\infty}} \frac{K_1(\tilde{x}_d/\tilde{\chi}_{\infty}) + \tilde{x}_d \sum_{m=1}^{\infty} \left(\frac{2K_1(m/\tilde{\chi}_{\infty})}{m} - \frac{K_2(m/\tilde{\chi}_{\infty})}{\tilde{\chi}_{\infty}} \right)}{K_0(\tilde{x}_d/\tilde{\chi}_{\infty}) + 2 \sum_{m=1}^{\infty} K_0(m/\tilde{\chi}_{\infty})}, \quad (23)$$

for $\tilde{x}_d \ll 1$ and where $K_{\nu}(\cdot)$ is the modified Bessel function of the second kind of order ν (see Appendix A).

We also consider the one-dimensional case for which the GB is an ideal (structureless) sink in the presence of irradiation, where the vacancy concentration $\bar{c}(x)$ satisfies

$$D_v \frac{d^2 \bar{c}}{dx^2} = D_v k^2 \bar{c} - K, \quad (24)$$

with boundary conditions

$$\bar{c}(0) = c_d \text{ and } \bar{c}(\pm\infty) = K/D_v k^2 \equiv \zeta_{\infty}. \quad (25)$$

Figure 3: (a) Sink efficiency η_r for the GB modeled as an array of dislocations in the presence of irradiation (Eq. (28)). The black line corresponds to $\eta_r = 0.9$; $\eta_r > 0.9$ to the right of this line corresponds to the case where the GB is a near ideal sink of point defects. (b) Relative error of the approximate sink efficiency η_r^a (Eq. (29)) compared with the exact formula of η_r , defined as $err = |\eta_r - \eta_r^a|/\eta_r$. (c) Sink efficiency η_r as a function of χ_∞ for several fixed values of the dislocation spacing p . (d) Relative error err as a function of χ_∞ for several dislocation spacings p .

The solution is

$$\bar{c}(x) = (c_d - \zeta_\infty)e^{-k|x|} + \zeta_\infty, \quad (26)$$

and the vacancy current into the GB in this ideal case in the presence of radiation I_r^i is

$$I_r^i = \frac{2D_v}{\Omega} \frac{\zeta_\infty - c_d}{\tilde{\chi}_\infty}. \quad (27)$$

The GB sink efficiency for a GB array of dislocations under radiation conditions is

$$\eta_r = \frac{I_r}{I_r^i} = \pi \tilde{x}_d \frac{K_1(\tilde{x}_d/\tilde{\chi}_\infty) + \tilde{x}_d \sum_{m=1}^{\infty} \left(\frac{2K_1(m/\tilde{\chi}_\infty)}{m} - \frac{K_2(m/\tilde{\chi}_\infty)}{\tilde{\chi}_\infty} \right)}{K_0(\tilde{x}_d/\tilde{\chi}_\infty) + 2 \sum_{m=1}^{\infty} K_0(m/\tilde{\chi}_\infty)}. \quad (28)$$

The value of η_r determined as a function of χ_∞/x_d ($= k^{-1}x_d^{-1}$) and p/x_d is shown in Fig. 3(a) and (c). Comparing Fig. 3(a) with Fig. 1(a), we see that η_r and η_0 appear very similar in both

distribution and magnitude when χ_∞ and x_∞ are treated in same way. In other words, we can estimate the sink efficiency η_r for an irradiation problem by solving a non-irradiation problem, where x_∞ is replaced by χ_∞ . Similar to η_0 , the value of η_r strongly depends on the ratio $\chi_\infty/p = (\chi_\infty/b)\theta$, and all of the properties of η_0 deduced from Fig. 1(a) also apply to η_r if we replace x_∞ in the expression for η_0 by χ_∞ in that for η_r .

