Complete characterization of sink-strengths for 1D to 3D mobilities of defect clusters

I. Extension to diffusion anisotropy analog cases.

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Abstract

Simulating more than seconds of microstructure evolution in systems involving almost athermally or very fast diffusing species such as self-interstitial atom (SIA) clusters currently relies on mean-field or coarse-graining techniques. Rate-equation cluster dynamics (RECD) is the most popular of those when dealing with irradiated microstructure or second phase precipitation by thermal ageing. The important input parameters of RECD are the absorption rates, also called cluster sink-strengths (CSS). These quantities crucially depend on the way clusters interact and diffuse and notably on the dimensionality of the involved random diffusion processes. As expected theoretically and experimentally confirmed, SIA clusters migrate in a one-dimensional fashion (possibly with random orientation changes, i.e. rotations of their Burgers vector). This complicates the calculation of the related CSS. When involving a 1D-mobile specie and an immobile reaction partner (a “1D-0” reaction) the expressions are quite well known as well as the extension including random rotations (a “1DR-0” reaction). Expressions of CSS for absorptions between identical 1D-mobile species were proposed in the literature, but the general case of 1D-1D absorptions between different cluster classes is unknown. Here we propose such general expressions which turn out to depend on the respective capture radii of interacting clusters classes, concentrations and notably on the ratio of their respective diffusion coefficients through a power-law. The same power-law formulation is found for 1D-3D absorptions but with different exponents, which thus appear as signatures of the dimensionality of the involved random motions. These limiting cases of CSS being established, they are finally implemented in an RECD calculation. The comparison with time consuming kinetic Monte-Carlo simulations completely validates their expression and without any need of “multi-sink terms” in the tested conditions.

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I. INTRODUCTION

Random walk are widely present in mathematical modeling, physics and biology at many different scales: from living beings movement, to colloidal particles aggregation at various length scales and even down to atomic diffusion processes. The latter process is mediated by crystalline point defects points. Point defect clusters are of primary importance for the concern of reactor lifetime management, because they condition the evolution of the pressurized water reactor materials macroscopic properties. The same considerations hold for fusion reactor components such as the tungsten divertor. In complement to accelerated irradiation experiments, simulation methods can provide both insight and validation of the mechanisms elementary mechanisms of defects and solute interactions. Among simulation methods, kinetic Monte-Carlo (KMC) type methods and rate-equations cluster-dynamics (RECD) type ones are commonly used, often to complement each other. Indeed, on one hand, with rigid lattice KMC type methods, reactions between defect clusters can be quite readily implemented, once elementary diffusion events frequencies are tabulated. One is then limited by the number of events that the computing units can perform to predict the long term evolution: the faster the diffusing species, the slower is the progression of the simulated physical time. Typically, for moderate temperatures (about one half of the melting temperature) and high temperatures, if very fast diffusing species are involved in the microstructure evolutions, such as self-interstitial atoms (SIA), then the accessible physical time is well below one second. On the other hand, RECD type mean-field methods do not suffer from such a limitation for long term simulation, basically because they consist in solving directly in time balance equations for the evolution of homogenized cluster concentrations. When the size of the system of balance equations is reasonable and numerical stiffness issues are not too critical, RECD simulations can easily simulate several decades of microstructure evolution. So, compared to KMC, RECD can be considered as an extremely efficient coarse-graining technique, but the price to pay is the non-trivial development of analytical absorption rates expressions (or the related cluster sink-strengths, abbreviated “CSS” hereafter). The CSS should account for the geometry, elastic field of the interacting clusters and most importantly for the dimensionality the random-walks they perform. The required CSS expressions for three-dimensionally mobile species (3D) are well know from the literature including cases where one of the reactants is a fixed sink (noted hereafter “$3D-0$", "$3D-0$"
“0” standing for the second reaction partner being immobile) as well as cases where both species have a mobility described by a 3D random-walk (noted “3D − 3D”). The state-of-the-art also encompasses absorptions of a one-dimensionally mobile specie by a fixed sink (“1D − 0”), which historically arose from the treatment of the recombination between a fast crowdion and a virtually immobile vacancy. Indeed, the two first stages of resistivity recovery experiments [2] can be interpreted with this single equation. At variance, for the RECD modeling of the evolution of a complete defect cluster population under irradiation or nucleation-growth-coalescence under simple thermal ageing [3] systems of thousand to millions of coupled ordinary differential equation are needed and the CSS expressions must be provided for all the possible reactions between clusters whatever the type of their mobility. More recent treatments [4] have included the observed possibility for small interstitial clusters to have a “mixed mobility”. This mixed mobility can be seen as an intermediate between a pure 3D-mobility and a pure 1D-mobility. It is often referred as “1D to 3D” in the literature, but we will note it hereafter ”1DR − 0” (standing for “1D random walk with random rotations of the glide direction with respect to a fixed sink”). Physically, this case corresponds to trajectories where the defect cluster perform sequences of 1D-jumps before rotating its glide direction and pursuing another 1D trajectory along a variant of the initial glide direction. Transmission electron microscopy investigations in both low alloy and concentrated irradiated steels [5–7] have confirmed the 1D-character of the motion of visible dislocations loops in total agreement with molecular dynamics simulations [8–11]. The latter also reveal that, from small to large clusters their should be a gradual transition from 3D-motion (relevant to dumbbell type SIA in some systems) to the pure 1D-motion that is expected for large dislocation loops. As a consequence, rate-theory modeling of defect clusters evolution should thus include CSS for 1DR − 1DR reactions, i.e. reactions between two clusters of any type mixed mobility (which also encompasses pure 3D and 1D mobilities). As such, state-of-the-art expressions of CSS for 1D − 0 or 1DR − 0 cases alone are of limited practical use if the whole RECD parameterization is not completed with the reactions between these mobiles species (1D − 1D or 1DR − 1DR type CSS).

