A projection-based reformulation of the coincident site lattice $\Sigma$ for arbitrary bicrystals at finite temperature

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The coincident site lattice and, specifically, the ‘$\Sigma$ value’ of a grain boundary are a ubiquitous metric for experimental classification of grain boundaries. However, the mathematical nature of $\Sigma$ – a pathological function taking values of either an integer or infinity – has been relatively unexplored. This work presents a framework for interpreting $\Sigma$ as the inverse of a projection defined using the standard $L^2$ inner product over continuous fields that represent lattices. ‘Pre-mollifiers’ are used to introduce thermal regularization in the context of the inner product, and a closed-form analytic result is derived. For all nonzero values of the regularization parameters, the formulation is mathematically smooth and differentiable, providing a tool for computationally determining experimental deviation from measured low-$\Sigma$ boundaries at finite temperatures. It is verified that accurate $\Sigma$ values are recovered for sufficiently low $\Sigma$ boundaries, and that the numerical result either converges towards an integer value or diverges to infinity.

1. Background and motivation

The coincident site lattice (CSL) and associated ‘$\Sigma$’ value are ubiquitous throughout grain boundary literature, providing a convenient metric for measuring the coincidence of a bicrystal. Early work on the CSL began with Fortes in 1972 who developed initial conditions for coincidence (Fortes, 1972); Santoro introduced shortly afterwards a mathematical quantification of the CSL and proposed an algorithm for computing the transformation matrix given a value for $\Sigma$ (Santoro & Mighell, 1973). Grimmer proved shortly afterwards that (i) the CSL exists only when the transformation matrix contains rational entries and (ii) $\Sigma$ is the least common integer divisor in the matrix (Grimmer, 1976). $\Sigma$ has been proposed and is frequently used as a measure of grain boundary character (Brandon et al., 1964; Brandon, 1966), although the legitimacy of this has been called into question (Goodhew & Smith, 1980). Because the CSL is agnostic regarding the interface inclination, it appears that ‘low $\Sigma$’ is a condition that is necessary only (not sufficient) for grain boundaries in bicrystals to have low energy (Randle, 2001).

Its ease of experimental measurement results in the frequent use of $\Sigma$; however, computing it for a known orientation relationship is considerably more complex. The determination of least common integer divisor is the most frequently used method (Banadaki & Patala, 2015); however, the determination of the least common divisor is highly dependent on either the user-determined cutoff or the round-off of the decimal components of the rotation matrix. $\Sigma$ is a highly pathological function of the orientation – integer-valued for all rational rotations and infinite otherwise – so the
above method is subject to significant error when estimating $\Sigma$ for rotations containing small deviations. Given a set of error-containing rotation parameters (e.g. Euler angles) the above method together with the metric provided via the Brandon criterion (Brandon, 1966) quantify the distance from whatever low-$\Sigma$ boundary was computed; however, there is no guarantee that the most relevant or accurate $\Sigma$ will be identified.

In this work, we develop a novel method for computing the $\Sigma$ value of a bicrystal. This work is primarily motivated by the aforementioned difficulties in straightforward $\Sigma$ computation of boundaries whose orientation parameters contain experimental error, but also seeks to introduce physical insight into the $\Sigma$ computation. As opposed to the conventional geometry-based approach to $\Sigma$ calculation, we develop a formalism that enables it to be expressed in the language of inner products and norms as a projection. We aim to develop a formulation that satisfies the following essential requirements: (i) it must recover the pathological form for $\Sigma$ of a rigid perfect bicrystal; (ii) numerical regularization must have a statistically or physically meaningful interpretation; (iii) the expression must be in closed form; and (iv) the form must be general enough for application to any type of periodic crystal structure.

2. Formulation

In this section we present the formulation of a thermalized $\Sigma$ expression. We begin by developing the structure necessary for the construction of a thermalized $\Sigma$ function using mollifiers, their square roots (referred to here for convenience as ‘pre-mollifiers’), density measures and density functions. We will show that the choice of mollifiers/pre-mollifiers can be made using physical reasoning and can generally be approximated using truncated Gaussians.