As η_0^a for the non-irradiation problem, we can also derive a simpler formula that approximates η_r in Eq. (28), which is

$$\eta_r^a = \left(1 + \frac{1}{\pi\tilde{\chi}_\infty} \ln \frac{1}{2\pi\tilde{x}_d}\right)^{-1} \quad (29)$$

(see Appendix B for derivation). The relative error of η_r^a with respect to its exact value η_r is shown in Fig. 3(b) and (d). As η_0^a , this approximation is also very accurate: the relative error is well controlled below 0.1% when $\chi_\infty/p \geq 1$, and it goes to 0 together with η_r as for very small χ_∞/p . Note that as $\chi_\infty/p \rightarrow 0$, the exact asymptotic behavior of the sink efficiency is $\eta_r \approx \pi\tilde{\chi}_\infty/\ln(\tilde{\chi}_\infty/\tilde{x}_d)$. From η_r^a in Eq. (29) and η_0^a in Eq. (13) for the non-irradiation problem, we have $\eta_r^a = \eta_0^a$ if $\chi_\infty = x_\infty$, which gives a quantitative correspondence between the sink efficiencies of the irradiation and non-irradiation problems.

The solution to the real GB (based on the dislocation model) under irradiation $c(x, y)$ is shown in Fig. 4 for five cases (points A-E labeled in Fig. 3(a)). Comparison is made among the profiles (averaged over y -axis) of the real GB (dislocation model) and the ideal sink. These vacancy concentration profiles are nonlinear rather than linear as shown in Fig. 2 for the non-irradiation problem. The comparison between the profiles of the real GB and the idea sink indicates that, when χ_∞/p is small (*e.g.* Fig. 4(a)), the concentration and flux near the GB plane deviate clearly from those of an ideal sink, while when $\chi_\infty/p \gg 1$ (*e.g.* Fig. 4(d) and (e)), the difference between the real and the ideal sink GB is negligible. This is consistent with the asymptotic behavior of η_r^a in Eq. (29).

If we replace the dislocation model of the GB with the Robin boundary condition in Eq. (14) for the irradiation problem and solve the one-dimensional diffusion equation Eq. (24), we find that

$$\bar{c}(x) = \frac{c_d - \zeta_\infty}{1 + k\alpha} e^{-k|x|} + \zeta_\infty, \quad (30)$$

$$\eta_r^R = \frac{1}{1 + \alpha/\chi_\infty}. \quad (31)$$

Setting $\eta_r^R = \eta_r^a$, we obtain exactly the same α as in the non-irradiation case, Eq. (18), with x_∞

Figure 4: Vacancy concentration in the presence of irradiation for the cases of (a) $\chi_\infty/x_d = 1000$ and $p/x_d = 400$, (b) $\chi_\infty/x_d = 1000$ and $p/x_d = 200$, (c) $\chi_\infty/x_d = 3000$ and $p/x_d = 400$, (d) $\chi_\infty/x_d = 3000$ and $p/x_d = 200$, (e) $\chi_\infty/x_d = 7000$ and $p/x_d = 200$, corresponding to the points A-E in Fig. 3(a). The top image in each panel shows the vacancy concentration distribution for the real GB modeled as a dislocation array, and the bottom image shows the concentration profiles, obtained by averaging over y -axis, for the real GB (green curve), the ideal sink (black curve), the GB modeled as Robin boundary (red dashed curve), and the real GB under the non-irradiation condition but with $c_\infty = \zeta_\infty$ and $x_\infty = \chi_\infty$ (blue curve). The vertical black dashed lines label the positions of $\pm\chi_\infty$.

replaced by χ_∞ . Again, the value of α only depends on features of the GB itself (p and x_d), regardless of the point defect annihilation that occurs within the grain (k) and the irradiation conditions (K). Vacancy concentration profiles solved using this Robin boundary condition at the GB are shown in Fig. 4. Comparison between the profiles of the dislocation and Robin description of the GB demonstrates that the Robin boundary condition provides an excellent description of the sink behavior of the dislocation GB in the presence or absence of radiation.

The vacancy concentration profile in the presence of irradiation can be approximated by the solution to the non-irradiation problem. We see, by examining the governing equation for the irradiation problem (Eq. 19) that, in the large x limit, the solution approaches a constant vacancy

concentration $\zeta_\infty = K/D_v k^2$; while in the small x limit, the diffusion equilibrium is dominated by the sink term and Eq. (19) reduces to Eq. (2). Thus, Eq. (2) with the boundary condition Eq. (4) is a reasonable approximation to Eq. (19) if we set the far-field vacancy concentration $c_\infty = \zeta_\infty$ ($\equiv K/D_v k^2$) and the cutoff distance $x_\infty = \chi_\infty$ ($\equiv 1/k$). Such correspondence is shown in Fig. 4, *i.e.*, the solution for the irradiation problem (green curves) can be approximated by the solution for the non-irradiation problem (blue curves); note that the slopes of the concentration profile at the GB are identical. This shows that GB sink efficiencies for these two problems are identical.