There are two main approaches to calculate CSS: a continuous medium pair-diffusion problem (as formulated by Waite [12]) with Smoluchowski type boundary conditions, or a “first-passage” formulation accounting for the random-walk character of the migration paths. When an analytical solution for the CSS exists, the first approach is in general more easy as
it relies on usual methods to solve differential equations. The drawback is that in the case of complex mobilities such as $1DR$ ones which imply two types of random events, it is very difficult to formulate the problem in terms of continuous pair-diffusion equation. The second method is somehow more flexible as it naturally accounts for the random-walk aspect of the mobilities, but it requires a larger variety of solving methods \cite{13} when they exist. A closed form solution to the problem of $1DR - 1DR$ CSS in the most general case seems currently out of reach so, in this paper, we will focus on finding expressions for the most important limiting cases. To this end, we will further develop the simple analogy that allowed G"osele and co-workers \cite{14} to propose an expression for the absorption rates of 1D-mobile species belonging to the same class. Because in realistic systems, there can only be a variety of mobile clusters, this expression is only useful for single equation cluster dynamics applied to the only experiment where defect reactions can be successively activated: resistivity recovery experiments. This is the reason why this relation will only be used as starting point to establish the more general case of interacting clusters from different populations (thus having different diffusion coefficients $D_A$, $D_B$, concentrations $C_A$, $C_B$ and radii $R_A$, $R_B$). The Annex will allow us reminds to unfamiliar reader the classical relations between absorption rates and CSS. Cases involving one immobile specie are important limiting cases that will play some roles in the new expressions that we will establish, so they are also briefly recalled in the annexes A, B and C. At section III a model is proposed to justify the equivalence between two 1D-random walks and a 2D one with respect to a fixed sink in a 3D-system. The asymptotic behavior of the associated diffusion problem suggest a new CSS expression in which $C_A$ and $C_B$ play a non-trivial role. This expression is well validated when compared with effective CSS object kinetic Monte-Carlo (OKMC) calculations for different couples of concentrations, radii and even for different glide directions families. Regarding the general $1D - 1D$ case, it only remains to establishing the effect of both diffusion coefficients ($D_A \neq D_B$). One can avoid the complexities of the associated pair diffusion problem and simply exploit the analogy of “1D-1D” diffusion problems with “2D-0” ones, as explained in section IV. The diffusion coefficients then appear in the CSS as a ratio elevated to an constant exponent. In fact, in section V the same type on analogy is exploited and results in a similar dependency of diffusion coefficients ratio but a with a different characteristic exponent.

These limiting cases of CSS being established, they are finally implemented in a complete
RECD calculation, in section VI. The comparison with time consuming kinetic Monte-Carlo simulations completely validates their expression and without any need of “multi-sink terms” in the tested conditions.

II. FRAMEWORK FOR SINK-STRENGTH ANALYTICAL CALCULATIONS

In rate equation cluster dynamics (RECD) implementing the absorption rates between interacting clusters classes (or equivalently cluster sink-strengths) is a crucial step for the built-up of the model. To its simplest form where the only reaction occurring is for two species A and B react \( \text{A} + \text{B} \xrightarrow{k(t)} \text{C} \), a rate equation could be written as:

\[
\frac{\partial C_A}{\partial t} = -k(t)C_AC_B,
\]

where \( k(t) \) is the reaction rate or absorption rate in the present case. In the framework of diffusion-controlled reactions theory ([12, 20, 21]), the case of a three-dimensional (3D) isotropic diffusion of A particle with coefficient \( D_A \) with respect to immobile B sink-particles can be formally described with the help of the pairs spatial distribution function \( U(r, t) \), \( r \) being the distance between A and B. The distribution \( U(r, t) \) is normalized with respect to the mean spatial concentration \( C_A(t) \). Both particles are assumed to be spherical with respective radii \( R_A \) and \( R_B \), their sum, the contact distance, is noted \( R = R_A + R_B \). As shown by Waite [12], the spatial distribution function satisfies the Fickian-like equation:

\[
\frac{\partial U(r, t)}{\partial t} = D_A\nabla^2U(r, t),
\]

but with specific boundary conditions depending on time and distance:

\[
U(r, 0) = 1, \forall r > R,
\]

which correspond to an initially uniform spatial distribution of A:

\[
U(\infty, t) = 1
\]

stating that far from the sink the mean concentration of the medium \( C_A(t) \) prevails. An additional boundary condition that has to be imposed is the Smoluchowski boundary condition [22]:

\[
U(R, t) = 0, \forall t > 0.
\]
This corresponds to the case of a diffusion-controlled process which assumes instantaneous reaction of partners upon contact. Then solving Eq. 2 for \( U(r,t) \) the reaction rate can be calculated according to the flux of the \( U \) gradient through the sink surface:

\[
k(t) = 4\pi R^2 \frac{\partial U}{\partial r} \bigg|_R
\]

(6)

For the most well known case of spherical reaction partners with 3D-diffusion of A with respect to the fixed sinks B (as they are immobile the dimensionality of their mobility is noted “0”), the reaction-rate is asymptotically:

\[
k(\infty) \simeq 4\pi D_A R = \kappa_{3D-0}^2 \frac{D_A}{C_B},
\]

(7)

where \( \kappa^2 \) is called the “sink-strength”.

III. SINK STRENGTHS IN THE 1D-1D ISOTROPIC CASE

The classical CSS expressions for \( 3D - 3D \) isotropic diffusion tensors, for \( 1D - 0 \) and for \( 1DR - 0 \) are respectively reminded in the appendix’ sections [A, B and C]. We will now focus on a case that is incompletely treated in the literature: the \( 1D_A - 1D_B \) CSS, even with \( D_A = D_B \) (isotropic case) was only proposed for a single specie reaction \( A = B \), as exemplified by the isolated reaction \{crowdion + crowdion \( \rightarrow \) di-interstitial\}. Clearly, the solution Gösele et al.\[20\] has a limited practical interest for the interaction defects with different concentration and radii. Also, as it was justified in a quite elusive manner, its validity deserves better understanding.