Using these constructions, we define a regularized expression for $\Sigma$ in terms of the $L^2$ norm on density functions for arbitrary collections of points. Finally, we exploit periodicity by using Fourier series to expand the density functions, allowing the projection operator to be evaluated in closed form.

2.1. Pre-mollifiers

We begin by reviewing the notion of ‘mollifiers’, which are defined as follows:

*Definition 1 (mollifiers in $\mathbb{R}^d$).* Let $\Phi: \mathbb{R}^d \to \mathbb{R}$. If $\Phi$ is (i) smooth, (ii) non-negative, (iii) has compact support, (iv) has unit integral $\int \Phi(x)\,dx = 1$ and (v) has a Dirac limit $\lim_{\epsilon \to 0} \Phi_\epsilon(x) = \delta(x)$ where $\Phi_\epsilon(x) = (1/\epsilon^d)\Phi(x/\epsilon)$, then $\Phi$ is a positive mollifier (Friedrichs, 1944).

An example of a mollifier with decreasing parameter is plotted in the top half of Fig. 1. The mollifier shown fully satisfies the properties of compact support and smoothness, but can also be approximated by a standard Gaussian.

We note that here and subsequently we work in three dimensions, although all results are easily generalized to any number of dimensions. All integrals are definite and over $\mathbb{R}^3$, and all measures used are Lebesgue unless otherwise noted.

Let $\langle \cdot, \cdot \rangle : L^2 \times L^2 \to \mathbb{R}$ be the $L^2$ inner product with respect to the Lebesgue measure and $| \cdot | : L^2 \to \mathbb{R}$ the induced norm. The definition of a mollifier implies that the norm of a mollifier $|\Phi_\epsilon|$ depends on $\epsilon$, and is undefined as $\epsilon \to 0$. This prompts the following definition:

*Definition 2 (pre-mollifiers).* If $\Phi$ is a mollifier and

$$\varphi = \Phi^{1/2} \quad \varphi_\epsilon = \Phi_\epsilon^{1/2}$$

then we refer to $\varphi$ as a pre-mollifier.

Examples of mollifiers with their corresponding pre-mollifiers are plotted in Fig. 1. We see that $\varphi$ inherits properties (i)–(iii) from $\Phi$. $\varphi$ does not inherit properties (iv)–(v); it is easy to show that $\int \varphi_\epsilon \,dx \to 0$ as $\epsilon \to 0$. However, $\varphi$ also possesses the desired property of simultaneously having a unit norm, i.e. $|\varphi_\epsilon| = 1 \quad \forall \epsilon > 0$. (Proof of both properties is given in Appendix A.) We now proceed to prove a simple but useful proposition for pre-mollifiers:

*Proposition 1.* Let $x^A, x^B \in \mathbb{R}^3, x^A \neq x^B$, and let $\Phi$ be a mollifier with pre-mollifier $\varphi$. Then

$$\lim_{\epsilon \to 0} \langle \varphi_\epsilon(x - x^A), \varphi_\epsilon(x - x^B) \rangle = 0. \quad (2)$$

![Figure 1](image-url)

Example of mollifiers (top) and pre-mollifiers (bottom) with numerical parameter $\epsilon$ going to zero. $\Phi$ for this example has the form of the exponential bump function $\Phi = \exp[-1/(1 - x^2)], x \in [-1, 1], 0 \text{else}$, which has compact support yet is infinitely differentiable. (In general, however, a truncated Gaussian function suffices.)
Proof. The proof follows simply by direct evaluation:

\[ \lim_{\varepsilon \to 0} \int \Phi^{1/2} \left( \frac{x - x_A^\varepsilon}{\varepsilon} \right) \Phi^{1/2} \left( \frac{x - x_B^\varepsilon}{\varepsilon} \right) \, dx = \lim_{\varepsilon \to 0} \int \Phi \, dx = \int d\mu_\varepsilon(x) = \#(\chi). \]  

(3)