4. Application of the Robin boundary condition: two examples

The analyses above demonstrate that the effects of the dislocation structure of a GB on its sink behavior is well described by a Robin boundary condition Eq. (14) with a parameter α that depends only on the GB structure (Eq. (18)) and not on irradiation conditions (K), external boundary conditions (x_∞), or the nature of the sinks within each grain (k). Because the Robin boundary condition provides a robust description of the GB sink effect, it can be directly implemented to solve time-dependent or steady-state point defect distribution problems in a polycrystalline microstructure. In this section, we show two simple examples that demonstrate the utility of this approach as well as the impact of finite grain size on the spatial distribution of point defects. In both examples, we solve for the steady-state point defect concentration profiles under irradiation conditions using a finite difference method applied to Eq. (19) with appropriate boundary conditions.

We first consider the case of a square grain of edge length q embedded in an otherwise single-crystal, square sample of edge length L with a misorientation angle between the two of θ . We employ Dirichlet boundary conditions at the edges of the sample, $c = c_0$, and describe the GBs using a Robin boundary condition. Two parallel GBs (labeled GB1 in Fig. 5) are composed of dislocations with spacing $p = p_0$ and Burgers vector $b = p_0\theta$ and the other two (labeled GB2) by dislocations with spacing $p = 4p_0$ and Burgers vector $b = 4p_0\theta$. This situation is realistic in the sense that the two sets of GBs will in general have different structures from each other in a cubic material with a $\langle 001 \rangle$ tilt axis. The results are shown in Fig. 5 for two different values of q/L .

Examination of Fig. 5 shows that the GBs are weaker point defect sinks than the free surface. Since the dislocation spacing in GB2 is four times larger than in GB1, GB2 is a less effective sink than GB1. The inequivalence of the GB structures breaks the four-fold symmetry of the concen-

Figure 5: Vacancy concentration in the sample of finite size $L = 200p_0$ (the concentration at the free surface fixed at $c_0 = 0$), which contains an embedded grain (with the misorientation angle $\theta = b/p_0$). The grain size is $q = 120p_0$ for (a) and $q = 40p_0$ for (b). The red dashed lines label the position of the GB. The vertical GBs (GB1) are composed by the dislocations with spacing p_0 while the horizontal GBs (GB2) by the dislocations with spacing $4p_0$.

tration field. The difference between Figs. 5(a) ($q/L = 0.6$) and (b) ($q/L = 0.2$) demonstrates that grain size affects the point defect concentrations within the interior of the grain (for the same irradiation conditions); larger grain sizes imply higher point defect concentrations within the grain. This is consistent with the results of other calculations [30, 31]. However, when the grain size is much larger than the decay length of the concentration profile χ_∞ , the grain size effect is negligible. (Note, the grain size where this transition occurs is a weak function of the sink efficiency α as well.)

Our second example is that of a polycrystal consisting of a periodic array of square grains (see Fig. 6). This microstructure consists of three different grain orientations and four distinct grain boundary types. Many of the same effects are present here as in Fig. 5; *e.g.*, we see variations in the GB structure produces differences in point defect concentration profiles and GBs with the largest dislocation spacing (GB1) show the largest concentrations at the GBs. A close examination of Fig. 6(b) reveals that the point defect concentrations in the grains is not determined by the grain orientations θ , but rather by their delimiting grain boundary characters; *i.e.*, by their values of α (or p and x_d). For example, of the two grains with the same orientation θ_1 , the one with grain boundaries GB3 and GB4 have lower point defect concentrations than the one delimited by GB1 and GB2. The average point defect concentration in the entire polycrystal is smaller at smaller grain size (*cf.* Figs. 6(a) and (b)); this is because smaller grain sizes implies larger GB length (area) per unit area (volume) of the system (*i.e.*, a higher density of point defect sinks). In toto, these