The main idea of Gösele and co-workers is to express the \( 1D - 1D \) CSS by analogy to the case of a \( 2D \)-mobile specie with respect to a fixed sink \[14, 20\]. To justify this approximation the authors invoked the additivity of diffusion tensors, which they simply assumed to be homogeneous in space and time, without any further justification. First, let us examine the \( 1D - 1D \Leftrightarrow 2D - 0 \) equivalence from the geometrical point of view. In the simplest case of non-colinear but co-planar glide directions, any pair of \( (A,B) \) reaction partners may be described by its midpoint (the center of the \([A,B]\) segment) as illustrated on figure [1]. The motion can then be described by the \( 2D \)-random walk of the midpoint in the plane until it reaches a the capture distance \( R \) from the intersection of the two glide directions and is then results in an absorption. Assuming both particles have the same jump frequencies \( \Gamma \) and
Figure 1. Schematic view of the geometric equivalence between the trajectory of two absorbing 1D-random walkers (black circles with $\ell_A$ and $\ell_B$ jump vectors) and the 2D-random walk of their midpoint (blue solid and dashed circles for the current and past positions respectively) being absorbed by a fictitious fixed sink sitting at the intersection of their glide directions.

Distances $d_j$, the lattice associated to the midpoint’s random walk is scaled down to $\sqrt{2}/2$ times the original one. Using the relation:

$$\Gamma = \frac{2ND}{fd^2},$$

(8)

where the diffusion correlation factor $f$ will here be neglected ($f = 1$) and where $N$ is the dimensionality of the random walk. Equating jump frequencies for $N = 1$ and $N = 2$ yields that relevant diffusion coefficient for the midpoint is four times smaller than the original one.

For the specific system considered in the isotropic case it is thus relevant to use 2D-0 absorption rates which are given by analogy with the solution 2D-heat flow [23, 24]:

$$\frac{\partial C}{\partial t} = -\frac{8D}{\pi} C^2 \int_0^\infty \frac{\exp(-Du^2t)}{u[J_0(Ru) + Y_0(Ru)]} du,$$

(9)

where $J_0$ and $Y_0$ are respectively Bessel and Neumann functions of zero order. For long
times, this expression is approximated by the equation:

$$\frac{\partial C}{\partial t} \simeq -2\pi DR\alpha(t)C^2,$$

(10)

where,

$$\alpha(t) = \frac{4}{\ln \left( \frac{4Dt}{\pi R^2} \right)},$$

(12)

using asymptotic expansions of integrals involving Bessel and Neumann functions. According to their analysis, the function $\alpha(t)$ is a slowly decreasing function of time, which bears further approximation for long times:

$$\overline{\alpha} \simeq \frac{4}{\ln(\pi^2C(0)R^3/2)},$$

(13)

As noted by the authors, if in practice the logarithmic terms actually stays quite constant, this results in apparently second order kinetics, just like $3D - 0$ ones and at variance with the third order ones for $1D - 0$ kinetics, as recalled in the Annex B.

We may now adapt Eq. (11) to the case of differentiable reaction partner $A$ and $B$ substituing the $C^2$ term by $C_AC_B$. One should also note that Eq. (11) only accounts for the non-colinear glides interactions, so it has to be complemented with a term for colinear glides interactions $\frac{\partial C_A}{\partial t} |_{//}$. In a time-independent form, it bears a similar expression as $1D - 0$ CSS:

$$\frac{\partial C_A}{\partial t} |_{//} = -6\pi^2R^4(C_A^2C_BD_B + C_B^2C_AD_A),$$

(14)

ensuing from the symmetric role of $A$ and $B$ mobilities. If the number of crystallographic variants of the glide direction is noted $v$ ($v = 4$ for the $1/2\langle 111 \rangle$ family), each variant has $(v - 1)$ non-colinear variants, and the overall reaction-rate would read:

$$\frac{\partial C_A}{\partial t} = f_v\frac{\partial C_A}{\partial t} |_{\perp} + (1 - f_v)\frac{\partial C_A}{\partial t} |_{//},$$

(15)

$$f_v = \frac{v - 1}{v},$$

(16)

keeping in mind that in typical cases where the initial volume fractions are small or moderate, the colinear part should often be negligible compared to the non-colinear part (see the appendix B for a justification).
Figure 2. Schematic view of the geometric condition for the interaction of two non-coplanar particles with glide direction $\vec{\ell}_A$ and $\vec{\ell}_B$ respectively.

Because this derivation relies on the initial assumption that the diffusion tensors are homogeneous in space, it may be questionable when dealing with small defect clusters whose spatial extend can be comparable to the relevant interplanar spacing $d$ because the interacting particles are actually distributed on a 3D lattice. Indeed, in a 3D-system, cases where we have non-collinear but also non-coplanar glide directions complicates this picture, as there are clearly situations where the distance between glide lines is larger than interaction distance and thus no absorption occurs at all.

The geometrical conditions for the $1D - 1D$ equivalence to $2D - 0$ will now be addressed by calculating an equivalent effective radius. A simplified geometrical necessary condition for the reaction of two non-collinear 1D-mobile species at a minimal distance $h$ is illustrated on figure 2: the contact condition between capture spheres of radii $R_A$ and $R_B$ is equivalent to the contact condition between a point and a sphere with radius $R_{eff} = \sqrt{(R_A + R_B)^2 - h^2}$.

Now we may weight this effective radius according to the distribution of $h$ values. Assuming an A-type particle sits at the center of a slab at $z = 0$, let $\rho$ be the density of B-type species in a slab at $z = h$ that are non-collinear to a given A orientation. If $C_B \geq C_A$, the interaction range of the A-particle with the B-particles is modeled by the Wigner-Seitz radius (as illustrated on figure 3): $a_{A}^{WS} = \left(\frac{3\nu}{4\pi C_A}\right)^{1/3}$ (assuming glide variants are evenly
Figure 3. Assignment of a linear density along \( \vec{z} \) of potentially non-colinearly interacting B-particle to an A-particle sitting in the center of slab delimited by its Wigner-Seitz distance.

distributed). Thus in the slab at \( z = h \), there are:

\[
d(a_A^{WS})^2 C_B(v - 1)
\]

B-particles assigned to A for potential non-colinear interaction, \( d \) being the relevant interplanar spacing and jump distance.