Changing variables \( \bar{x} = x/\varepsilon, \, d\bar{x} = dx/\varepsilon^3 \) (note that \( dx \) is the differential volume element, which in three dimensions results in the cubic \( \varepsilon \) term)

\[ \lim_{\varepsilon \to 0} \int \Phi^{1/2} \left( \frac{x - x_A^\varepsilon}{\varepsilon} \right) \Phi^{1/2} \left( \frac{x - x_B^\varepsilon}{\varepsilon} \right) \, d\bar{x}. \]  

(4)

Because \( x_A^\varepsilon \neq x_B^\varepsilon \), the distance between the mollifiers’ centers grows to infinity. By the condition of compact support, (4) goes to zero. \( \square \)

2.2. Projection formulation of \( \Sigma \)

Let \( \chi_A, \chi_B \subset \mathbb{R}^3 \) denote the locations of two discrete groups of atoms, labeled \( A \) and \( B \). \( \chi_A, \chi_B \) generally represent lattice sites but can be any collections of atoms. The CSL is then represented simply as

\[ \chi_{AB} = \chi_A \cap \chi_B, \]  

(5)

the intersection of the sets. We now define the \( \Sigma \) value as a discrete function of these two sets.

Definition 3 (\( \Sigma \) value). Given two sets of points \( \chi_A, \chi_B \subset \mathbb{R}^3 \), the \( \Sigma \) value is defined as

\[ \Sigma(\chi_A, \chi_B) = \frac{\#(\chi_A) \#(\chi_B)^{1/2}}{\#(\chi_A \cap \chi_B)} \]  

(6)

where \( \#() \) is the cardinality of ( ), alternatively the counting measure on ( ).

Note that this definition is not restricted to bicrystals composed of two identical lattices, but recovers the standard definition when both lattices are the same.

We now proceed to regularize this definition, allowing us to pass from the ‘discrete case’ (wherein atomic sites correspond to lattice sites in \( \mathbb{R}^3 \)) to the smooth case, where atomic sites correspond to probability densities centered around the lattice site. To do this we introduce one final construction:

Definition 4 (regularized lattice field). Let \( \mu_\varepsilon \) be a collection of point (i.e. Dirac) measures centered at \( \chi \subset \mathbb{R}^3 \), a collection of discrete points corresponding to atomic locations. Let \( \Phi \) be a mollifier with pre-mollifier \( \varphi \). Then

\[ \rho_\varepsilon(x) = (\varphi_\varepsilon \ast \mu_\varepsilon)(x) = \sum_{i \in \chi} \varphi_\varepsilon(x - x_i) \]  

(7)

is the lattice field corresponding to \( \{x_i\} \), regularized by a numerical parameter \( \varepsilon \).

Now we show that the counting measure \( \# \) on a discrete set corresponds to the Lebesgue measure \( dx \) on the corresponding lattice field. That is, given a set \( \chi \) with corresponding lattice density field \( \rho_\varepsilon \), then it is clear that \( \# \) is the limit of the Lebesgue measure on the squared density field:

\[ \lim_{\varepsilon \to 0} |\rho_\varepsilon|^2 = \lim_{\varepsilon \to 0} \int \rho_\varepsilon^2 \, dx = \int d\mu_\varepsilon(x) = \#(\chi). \]  

(8)

We now extend this regularization in the context of inner products. Let \( \langle \cdot, \cdot \rangle : L^2 \times L^2 \to \mathbb{R} \) be the usual inner product on \( L^2 \), with \( |\cdot| \) the norm induced by it. In the following, we identify the limit of the inner product of two density fields as the cardinality of their discrete intersections:

Theorem 1. Let \( \chi_A, \chi_B \subset \mathbb{R}^3 \) and let \( \Phi \) be a mollifier. Let \( \rho_A^\varepsilon \) and \( \rho_B^\varepsilon \) be lattice fields corresponding to \( \chi_A, \chi_B \) with mollifier \( \Phi_\varepsilon \). Then

\[ \lim_{\varepsilon \to 0} \langle \rho_A^\varepsilon, \rho_B^\varepsilon \rangle = \#(\chi_A \cap \chi_B). \]  

(9)

Proof. The proof follows directly by evaluation of the integral and application of Proposition 1. \( \square \)