Figure 6: Vacancy concentration in a model polycrystal consisting of a periodic array of square grains. In (a), the grain size is $q = 100p_0$, and only one period of the microstructure is shown. In (b), the grain size is $q = 50p_0$, and four periods of the microstructure are shown (one period is framed by the red solid lines). There are three grain orientations $\theta_1 = 0$, $\theta_2 = 0.05$, and $\theta_3 = 0.005$. The red dashed lines label the positions of the GBs. There are four distinct GB types, labeled by GB1 ($p_1 = 4p_0$, $b_1 = 0.02p_0$), GB2 ($p_2 = 0.2p_0$, $b_2 = 0.01p_0$), GB3 ($p_3 = 0.8p_0$, $b_3 = 0.04p_0$), and GB4 ($p_4 = p_0$, $b_4 = 0.005p_0$).

examples demonstrate that grain refinement should help mitigate radiation damage in polycrystals (consistent with a wide range of experimental results [32, 33]), and (ii) that the variability of GB efficacy as point defect sinks is increasingly important when the grain size is small.

5. Discussion and Conclusions

In this paper, we examined the common assumption that grain boundaries are ideal sinks and sources for point defects by comparing and contrasting its implications with a structure-aware description of grain boundaries for the specific case of a low-angle tilt GB described by an array of straight, parallel edge dislocations. In the latter case, the constituent dislocations absorb point defects by climbing within the GB plane. We solve the resultant diffusion equation in the presence and absence of radiation-induced point defects within the grains. The grain boundary sink efficiency η is a simple function of two parameters; the first, α , depends only on the GB structure and the second, x_∞ (non-irradiation case) or χ_∞ (irradiation case), depends on the characteristic diffusion length within the grain – see Eqs. (17) and (31).

When the dislocation spacing p is small (*i.e.*, large misorientation angle) or the characteristic length of diffusion x_∞ (or χ_∞) is much larger than p , the sink efficiency approaches that of the ideal

sink. However, for small misorientations or small x_∞ (or χ_∞), the sink efficiency drops rapidly to zero and the ideal sink assumption for the GB fails dramatically.

We have reformulated the grain boundary sink effect within a Robin boundary condition framework. In this approach, the variation of the structure along the grain boundary is replaced by a single boundary condition on the entire GB plane and hence can be thought of as a reduced order model. The Robin boundary condition contains a single parameter α that characterizes the GB structure. By comparing our dislocation model for the grain boundary sink behavior with the solution based on the Robin boundary condition, we obtain an explicit form for α in terms of only the dislocation spacing and dislocation core size, and demonstrate that this yields excellent agreement between the dislocation and the Robin models for GB sink efficiency and point defect profiles. This allows us to capture the structure dependence of the GB sink behavior by solving a bulk governing equation with a Robin boundary condition without resolving the details of the GB structure. The same Robin boundary condition can be used both in steady-state and time-dependent solutions of the governing diffusion equation.

The physical interpretation of the Robin boundary condition is that it describes a mixed rate-controlled process. If the absorption of point defects into the GB is purely diffusion-controlled, the concentration will be fixed at c_d at $x = x_d$, which corresponds to $\alpha \rightarrow 0$. If the absorption is purely reaction-controlled, there will be no concentration gradient throughout the grain; *i.e.*, $\alpha \rightarrow \infty$. Hence, for finite α , the Robin boundary condition describes a mixed rate-controlled process. From Eq. (18), we find that α increases with increasing dislocation spacing in the GB, p . With increasing p , the constituent dislocations in the GB become further separated and, hence, the point defect absorption rate will be controlled by the density of isolated dislocations – this is typical of reaction rate control.

We note that the analysis above is based on two main simplifications: (i) the GB can be described by a uniform set of straight, equally spaced lattice dislocations and (ii) we can adequately reduce the radiation damage problem to a case of a single point defect species. The assumption (i) that the dislocations are straight ignores the details of how point defects are actually absorbed along dislocations and the rapidity of point defect transport along dislocations. Point defects are generally absorbed at jogs. The straight dislocation assumption should be valid if point defect transport along the dislocation between jogs is extremely rapid, there is zero barrier for formation

of a jog pair, or the temperature is above the dislocation line roughening transition or some combination of these. Nonetheless, the assumptions we make here are consistent with those of most of the community modeling dislocation climb.