Casting this quantity into a linear density along the \( \vec{z} \) axis yields:

\[
\rho = \frac{(3 \pi C_A^2)^{1/3}}{4 \pi C_A} C_B^{v-1/2}.
\]

When \( C_B \geq C_A^{2/3}/d \) there are on average more than one B in each slab and the average effective radius is greater than \( R \):

\[
\overline{R_{eff}} = \frac{1}{2R/d} \sum_{i=-R/d}^{i=R/d} d\sqrt{R^2 - (id)^2}
\]

\[
\simeq \frac{1}{R} \int_0^R \sqrt{R^2 - h^2} dh = \frac{\pi}{2} R
\]

In other cases, \( \overline{R_{eff}} < R \), and we now model the distribution of distances \( h \) as nearest neighbor distances along the \( z \) direction for example with a Poisson distribution \( P(\rho, h) \):

\[
P(\rho, h) = \rho \exp(-\rho h) H(R - h) \frac{1 - \exp(-\rho R))}{(1 - \exp(-\rho R))},
\]

assuming \( \rho R < 1 \), and including the Heaviside function \( H \) to impose that pairs for which \( h > R \) do not contribute.
Then the average effective radius may be taken as an average of $R_{eff}$ being distributed according to Eq. 20:

$$R_{eff} = \int_0^\infty \sqrt{R^2 - h^2} P(\rho, h) dh$$

$$= \int_0^R \sqrt{R^2 - h^2} \frac{\exp(-\rho h)}{\frac{1}{\rho}(1 - \exp(-\rho R))} dh$$

$$= \frac{\pi R(I_1(\rho R) - L_1(\rho R))}{2(1 - \exp(-\rho R))},$$  \hspace{1cm} (21)

where $I_1$ and $L_1$ are the modified Bessel function of the first kind and the Struve function respectively. This can be further approximated for small $\rho R$ values:

$$R_{eff} = \int_0^R \sqrt{R^2 - h^2} \frac{1 - \rho h}{R(1 - \frac{\rho}{2} R)} dh$$  \hspace{1cm} (22)

which after Taylor-expanding the rational function of $\rho R$ leads to:

$$R_{eff} \simeq R \left( \frac{\pi}{4} + \frac{3\pi}{12} - 4R\rho \right) \simeq \frac{\pi}{4} R$$  \hspace{1cm} (23)

This approximation happens to be very close to the evaluations of Eq. 21 whenever $\rho R \lesssim 0.1$. This can also be used as condition for the validity of this last approximation: for example assuming $C_A = C_B$ and a radii sum of 4 nm, the order of magnitude of the maximum $C_A$ compatible with the approximation is about $C_A^{max} \simeq 10^{16} cm^{-3}$. This limit is often above densities we expect in typical condition for such large objects (compared to monomers).

Note that Eq. 21 account the effect of the number of variants $v$ (through $\rho$) in a more complex manner than Eq. 15. When passing to the small $\rho R$ limit at Eq. 23 the $v$-dependencing disappers, so this final approximation could less accurate than Eq. 15. At figure 4 we see that both approximations globally perform similarly: Eq. 23 (the black $y = 1$ straight line) matches better the effective CSS calculated by OKMC when dealing with <110> glides. When it comes to <111> glides, they perform similarly up to $C_A^{max} \simeq 10^{16} cm^{-3}$ and then Eq. 15 (dashed blue line) matches almost perfectly the effective CSS. Concerning <100> type mobilities, Eq. 15 performs better (about 5% discrepancy without OKMC, while the effective radius correction make a 10% discrepancy with OKMC estimates).

Now that the grounds of the equivalence of $1D - 1D$ to $2D - 0$ for CSS expression are better understood and were validated against OKMC simulation when $D_A = D_B$ and $C_A = C_B$, we will first extend it to the case $D_A = D_B$ and $C_A \neq C_B$. We use as a guideline
Figure 4. Ratio of the analytical CSS including the effective radius correction Eq. 21 ($\kappa_{1D-1D}^2$) over the effective CSS estimated by OKMC ($\kappa_{est}^2$) as a function of the decimal logarithm of $C_A = C_B$ in cm$^{-3}$. The effective CSS were calculated according to the convergence conditions detailed in the companion paper [1]. Cluster radii sums are 4 nm (cluster radii sums of 2 to 6 nm did not show any significant difference). Glide direction families are indicated in the legend. For comparison with an older approach, the evaluation of Eq. 16 for the corresponding families are represented as accordingly colored dashed lines, while the effective radius simplification Eq. 21 corresponds to the black line $y = 1$.

A steady-state approximation (see Annex B for original references applying it to 1D - 0 reactions) and then we validate it. Now assuming $C_A > C_B$ and that no other reaction interferes, we always have:

$$C_A(t) = C_B(t) + \delta, \quad \delta > 0, \quad \forall t \geq 0,$$

$$\dot{C}_A(t) = \dot{C}_B(t),$$

$$\dot{C}(t) = -C(C + \delta) \left[ \beta_\perp \alpha(t) + \beta_\parallel \gamma t^{-1/2} \right],$$

$$\beta_\perp = 2\pi DR_{eff},$$

$$\beta_\parallel = 2\pi DR,$$

$$\gamma = \frac{\pi R}{2\sqrt{\pi D}}.$$  

The time dependent solution is easily obtained assuming again that $\alpha(t) = \bar{\alpha}$ but this constant has to be determined self-consistently. Then solving for the half-reaction time and inserting it back into $\alpha$ yields a steady-state proposal the CSS expression. After additional
Taylor expansions for small $\delta/C_B^0$, this leads to the following simple yet physically non-trivial absorption rate expression:

$$2\pi R_{\text{eff}} \left[ \frac{8}{-\ln \left( \frac{\pi^2/2(C_A + C_B)R^3}{DA} \right)} \right]$$

(24)

A validation of this expression is displayed on figure 5, where the ratio of the previous expression over the effective absorption rate is represented depending on logarithm of both concentrations. We see that the proposed expression matches the OKMC-estimated CSS with only about 5% discrepancy all over the range of concentrations investigated for $1/2\langle 111 \rangle$. For $1/2\langle 110 \rangle$, the agreement is also important, but the discrepancy may exceed 10% when the concentration ratio exceeds a factor 3.