We now use this fact to construct a regularized \( \Sigma \). Let \( \rho_A^\varepsilon, \rho_B^\varepsilon \) be lattice fields corresponding to sets of atomic locations \( \chi_A, \chi_B \). Then, the regularized \( \Sigma \) value (referred to as \( \Sigma_\varepsilon \)) is defined conveniently (in terms of its reciprocal, \( \Sigma_\varepsilon^{-1} \)) as a projection in terms of the \( L^2 \) inner product and the \( L^2 \) norm:

\[ \Sigma_\varepsilon^{-1} = \frac{\langle \rho_A^\varepsilon, \rho_B^\varepsilon \rangle}{|\rho_A^\varepsilon|^2 |\rho_B^\varepsilon|^2}. \]  

(10)

It is easily verified that the discrete case is recovered as \( \varepsilon \to 0 \). \( \Sigma \) is most frequently used when one lattice is a rotation of the other; i.e. \( \rho_B^\varepsilon = \rho_A^\varepsilon \circ R, R \in SO(3) \). Then the value is expressed simply as

\[ \Sigma_\varepsilon^{-1} = \frac{\langle \rho_A^\varepsilon, \rho_B^\varepsilon \circ R \rangle}{\langle \rho_A^\varepsilon, \rho_B^\varepsilon \rangle}. \]  

(11)

The projection formulation allows some already known facts about \( \Sigma \) to be proven in a different way; for example:

Theorem 2 (\( \Sigma \) inequality). For non-empty density fields with at least one coincident point, \( \Sigma \geq 1 \).

Proof. The proof follows by application of the Cauchy–Schwartz inequality to (10). Let \( \rho_A^\varepsilon, \rho_B^\varepsilon \) be taken as before. Since each lattice field contains at least one coincident point, then \( \langle \rho_A^\varepsilon, \rho_B^\varepsilon \rangle \geq 1 \). By the above and by the Cauchy–Schwartz inequality we have \( |\rho_A^\varepsilon|^2 |\rho_B^\varepsilon|^2 \geq \langle \rho_A^\varepsilon, \rho_B^\varepsilon \rangle^2 \geq \langle \rho_A^\varepsilon, \rho_A^\varepsilon \rangle \), which shows \( \Sigma \geq 1 \). \( \square \)

A full discussion of what can be proven using this framework is out of the scope of this work, but may include (i) proof of \( \Sigma \) parity for cubic lattices and (ii) proof that f.c.c. (face-centered cubic) and b.c.c. (body-centered cubic) lattices with the same orientation relationship possess the same \( \Sigma \) value, by virtue of Parseval’s theorem and the fact that f.c.c. and b.c.c. lattice measures possess Pontryagin duality.
2.3. Fourier representation of periodic lattice fields

To compute $\Sigma$ using the above formulation for lattices with crystal symmetry, it is advantageous to find a Fourier representation for the lattices’ density fields, $\rho_\alpha$. We follow a procedure similar to that described in §3.1.4 of Runnels (2016), and a general reference for the treatment of periodic tempered distributions is pp. 162–163 of Donoghue (1969). Let $\chi \subset \mathbb{R}$ be the atomic locations for a one-dimensional lattice with spacing $a$. $\Phi$ is a mollifier having a pre-mollifier $\varphi$ with Fourier transform $\hat{\Phi}$. Then, a regularized form for $\rho_\alpha$ is given in terms of $\varphi$:

$$\rho_\alpha(x) = \sum_k \mu_k \exp(2\pi ikx/a) \hat{\Phi}(2\pi k/a).$$  \hspace{1cm} (12)

In the following sections we use this form for $\rho$ extended to three dimensions.

2.4. Physical interpretation of lattice regularization

Regularization of periodic lattice fields is convenient from a computational perspective, but it carries with it physical significance. Given a lattice field as defined above, the square $\rho_\alpha^2(x)$ has the interpretation as a probability density field (multiplied by the number of atoms). The MaxEnt procedure (Jaynes, 1957a,b; Kulkarni, 2007; Niven, 2009) was used in §3.1.3 of Runnels (2016) to pass from point masses at absolute zero to smoothed density functions at finite temperature. The primary difference in this treatment is that we work with pre-mollifiers; however, it is clear that the interpretation is identical for $\rho_\alpha^2$.