In general, GB structures are much more complicated than can be represented by the simple assumption (i). As the misorientation angle increases, lattice dislocation cores overlap and the low-angle grain boundary model becomes inapplicable. However, at higher misorientation angles, GBs can be thought of as “ideal” structures plus an array of secondary grain boundary dislocations [12]. Ignoring first the “ideal” structure, we can apply the same type of dislocation model we employed for low-angle grain boundaries to model the climb of the secondary GB dislocations. The “ideal” structures, may also absorb point defects as they transform between metastable structures [34, 35]. We expect the contribution of the “ideal” structures to GB sink efficiency to be less important than the secondary GB dislocations. Hence, the present analysis can be extended to more general GBs, provided that an adequate model of the GB structure (compatible with the bicrystallography) is employed. Nonetheless, the Robin boundary condition approach, which characterizes the GB structure in terms of a single parameter α is still applicable, even when assumption (i) fails. When this occurs, the value of α characterizing a boundary structure will require either more sophisticated descriptions of the GB structure or it can be viewed as an empirical descriptor for each GB structure (or five macroscopic geometric degrees of freedom associated with grain misorientation and boundary normal).

The manner in which we treat the point defect population during irradiation is clearly oversimplified, *i.e.*, due to assumption (ii). A full treatment requires consideration of both the interstitial and vacancy concentration profiles throughout the grain, as well as the vacancy/interstitial recombination, vacancy and interstitial clusters, dislocation loops, voids, *etc.* [1] and the evolution of the populations of all of these clusters/voids/loops. This is further complicated by the unequal defect diffusivities and stresses within the material [1]. Nonetheless, the simple radiation damage scenario presented here demonstrates what we believe to be the main effect in describing how and why different grain boundaries exhibit different sink efficiencies in a radiation environment. The main conclusions, and especially the simplified (and GB-structure parameterized) Robin boundary condition approach, may be incorporated directly into models that describe the much richer phenomena that occur during the irradiation of polycrystalline materials.

Finally, we note that the effects discussed above are especially important when considering the role of GBs in point defect annihilation in nanocrystalline materials, where grain sizes are especially small and which are currently being considered for application in environments with significant radiation fluxes. Physically, there are several important length scales, including the dislocation spacing in the grain boundary (p), grain size, the characteristic length between the sinks within the grain (k^{-1}), and the sample size (considering that the point defect concentration is fixed at free surfaces). The analysis presented above shows the interplay between these length scales and the relevant physical parameters (*e.g.* temperature – through the diffusivities and equilibrium point defect concentrations) on the grain boundary sink efficiency.

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Appendix A. Derivation of Eq. (23)

We present a derivation of the vacancy current I_r in Eq. (23) from the vacancy concentration field $c(x, y)$ in Eq. (22). We first write $c(x, y)$ in a polar coordinate system with the origin at the center of a GB dislocation as

$$c(r, \varphi) = (c_d - \zeta_\infty) \frac{\sum_{m=-\infty}^{\infty} K_0(\sqrt{\tilde{r}^2 - 2m\tilde{r}\cos\varphi + m^2}/\tilde{\chi}_\infty)}{\sum_{m=-\infty}^{\infty} K_0(\sqrt{\tilde{x}_d^2 + m^2}/\tilde{\chi}_\infty)} + \zeta_\infty. \quad (\text{A.1})$$

The derivative of $c(r, \varphi)$ with respect to r at $r = x_d$ is

$$\begin{aligned} \left. \frac{\partial c}{\partial r} \right|_{r=x_d} &= \frac{1}{p\tilde{\chi}_\infty} \frac{c_d - \zeta_\infty}{\sum_{m=-\infty}^{\infty} K_0(\sqrt{\tilde{x}_d^2 + m^2}/\tilde{\chi}_\infty)} \\ &\quad \cdot \sum_{m=-\infty}^{\infty} \frac{(m \cos \varphi - \tilde{x}_d) K_1(\sqrt{\tilde{x}_d^2 - 2m\tilde{x}_d \cos \varphi + m^2}/\tilde{\chi}_\infty)}{\sqrt{\tilde{x}_d^2 - 2m\tilde{x}_d \cos \varphi + m^2}}. \end{aligned} \quad (\text{A.2})$$