Figure 5. Analytical sink-strength from Eq. 24 over the OKMC-estimated CSS ($\kappa_{\text{est}}^2$) as a function of the decimal logarithm of $C_A$ and $C_B$ in cm$^{-3}$ (x and y axis on the horizontal plane). Green points correspond to conditions with $1/2\langle 111 \rangle$ glide and red ones to $1/2\langle 110 \rangle$. Surfaces are displayed for eye guidance.
IV. SINK STRENGTHS IN THE 1D-1D ANISOTROPIC CASE

We are now addressing the most general case for two 1D random walks where \( D_A \neq D_B \). Having established in section III the correcting factor allows the 1D − 1D equivalence to \( 2D - 0 \), we may now exploit further this analogy. The 2D equivalent diffusion problem should now be that of an anisotropically diffusing specie, with diffusion tensor

\[
D = \begin{bmatrix}
D_A & 0 \\
0 & D_B
\end{bmatrix}
\]

Explicit statement of the steady-state pair probability density diffusion yields:

\[
D_A \frac{\partial^2 U}{\partial x^2} + D_B \frac{\partial^2 U}{\partial y^2} = 0
\]  \hspace{1cm} (25)

The solution shares some similarities with isotropic case, with the difference that the circular symmetry-related Bessel functions have to be replaced by their elliptical symmetry-related counterpart: Mathieu functions \[26\]. For an explicit analytical resolution of absorption rates, one should then, in principle, calculate the stationary flux of pair concentration current through the capture surface as reminded in section II. Theses steps might be much more difficult that in the isotropic case because Mathieu’s functions asymptotic expansions are much more difficult to manipulate that Bessel’s one \[27\] and even the numerical evaluation of the multiple summations that they involve can be a challenge in itself \[28\].

Fortunately, further exploiting the \( 2D − 0 \) analogy completely alleviates these difficulties: we can directly establish the needed CSS expressions by analogy to the 2D anisotropic case. After a series of non-trivial simplifications, Woo and co-workers \[29, 30\] have established the general form of this absorption rate for anisotropically diffusing species absorbed at a dislocation line of given orientation. Their result is better known for its use in the so-called “DAD model” for “Diffusion Anisotropy Driven” growth of loops in hcp crystals. Adapting it to the geometry of our analog problem yields (following the definition of \( \lambda \) from \[29\],
\[ \lambda = \pi/2 \):

\[
\kappa_{1D-1D}^2(D_A, D_B, R)D_A
\approx \kappa_{2D-0}^2(D_A, D_B, \overline{R}_{\text{eff}})\overline{D} \\
\approx \kappa_{2D-0}^2(D_A, D_A, \overline{R}_{\text{eff}})\overline{D} \left( \frac{D_A}{D_B} \right)^{1/6} \\
\approx \kappa_{2D-0}^2(D_A, D_A, \overline{R}_{\text{eff}})D_A \left( \frac{D_A}{D_B} \right)^{-1/3},
\]

(26)

for \( D_A > D_B \) and \( \overline{D} \) being here the rescaled average diffusion coefficient relevant to 2D diffusion: \((D_A D_B)^{1/2}\). We note here the non-trivial dependency of the CSS to the diffusion coefficient ratio to the power \((-1/3)\), which will be central in the interpretations of the companion paper [1]. Strictly speaking, the preceding result is valid only when the glide direction variant are orthogonal, which is only the case for the \( \langle 100 \rangle \) system. When it is not the case, one should correct the diffusion coefficient ratio for non-orthotropy using the formulas from the Appendix D.

V. SINK STRENGTHS IN THE 3D ANISOTROPIC CASE

In a realistic irradiated microstructure, some small vacancy clusters and interstitial clusters will be mobile and interact intensively. As these two types of clusters generally have 3D and 1D mobilities respectively, the general expression of 3D - 1D CSS is also needed for a comprehensive RECD parameterization. Just as in the previous case, we may directly derive this expression from equivalent diffusion problems. Here also, we start by examining the assumption of additivity of diffusion tensors. This assumption holds more naturally than in the 1D - 1D because, in the present case, one of the reactants has a 3D mobility, so the geometric condition for interaction does not require any specific treatment (whatever the geometric configuration the relevant capture distance is always \( R = R_A + R_B \)). The rate for \( A - B \) absorptions, with respective diffusion tensors \( D_A \) and \( D_B \), are then equivalent to the rates for a specie with diffusion tensor \( D_A + D_B \) with respect to a fixed sink. This assumption made, the case of \( A \) having an isotropy 3D-random walk while \( B \) moves 1D, is easily handled with the “3D-anisotropy” results that follow.

If we consider that the total diffusion tensor has three diagonal components \( D_x = D_y = D_\rho \) and \( D_z \), the absorption rate can be cast in analytical forms in the following three limiting
cases:

$$\frac{\partial C_A}{\partial t} = -C_A C_B \overline{D}$$

\[
\left\{ \begin{array}{l}
4\pi \left( \frac{D_A}{D_z} \right)^{1/3} R/\ln \left[ 2 (D_\rho / D_z)^{1/2} \right], \text{for } D_z \ll D_\rho ,
4\pi R, \text{for } D_z \simeq D_\rho ,
8 \left( \frac{D_z}{D_\rho} \right)^{1/6} R, \text{for } D_z \gg D_\rho
\end{array} \right.
\]

where only the long time terms were retained from the developments of Woo \cite{30} and $\overline{D} = (D_\rho^2 D_z)^{1/3}$ is the rescaled average diffusion coefficient relevant to this type of anisotropy. It is generally convenient in RECD to have CSS proportional to the sum of diffusion coefficients $D_A + D_B$ that we can state as $D_z$ and assume to be constant without loss of generality. Indeed, the diffusion coefficient dependencies of the previous cases can be cast in the following form:

$$D \left( \frac{D_z}{D_\rho} \right)^{\delta} = D_z \left( \frac{D_z}{D_\rho} \right)^{\delta - \frac{2}{3}}$$

(28)

Now, to establish the CSS expression relevant to our case, we can choose $D_\rho = D_B$, which yields $D \left( \frac{D_z}{D_\rho} \right)^{\delta} = D_z \left( \frac{D_A}{D_B} \right)^{-\frac{1}{2}}$ diffusion ratio dependency when $D_A \gg D_B$ (third case of Eq. 27), thus exhibiting a characteristic exponent ($-1/2$) for the diffusion coefficient ratio.