The choice of mollifier $\Phi$, therefore, may be determined physically, where the parameter $\epsilon$ is linearly proportional to the temperature of the lattice. The degree of regularization then corresponds to the temperature of the specimen. Pragmatically, a Gaussian-type mollifier approximant will suffice.

2.5. Closed-form inner product evaluation

We now consider the evaluation of the inner product as previously defined. Let us consider two periodic lattice fields $\rho_\alpha^A, \rho_\alpha^B$ with mollifier $\Phi$, where $\rho^B = \rho^A \circ R, R \in \text{SO}(3)$; i.e. $\rho^B$ is a rotated copy of $\rho^A$. Because the lattices are no longer finite, localization is necessary for computability. Let $\Psi$ be a mollifier with Fourier transform $\hat{\Psi}$, where $\hat{\Psi}_\sigma \rightarrow 1$ as $\sigma \rightarrow 0$.

Using $\hat{\Psi}$ as a localization function, we approximate the inner product as

$$\langle \rho_\alpha^A, \rho_\alpha^B \rangle_{\alpha} = \int \rho_\alpha^A(x) \overline{\rho_\alpha^B(x)} \hat{\Psi}_\alpha(x) \, dx,$$  \hspace{1cm} (13)

where the overbar indicates complex conjugation. We note that the strict use of a mollifier for $\Phi$ is not entirely necessary as the condition of compact support is not needed by any of the proofs presented here. We also note that the inclusion of $\hat{\Psi}_\alpha$ could be viewed as a redefinition of the $L^2$ inner product with respect to some measure $d\mu_\alpha(x) = \hat{\Psi}_\alpha(x) \, dx$. \hspace{1cm} (14)

For convenience, we introduce $k(n) = \lfloor 2\pi n_1/a_1, 2\pi n_2/a_2, 2\pi n_3/a_3 \rfloor$, where $a_i$ are the dimensions of the periodic cell in each dimension.

For simple cubic lattices such as f.c.c. and b.c.c., $a_1 = a_2 = a_3 = a$, the lattice constant. Even for non-cubic lattices, such as h.c.p. (hexagonal close-packed), it is usually...
possible to find a rectangular periodic cell. Fig. 2 illustrates the repeating cell choices for f.c.c., b.c.c. and h.c.p. lattices.

With this notation, the Fourier series formulation is

$$\rho_x = \sum_{n \in \mathbb{Z}^3} \mu_n \exp[k(n) \cdot x] \hat{\varphi}(k(n))$$  \hspace{1cm} (15)

resulting in the following expression for the inner product:

$$\langle \rho_x^\alpha, \rho_x^\beta \rangle = \int \sum_{m,n \in \mathbb{Z}^3} \mu_m^\alpha \mu_n^\beta \exp\{[k^\alpha(m) - k^\beta(n) \cdot x]\}
\times \hat{\varphi}^\alpha[k^\alpha(m)] \hat{\varphi}^\beta[k^\beta(n)] \Psi(x) \, dx
= \sum_{m,n \in \mathbb{Z}^3} \mu_m^\alpha \mu_n^\beta \hat{\varphi}^\alpha[k^\alpha(m)] \hat{\varphi}^\beta[k^\beta(n)]
\times \Psi_x[k^\alpha(m) - k^\beta(n)].$$  \hspace{1cm} (16)

Reducing to the case where $\rho^\beta = \rho^\alpha \circ R$, the lattice has cubic symmetry, and all mollifiers are assumed to depend on $|x|$ only, we arrive at the expression

$$\langle \rho_x^\alpha, \rho_x^\beta \rangle = \sum_{m,n \in \mathbb{Z}^3} \mu_m^\alpha \mu_n^\beta \hat{\varphi}^\alpha[k^\alpha(m)] \hat{\varphi}^\beta[k^\beta(n)] \Psi_x[k^\alpha(m) - R^T k^\beta(n)].$$  \hspace{1cm} (17)

This formulation can be readily implemented and used to compute $\Sigma$ directly. In the following section we test the method for the familiar f.c.c.–f.c.c./b.c.c.–b.c.c. bicrystal case. However, the method in its current formulation can be applied to hexagonal structures and bimetal interfaces. We leave the further exploration of these cases for subsequent studies.