Using the assumption $\tilde{x}_d \ll 1$ and the properties of modified Bessel functions, we have the approximations

$$\sum_{m=-\infty}^{\infty} K_0(\sqrt{\tilde{x}_d^2 + m^2/\tilde{\chi}_\infty}) \approx K_0(\tilde{x}_d/\tilde{\chi}_\infty) + 2 \sum_{m=1}^{\infty} K_0(m/\tilde{\chi}_\infty), \quad (\text{A.3})$$

and

$$\begin{aligned} & \sum_{m=-\infty}^{\infty} \frac{(m \cos \varphi - \tilde{x}_d) K_1(\sqrt{\tilde{x}_d^2 - 2m\tilde{x}_d \cos \varphi + m^2/\tilde{\chi}_\infty})}{\sqrt{\tilde{x}_d^2 - 2m\tilde{x}_d \cos \varphi + m^2}} \\ & \approx -K_1(\tilde{x}_d/\tilde{\chi}_\infty) + 2 \sum_{m=1}^{\infty} \frac{m \cos \varphi - \tilde{x}_d}{m(1 - \tilde{x}_d \cos \varphi/m)} \\ & \quad \cdot \left[K_1(m/\tilde{\chi}_\infty) + (K_2(m/\tilde{\chi}_\infty)m/\tilde{\chi}_\infty - K_1(m/\tilde{\chi}_\infty))\tilde{x}_d \cos \varphi/m \right]. \end{aligned} \quad (\text{A.4})$$

Finally, the current towards the dislocation core at $r = x_d$ is

$$\begin{aligned} I_r &= \frac{D_v x_d}{\Omega} \int_0^{2\pi} \frac{\partial c}{\partial r} \Big|_{r=x_d} d\varphi \\ &\approx \frac{2\pi D_v}{\Omega} (\zeta_\infty - c_d) \frac{\tilde{x}_d}{\tilde{\chi}_\infty} \frac{K_1(\tilde{x}_d/\tilde{\chi}_\infty) + \tilde{x}_d \sum_{m=1}^{\infty} [2K_1(m/\tilde{\chi}_\infty)/m - K_2(m/\tilde{\chi}_\infty)/\tilde{\chi}_\infty]}{K_0(\tilde{x}_d/\tilde{\chi}_\infty) + 2 \sum_{m=1}^{\infty} K_0(m/\tilde{\chi}_\infty)}. \end{aligned} \quad (\text{A.5})$$

Appendix B. Derivation of Eq. (29)

We derive an approximate formula for η_r^a (29) from the exact formula η_r (28). The derivation is based on the assumption that $\tilde{x}_d \ll 1 \ll \tilde{\chi}_\infty$. The relevant expansions are listed below:

$$K_0(z) = -\gamma + \ln 2 - \ln z + O(z^2 \ln z), \quad z \rightarrow 0, \quad (\text{B.1})$$

$$K_1(z) = \frac{1}{z} - \frac{z}{4} + \frac{\gamma z}{2} - \frac{z \ln 2}{2} + \frac{z \ln z}{2} + O(z^2), \quad z \rightarrow 0, \quad (\text{B.2})$$

$$K_2(z) = \frac{2}{z^2} - \frac{1}{2} + O(z^2), \quad z \rightarrow 0, \quad (\text{B.3})$$

where $\gamma = 0.5772 \dots$ is the Euler-Mascheroni constant. A useful integration is

$$\int_0^\infty K_0(z) dz = \frac{\pi}{2}. \quad (\text{B.4})$$

Firstly, we consider the approximation of the denominator in Eq. (28). From Eq. (B.1),

$$K_0(\tilde{x}_d/\tilde{\chi}_\infty) = \ln \frac{\tilde{\chi}_\infty}{\tilde{x}_d} - \gamma + \ln 2 + O\left(\frac{\tilde{x}_d^2}{\tilde{\chi}_\infty^2} \ln \frac{\tilde{x}_d}{\tilde{\chi}_\infty}\right). \quad (\text{B.5})$$