VI. APPLICATION TO CLUSTER DYNAMICS

A practical application of the CSS development is now exposed. For the sake brevity, it can only be sketched. For a general description of RECD, one may refer to \cite{19} and to the historical references it contains. For validation purposes, the CSS expression Eq. 24 is has been implemented with a finite difference Jacobian calculation and the results were compared with massive OKMC simulations using the LAKIMOCA code \cite{31}. Due to the limitations of OKMC to the early stages of microstructure evolution in systems with fast species, we do not need any specific method for large cluster (such as the Fokker-planck approximation or the grouping method) in this case: all the cluster sizes can be solved exactly. To test the validity of the generic CSS expressions proposed, the parameterization and simulation conditions do not need to be representative of a totally realistic system. It is more important that, on one hand, they are simple enough to probe reaction couples sequentially, and on the other
hand, complex enough to test a variety of cluster reaction couples with different radii, concentrations and diffusion coefficients ratios as this generality is the main novelty of this CSS development. This has been realized starting from a fixed initial concentration of 1D-mobile SIA that will progressively react and populate 1D-mobile dimers, trimers ... up to mobile clusters of ten interstitials. Above this size, clusters will be immobile and their reactions rates will follow the expression Eq[B3]. To that purpose, decreasing 1D diffusion coefficients are imposed increasing cluster size: $2.314 \times 10^{-6}$, $2.158 \times 10^{-6}$, $2.024 \times 10^{-6}$, $1.908 \times 10^{-6}$, $1.805 \times 10^{-6}$, $1.714 \times 10^{-6}$, $1.633 \times 10^{-6}$, $1.560 \times 10^{-6}$, $1.494 \times 10^{-6}$, $1.434 \times 10^{-6}$ cm$^{2}$s$^{-1}$.

The cluster’s capture radius to volume relation is assumed spherical with an atomic volume value of $1.182 \times 10^{-23}$ cm$^{3}$, which is typical to BCC iron. Although 1D-mobility rules are quite straightforward to implement in OKMC, generating an initial OKMC configuration with correct and converged statistics for a comparison with RECD reveals to be technically nontrivial. Indeed, it appears that starting from a purely random distribution of monomers (i.e. simply assigning random positions with the only constraint of avoiding capture distances) leads to a significant discrepancy compared to a distribution equilibrated with respect to 1D-absorptions.

Equilibration here consists in evolving the system until a significant fraction of clusters have interacted. After each reaction, the two clusters are randomly replaced with the constraint of having their distance to the existing clusters greater that the sum of capture radii. In such way, density fluctuations (see for instance [32]) which are characteristic from 1D-reaction kinetics are properly accounted for. The only remaining task is to extend the OKMC statistics for comparison with the RECD result by repeating the runs from different 1D-equilibrium snapshots. Depending on the initial monomer density, the typical number of necessary OKMC runs ranges from hundreds to thousands. For the conditions of Figure [6] ($C_{\text{initial}} = 2 \times 10^{16}$ cm$^{-3}$) a hundred of runs were needed to have the same precision on concentration as RECD for cluster of size ten after 10 ms of physical time. This represents a paramount quantity of CPU time compared to the RECD calculation: the total CPU time spent for the OKMC runs is more than 3.2 million times larger than for RECD. Even better, with RECD because there is no major source of numerical stiffness in this type of simulation conditions, the RECD numerical scheme can substantially increase the time step and it takes less than a minute to simulate several decades of system evolution (the results are not displayed because the comparison with OKMC is completely out of reach).
Figure 6. Defect clusters distribution (x-axis is the cluster size in number of monomers, and the y-axis in the cluster concentration in cm$^3$). Starting from a population of $2 \times 10^{16}$ cm$^{-3}$ 1D-mobile monomers, the time evolution of the distribution was obtained by averaging one hundred OKMC runs (points) and an RECD calculation (lines).

From Figure 6, the comparison between RECD and OKMC appear as completely satisfactory, which is a strong validation the CSS developments. To our knowledge, this is the first RECD calculation accounting for absorptions of several types of 1D-mobile clusters. An important conclusion that can be drawn from the agreement of both methods is that multi-sinks terms are not necessary to the lowest order for 1D − 1D interactions. Multi-sink terms are CSS terms introducing the influence of the all possibly interfering microstructural features the absorption. These terms are only second order for the 3D − 3D CSS [33] but they are first-order for 1D − 0 interactions [34]. Note that the present CSS derivations did not consider the possibility for these terms and because the OKMC validation at section III was on single reaction types, it was not an assessment for potential multi-sink terms. The situation is different for this last OKMC validation on a complete microstructure evolution: because absorptions now actually result in a extended distribution of clusters sizes, it is a adequate probe for potential multi-sink effects. The fact that the RECD implementation of 1D − 1D CSS without multi-sink terms is perfectly capable of reproducing the OKMC kinetics (naturally accounting for them) shows they may not be first order in the 1D − 1D case. This result has important consequences on the overall kinetics of 1D − 1D interactions: from their practical implementation, to the estimation of nucleation rates.
VII. SUMMARY AND CONCLUSIONS

To summarize, because realistic RECD parameterization should include CSS for all relevant cluster reaction couples, there is a need for $1D - 1D$ CSS expressions (at least, as a limiting case of $1DR - 1DR$ CSS expressions). For any practical use in microstructure evolution simulation, this limiting case should depend on the couples of concentrations, radii and diffusion coefficients involved. The much restricted case of the 1D-absorptions of defects from the same class is taken as a starting point. First, the grounds of the equivalence between $1D - 1D$ and $2D - 0$ were better established thanks to a simple stochastic geometry model. From the asymptotics of this model, a simple correction arose, which in practice differs a little from seminal developments and compares better with OKMC effective CSS calculations at least for the $<111>$ glide family. It is also established that this equivalence is well justified for moderate to low volume fractions. Next, a self-consistent resolution of the diffusion asymptotics allowed us to extend the CSS formula to the case of distinct cluster classes ($C_A \neq C_B$) in an “isotropic diffusion” situation ($D_A = D_B$). This was also validated with OKMC simulations. It only remained to extend this result to $D_A \neq D_B$. Exploiting the previously established analogy with $2D - 0$, we adapted $2D$ anisotropic diffusion results to establish that the CSS must be corrected with the diffusion coefficient ratio to the power ($-1/3$). Similarly, for the equally important case of $3D - 1D$ interactions, a similar equivalence can be used and results in the same correction but with a ($-1/2$) exponent. These exponents thus appear to be characteristic of the dimensions involved in both random-walks. This fact will be extensively exploited in a companion paper [1] where these limiting cases will be used as the backbone of an even more general semi-empirical CSS expression encompassing all combinations of mixed-mobilities. Last but not least, we have seen that the established CSS compare very well with complete cluster nucleation OKMC simulations, provided that the latter have adequate initial structures and that statistics are extensive enough. This very good agreement also shows $1D - 1D$ CSS are not expected to have significant multi-sink terms, at variance with theoretical results on $1D - 0$ ones.
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IX. FUNDING