3. Results and discussion

The thermalized $\Sigma$ method was implemented using the C++ WIELD framework (Runnels et al., 2015, 2016). Truncated Gaussian functions were used as approximants for the mollifiers $\Phi$ and $\Psi$. A generic f.c.c. bicrystal was considered, although the results are the same with b.c.c. Four sets of bicrystals are generated by rotating one lattice by an angle $\theta$ about the [001], [110], [111], [112] axes, and $\Sigma(\theta)$ is evaluated continuously over the region. Results are generated for two values of $\sigma$. A constant value of $\sigma = 0.25$ is used; however, we note that changing this value does not significantly alter the results or computational efficiency. The results are plotted in Figs. 3–6.

The two curves give an indication of the behavior as $\varepsilon \to 0$; points corresponding to rational rotations converge to some integer value, as illustrated with the $\Sigma$5 case in [001] or the $\Sigma$3 case in [110]. On the other hand, the value of the other points diverges to infinity.

Interpretation of the results prompts the following notes: (i) $\Sigma$ can be formulated in such a way as to have the structure of a projection under the $L^2$ norm and inner product. (ii) It is possible to define a continuous $\Sigma$ function using thermal regularization. (iii) At high temperatures, thermal fluctuations cause $\Sigma$ above a certain value to become irrelevant. (iv) $\Sigma$ has no apparent correlation to grain boundary energy; low $\Sigma$ is at best necessary but not sufficient for low energy. [A full

- **Figure 4** Thermalized $\Sigma$ generated for symmetric rotation about (110).
- **Figure 5** Thermalized $\Sigma$ generated for symmetric rotation about (111).
- **Figure 6** Thermalized $\Sigma$ generated for symmetric rotation about (112).
discussion of the definition of grain boundary energy as well as a comprehensive set of grain boundary energy computations are available in Olmsted et al. (2009).]

4. Conclusion
In summary, in this work we have presented a novel framework for computing $C_6$ for arbitrary sets of points; we have shown that $C_6$ possesses the mathematical structure of a projection of pre-mollified lattice density measures, and that exploitation of thermalization and periodicity enables $C_6$ to be computed in a closed-form expression. The full ability of this framework for proving properties of $C_6$ has yet to be exploited and is left to future work. Additional future applications include the evaluation of $C_6$ for h.c.p. and other more complex lattice structures.

APPENDIX A
Properties of pre-mollifiers
Pre-mollifiers are unique in that they always have a unit norm, but have an integral decreasing to zero as their numerical parameter goes to zero. To demonstrate this, we first establish the following: for mollifier $\Phi_\varepsilon$ with pre-mollifier $\varphi_\varepsilon$, we have

$$|\varphi_\varepsilon| = \left[ \int \varphi_\varepsilon^2 \, dx \right]^{1/2} = \left[ \int \Phi_\varepsilon \, dx \right]^{1/2} = 1 \forall \varepsilon > 0$$

(18)

by property (4) of mollifiers. On the other hand, we consider the following integral:

$$\lim_{\varepsilon \to 0} \int \varphi_\varepsilon(x) \, dx.$$

(19)

By changing variables $\tilde{x} = x/\varepsilon$, $d\tilde{x} = dx/\varepsilon^3$ (working in three dimensions, so that dx is a differential volume term with $1/\varepsilon^3$ scaling) we find that

$$\lim_{\varepsilon \to 0} \int \Phi_\varepsilon^{1/2}(x) \, dx = \lim_{\varepsilon \to 0} \frac{1}{\varepsilon^{3/2}} \int [\Phi(x/\varepsilon)]^{1/2} \, dx = \lim_{\varepsilon \to 0} \varepsilon^{3/2} \int \Phi_\varepsilon^{1/2}(\tilde{x}) \, d\tilde{x} = 0$$

(20)

by smoothness of $\Phi$.

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References