The other term in the denominator can be rewritten as

$$2 \sum_{m=1}^{\infty} K_0(m/\tilde{\chi}_\infty) = \tilde{\chi}_\infty \left(\sum_{m=-\infty, m \neq 0}^{\infty} K_0(|m\Delta z|) \Delta z \right), \quad (\text{B.6})$$

where we define the small quantity $\Delta z = 1/\tilde{\chi}_\infty$. The discrete sum in Eq. (B.6) can be evaluated using theorem 4.1 in Ref. [36]:

$$\begin{aligned}
& \sum_{m=-\infty, m \neq 0}^{\infty} K_0(|m\Delta z|)\Delta z \\
&= \int_{-\infty}^{\infty} K_0(|z|) dz - \int_{-\Delta z/2}^{\Delta z/2} K_0(|z|) dz + (1 - \ln \pi)\Delta z + O(\Delta z^2) \\
&= 2 \int_0^{\infty} K_0(z) dz - 2 \int_0^{\Delta z/2} (-\gamma + \ln 2 - \ln z + O(z^2 \ln z)) dz + (1 - \ln \pi)\Delta z + O(\Delta z^2) \\
&= \pi + \left(\ln \frac{1}{4\pi\tilde{\chi}_\infty} + \gamma \right) \frac{1}{\tilde{\chi}_\infty} + O\left(\frac{1}{\tilde{\chi}_\infty^2}\right). \tag{B.7}
\end{aligned}$$

Finally, from Eqs. (B.5) and (B.7), the denominator of the sink efficiency is

$$K_0(\tilde{x}_d/\tilde{\chi}_\infty) + 2 \sum_{m=1}^{\infty} K_0(m/\tilde{\chi}_\infty) \approx \pi\tilde{\chi}_\infty - \ln 2\pi\tilde{x}_d. \tag{B.8}$$

Next, we approximate the numerator in Eq. (28). Using Eq. (B.2), the first term in the numerator is

$$K_1(\tilde{x}_d/\tilde{\chi}_\infty) = \frac{\tilde{\chi}_\infty}{\tilde{x}_d} + O\left(\frac{\tilde{x}_d}{\tilde{\chi}_\infty} \ln \frac{\tilde{x}_d}{\tilde{\chi}_\infty}\right). \tag{B.9}$$

For the second term, we use the following inequalities [37],

$$K_1(z) < \frac{z_0 K_1(z_0)}{z} \text{ for } z > z_0 > 0, \tag{B.10}$$

$$K_2(z) < \frac{z_0^2 K_2(z_0)}{z^2} \text{ for } z > z_0 > 0. \tag{B.11}$$

These inequalities imply that

$$0 \leq \sum_{m=1}^{\infty} \frac{K_1(m/\tilde{\chi}_\infty)}{m} < K_1(1/\tilde{\chi}_\infty) \sum_{m=1}^{\infty} \frac{1}{m^2} = \frac{\pi^2}{6} \tilde{\chi}_\infty + O\left(\frac{1}{\tilde{\chi}_\infty}\right), \tag{B.12}$$

$$0 \leq \sum_{m=1}^{\infty} K_2(m/\tilde{\chi}_\infty) < K_2(1/\tilde{\chi}_\infty) \sum_{m=1}^{\infty} \frac{1}{m^2} = \frac{\pi^2}{3} \tilde{\chi}_\infty^2 + O(1), \tag{B.13}$$

where we have also used the asymptotic behavior in Eq. (B.2). Thus, the numerator in Eq. (28) can be approximated by

$$K_1(\tilde{x}_d/\tilde{\chi}_\infty) + \tilde{x}_d \sum_{m=1}^{\infty} \left(\frac{2K_1(m/\tilde{\chi}_\infty)}{m} - \frac{K_2(m/\tilde{\chi}_\infty)}{\tilde{\chi}_\infty} \right) \approx \tilde{\chi}_\infty/\tilde{x}_d + O(\tilde{x}_d\tilde{\chi}_\infty) \approx \tilde{\chi}_\infty/\tilde{x}_d. \tag{B.14}$$

Therefore, using Eqs. (B.8) and (B.14), we have the approximation of Eq. (28)

$$\eta_r \approx \left(1 + \frac{1}{\pi\tilde{\chi}_\infty} \ln \frac{1}{2\pi\tilde{x}_d} \right)^{-1} \equiv \eta_r^a. \tag{B.15}$$

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