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Appendix A: Sink strengths in the 3D-0 and 3D-3D isotropic cases

In the case of spherical partners and 3D-diffusion of A with respect to the fixed sinks B (as they are immobile the dimensionality of their mobility is noted “0”), the reaction-rate can be further evaluated as:

\[ k(t) = 4\pi D_A R \left( 1 + \frac{R}{\sqrt{\pi D_A t}} \right). \] (A1)

The most well known form corresponds to its asymptotic form, where the short-time component has been neglected:

\[ k(\infty) \simeq 4\pi D_A R = \kappa_{3D-0}^2 D_A C_B, \] (A2)

where \( \kappa_{3D-0}^2 \) is strictly speaking a sink-strength, a quantity which is connected with reaction (here absorption) rate by \( \kappa_{AB}^2 = k(\infty) C_B / D_A \). The case where both species A and B undergo a 3D-random walk with respective diffusion coefficient \( D_A \) and \( D_B \) can be rigorously handled in random-walk calculations and results in the simple reaction rate expression where the sum of diffusion coefficients appears:

\[ 4\pi(D_A + D_B)R. \] (A3)

The apparent simplicity of this result may be the origin of the misleading conception that CSS expressions for two mobile partners can always simply be adapted from the fixed sink case by substituting the diffusion coefficient with a sum diffusion coefficients. As we will see in the next sections, this is valid only for purely isotropic 3D mobilities.

Appendix B: Sink strengths in the 1D-0 case

The case of one-dimensional diffusion of A mobile species with respect to a fixed density of sinks B (1D−0) can also be treated with in framework of pairs diffusion, but the analytical resolution is more difficult. It leads first to time-dependent reaction rate [20]:

\[ \frac{\partial C_A}{\partial t} = -C_A C_B 2\pi R^2 \left( \frac{D_A}{\pi t} \right)^{1/2}, \] (B1)
The variations of the $t^{-1/2}$ term will be significant at short times. Physically, this corresponds to cases where some sinks are initially in the glide trajectory of the mobile and are, by chance, close enough for a fast reaction. In these specific situations, the $1D - 0$ absorption rates can be quite large and comparable with (even possibly larger than) their $3D - 0$ counterparts. At longer times, the time-dependent term will vary slowly, and may lead to much lower absorption rates compared to the 3D case. With the preceding considerations, we see that it may then be legitimate to solve this equation for steady state conditions and then to input the steady state concentration back into the differential equation as done by Barashev et al. [4]:

$$\frac{\partial C_A}{\partial t} = - 4 \left[ 4 \left( \frac{\pi R^2 C_B}{\pi} \right)^2 \frac{D_A}{D} \right] C_A \times \left( \frac{1}{1 - C_A/C_A(t = 0)} \right),$$

which, apart from a factor $\frac{8}{3\pi}$ and neglecting that the last term on the right, is identical to the expression classically obtained by a statistical mechanics treatment of 1D random-walks towards a distribution of sink pairs (see [4, 34]):

$$\frac{\partial C_A}{\partial t} = - \kappa_{1D-0}^2 D_A C_A$$

$$= - 6\pi^2 R^4 C_B^2 D_A C_A$$

(B3)

To stress out how it compares to $3D - 0$ CSS in term of orders of magnitude, let us consider the following approximate relation:

$$\kappa_{1D-0}^2 = \frac{9}{8} (4\pi R C_B)(4/3\pi R^3 C_B)$$

$$\approx \kappa_{3D-0}^2 \Phi_B \text{ (if } R \approx R_B \text{)},$$

(B4)

where $\Phi_B$ is the volume fraction of sinks $B$. Thus, when the size of immobile sinks is large compared to that of the mobile clusters and when both volume fractions are small, then the $1D - 0$ CSS is also very small compared to its 3D counterpart.

Appendix C: Sink strengths in the 1DR-0 case

The case of absorption rates for species with a mixed 1D to 3D mobility towards a fixed sinks ($1DR - 0$ in our notation) has been solved by several authors [4, 33, 36]. Their work intents to account for the complex random walks observed for some small defects clusters...
as observed in molecular dynamics simulations \[8-11\] or as suspected from transmission electron microscopy (TEM) observations \[37\]. Several seminal HVEM (high voltage electron microscopy) observations \[5, 6\] have clearly pointed out the 1D character of the mobility of large dislocation loops when untrapped from impurities. Other studies \[37\] have also suggested the direct observation of the theoretically expected Burger’s vector changes of visible loops, but because this phenomenon is a priori more likely for very small loops which are not resolved in classical TEM observation conditions, these observations seem to be rare. The usual derivation of the related CSS relies on the parameterization of the average mean free-path before rotation \(\ell_{ch} = d_j \sqrt{\exp(E/k_BT)}\) by introducing a so-called rotation energy \(E\), and where \(d_j\) is the atomic jump distance, \(k_B\) Boltzmann’s constant and \(T\) the temperature. This energy should be related to the minimization of the elastic interaction of the loop and the surroundings field \[38\], but here we shall simply consider it as a “black box” parameter continuously describing the whole range of mixed 1DR mobilities from pure 3D mobility \((E = 0\) or \(\ell_{ch} \leq d_j\)) to pure 1D mobility \((E = \infty\) or large enough so that \(\ell_{ch}\) is larger than the average distance before absorption, the inverse square root of the 3D-CSS).

Using either random-walk statistical treatment \[4\] or diffusion equations \[35\] both yield the same result:

\[
\frac{\partial C_A}{\partial t} = -y\kappa_{1D-0}^2 D_A C_A, \tag{C1}
\]

where

\[
y = \frac{1}{2} \left( 1 + \sqrt{1 + \frac{4}{x^2}} \right), \tag{C2}
\]

\[
x^2 = \frac{\ell_{ch}\kappa_{1D-0}^2}{12} + \frac{\kappa_{1D-0}^4}{\kappa_{3D-0}^4}. \tag{C3}
\]

**Appendix D: Correction for the diffusion non-orthotropy**

The preceding results on sink strengths all rely on the implicit but important assumption that the diffusion is orthotropic so that diagonal diffusion tensors are given on an orthonormal base. Otherwise, pair diffusion equations would not have a Laplacian form and would have a cumbersome \(\frac{\partial^2 C}{\partial x \partial y}\) cross-term to be treated. Of course, this only happens in the present very specific case where we use continuous diffusion to model random walks along a discreet directions. Indeed the highlighted cases of interest, species correspond to \(1/2\langle111\rangle\) gliding
loops. There are four crystallographic variants of this directions and the angle between any pair of them is \( \beta = \arccos(1/3) \simeq 0.39\pi \). One classical way, to deal with it is to apply variable transformation to cast the partial differential equation (PDE) into its canonical form (i.e. is without cross-terms). A systematic way of operating these transformations can be obtained using singular values decomposition. We will now use a particular case of this procedure, resorting on rotations only, and determine the series of transformations needed to cast the PDE in a canonical form. This will provide us the rescaling factors that must be applied to the diffusion coefficients when we adapt CSS results for orthotropic diffusion to our non-orthotropic cases.

Formally, working either with the PDE, the diffusion tensor \( \mathbf{D} \), or the related elliptic equation are all equivalent and for manipulation purposes we choose the latter two formulation because of their intuitive geometrical interpretation. In the non-orthogonal coordinate system of glide directions \( R' = \{0, \vec{x'}, \vec{y'}\} \) (see Fig. 7) writes:

\[
\mathbf{D}' = \begin{bmatrix}
D_A & 0 \\
0 & D_B
\end{bmatrix}_{R'}.
\]  

(D1)

If we express the diffusion tensor in the \( R = \{0, \vec{x}, \vec{y}\} \) orthonormal system using the transfer matrix \( \mathbf{P} \):

\[
\mathbf{P}_{R \rightarrow R'} = \begin{bmatrix}
1 & \cos \beta \\
0 & \sin \beta
\end{bmatrix},
\]  

(D2)

\[
\mathbf{D} = \mathbf{P}_{R \rightarrow R'} \mathbf{D}' \mathbf{P}_{R' \rightarrow R} = \begin{bmatrix}
D_A & \alpha \\
0 & D_B
\end{bmatrix}_{R},
\]  

(D3)
where $\alpha = (D_A - D_B) \cos \beta$

Then,

$$D \times \begin{bmatrix} \cos \theta \\ \sin \theta \end{bmatrix} = \begin{bmatrix} D_A \cos \theta + \alpha \sin \theta \\ D_B \sin \theta \end{bmatrix} = \begin{bmatrix} a \cos(\theta + \Delta) \\ b \sin \theta \end{bmatrix} = \begin{bmatrix} x \\ y \end{bmatrix}$$

(D4)

which translates into the implicit equation:

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} - 2 \sin \Delta \frac{x y}{a b} = \cos^2 \Delta,$$

(D5)

where $\Delta$ is introduced for commodity and bares the relations:

$$\cos \Delta = \frac{D_A}{a},$$
$$\sin \Delta = \frac{\alpha}{a},$$
$$a = \sqrt{D_A^2 + \alpha^2},$$
$$b = D_B.$$

(D6)

Our goal now is to convert this equation into the usual elliptic form

$$\left( \frac{x''}{D_A''} \right)^2 + \left( \frac{y''}{D_B''} \right)^2 = 1$$

(D7)

in a $R'' = \{0, x'', y''\}$ system which corresponds to the $R$-system rotated to an angle $\gamma$ as illustrated on Fig. [7] Inserting

$$x = x'' \cos \gamma - y'' \sin \gamma,$$
$$y = x'' \sin \gamma + y'' \cos \gamma,$$

(D8)

into the previous equation and imposing the cancellation of the cross-term yields

$$\tan 2\gamma = \frac{2\alpha b}{b^2 - a^2},$$

(D9)
and identification of ellipse factors gives:

\begin{align}
D'_A &= D_A \left[ 1 + \sin^2 \gamma \left( \frac{a^2}{b^2} - 1 \right) + \frac{\alpha}{b} \sin 2\gamma \right]^{-1/2} \\
D'_B &= D_A \left[ 1 + \cos^2 \gamma \left( \frac{a^2}{b^2} - 1 \right) - \frac{\alpha}{b} \sin 2\gamma \right]^{-1/2}
\end{align}

(D10)

(D11)

These are the effective diffusion coefficients to be substituted in place of $D_A$ and $D_B$ inside the CSS expressions to account for the non-orthotropy. They can be more directly estimated by Taylor-expanding $A$ and $B$ to the first order of $b/a$ (or equivalently $D_B/D_A$ being small enough) leads to the much simpler formulas:

\begin{align}
D'_A &\simeq a, \\
D'_B &\simeq b \cos \Delta,
\end{align}

(D12)

and thus

\[
\frac{D'_A}{D'_B} \simeq \frac{D_A}{D_B} \simeq 1 + \cos^2 \beta.
\]

(D13)

For the case of $1/2\langle 111 \rangle$ glides which is highlighted in this paper, because the angle between crystallographic variants $\arccos(1/3)$ is somehow not so far from $\pi/2$, the correction on CSS for non-orthotropic diffusion happens to be relatively modest even when $D_A \gg D_B$: it is about a factor 0.9 (of course for $D_A = D_B$ the ratio is one, as no correction is needed). The correction is more substantial when considering, for example, absorptions between $1/2\langle 111 \rangle$ loops and $\langle 100 \rangle$ ones (which are known to coexist in irradiated bcc-iron [39, 40]). The smallest angle between glide directions would then be divided by two, so the correction on CSS could then become quite significant (about 0.6).