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METHOD TO CALCULATE THE GRAIN BOUNDARY ENERGY DISTRIBUTION OVER THE SPACE OF MACROSCOPIC BOUNDARY PARAMETERS FROM THE GEOMETRY OF TRIPLE JUNCTIONS

A. MORAWIEC†

Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA

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Abstract—Details of a numerical method for reconstructing the grain boundary energy distribution over the complete space of macroscopic boundary parameters are presented. The reconstruction is based on the analysis of the dihedral angles between homophase grain boundaries of polycrystalline triple junctions. Instead of the Herring equilibrium condition, the procedure uses the Hoffman–Cahn formalism of the capillarity vector. This turns the reconstruction into the problem of solving a homogeneous system of algebraic linear equations. A numerical example demonstrating a reasonably good performance of the method is also given. © 2000 Acta Metallurgica Inc. Published by Elsevier Science Ltd. All rights reserved.

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1. INTRODUCTION

An effort is under way to develop a procedure for determination of the relative grain boundary energy from the geometry of equilibrated polycrystalline microstructures [1, 2]. The objective is to map the relative energy function over the whole space of macroscopic boundary parameters. The project poses considerable experimental challenges, mostly due to the enormous number of triple junctions to be characterized and analyzed. Also, from the numerical point of view, the task of calculating the relative energy from geometrical data is not trivial. This paper is meant to provide computational particulars of the energy reconstruction.

The analysis of dihedral angles at triple lines is a well-known method to investigate the anisotropy of grain boundary energy. Some works of this kind were limited to the energy dependence on grain misorientation [3–7], others take into account boundary inclinations with respect to the crystal lattice [8–12]. The mentioned project differs from all previous studies because it attempts to cover the complete space of five macroscopic boundary parameters.

The equilibrium condition for a triple junction in the presence of anisotropy was given by Herring [13]. The Herring relationship involves differentials in the so-called “torque term”. This makes the application of that equation difficult. The problem of energy reconstruction is purely algebraic using the Hoffman–Cahn formalism of the capillarity vector [14, 15]. The equilibrium condition expressed in terms of the capillarity vector allows one to determine the vector (times a constant factor) from the geometry of the junctions. Then, a simple relationship between the capillarity vector and the free energy is applied to calculate the distribution of the latter.

From the formal point of view, investigation of grain boundaries is related to the analysis of a surface stretched over a fixed frame (anisotropic Plateau problem), or the problem of the equilibrium shape of a particle. However, the polycrystal’s boundary network, as a whole, has its own features involving triple junctions and quadruple points. In this work, only isolated triple junctions are taken into account; the influence of quadruple points is neglected.

The relation to the equilibrium shape brings us to the question of solvability of the problem. In the case of anisotropic material, energies for some high energy regions of the parameter space can be inaccessible. The question is, which part of the energy

† Present address: Instytut Metalurgii i Inżynierii Materiałowej PAN, Reymonta 25, Kraków, Poland.

E-mail address: nmmorawi@cyf-kr.edu.pl (A. Morawiec).

distribution can be obtained from purely geometrical information? For the problem of reconstructing the *surface* energy distribution from the shape of a particle surrounded by a homogeneous medium, the answer is clear: only the convex hull of the $1/\gamma$ -plot can be determined [16, 17]. The situation is more complex for the polycrystalline boundary networks [18]. We limit our discussion of this subject to the assumption that, apart from experimental errors, the geometry of equilibrated microstructure can provide an approximation of the relative energy; for low level of anisotropy, the approximation may coincide with the actual energy distribution.

Formally, the energy function with cusps corresponding to faces with integer Miller indices is continuous, but not differentiable [19]. On the other hand, the function is “smoothed” by only *near-equilibrium* conditions, and by flaws in a real material. From the viewpoint of measurements, additional spread comes from experimental errors. With Herring or Hoffman and Cahn equilibrium equations, one assumes not only continuity but also (piecewise) differentiability of the energy function with respect to its arguments.† That assumption applies to the Hoffman–Cahn formalism of the capillarity vector in general. Essential relations of that formalism are re-derived in an appendix to this paper. They are, however, obtained in a way different than presented in Hoffman and Cahn [14].

1.1. Preliminaries

Let the orientations of two neighboring crystallites with respect to an external (sample) Cartesian coordinate system be given by the special orthogonal matrices $\bar{\mathbf{o}}^1$ and $\bar{\mathbf{o}}^2$. (Quantities specified in the external coordinate system are over-lined.) Locally, the grain boundary between the *first* grain and the *second* one is determined by two elements: first, the misorientation matrix $\mathbf{m} = \bar{\mathbf{o}}^1(\bar{\mathbf{o}}^2)^T$, and second, by a unit vector \mathbf{n} normal to the boundary and directed towards the second grain, with coordinates specified in the Cartesian coordinate system of the first crystallite. Instead of the pair (\mathbf{m}, \mathbf{n}) , however, it is frequently more convenient to use a 4×4 matrix \mathbf{b} defined by

$$\mathbf{b} = \begin{bmatrix} \mathbf{m} & \mathbf{n} \\ -\mathbf{n}^T \mathbf{m} & 0 \end{bmatrix}; \quad (1)$$

cf. Morawiec [22]. If \mathbf{b} represents the boundary between the first and the second grain, the boundary between the second grain and the first one is represented by \mathbf{b}^T . The pair (\mathbf{m}, \mathbf{n}) and the matrix \mathbf{b} will be used interchangeably. We will write $\mathbf{b} \triangleq (\mathbf{m}, \mathbf{n})$ if \mathbf{b} is related to the pair (\mathbf{m}, \mathbf{n}) by (1). To express \mathbf{m}

and \mathbf{n} corresponding to \mathbf{b} , we will use $\mathbf{m} = P_1(\mathbf{b})$ and $\mathbf{n} = P_2(\mathbf{b})$.

Due to crystal symmetries, numerous different sets of boundary parameters, or different matrices of the type (1), may represent physically indistinguishable boundaries. The boundary energy distribution γ has the same value for all symmetrically equivalent configurations, i.e.

$$\gamma(\mathbf{b}) = \gamma(S_q(\mathbf{b})), \quad (2)$$

where $S_q(\mathbf{b})$ is the q th element of the list of matrices equivalent to \mathbf{b} . Let \mathbf{C}_i be a 4×4 matrix given by

$$\mathbf{C}_i = \begin{bmatrix} \mathbf{c}_i & 0 \\ 0 & 1 \end{bmatrix},$$

with \mathbf{c}_i being a 3×3 special orthogonal matrix representing a symmetry operation of the crystal point group; the range of i is from one to the number of such symmetry operations. (We assume here that the crystal symmetry point group contains inversion.) With $\mathbf{b} \triangleq (\mathbf{m}, \mathbf{n})$, the complete list of matrices $S_q(\mathbf{b})$ equivalent to \mathbf{b} consists of $\mathbf{C}_i \mathbf{b} \mathbf{C}_j$, $\mathbf{C}_i \mathbf{b}^T \mathbf{C}_j$, $\mathbf{C}_i \mathbf{b}^- \mathbf{C}_j$ and $\mathbf{C}_i (\mathbf{b}^-)^T \mathbf{C}_j$, where $\mathbf{b}^- \triangleq (\mathbf{m}, -\mathbf{n})$, and the indices i and j cover all their range.

We will also need the relation between the capillarity vector and the surface tension [14]. Let the vector $\bar{\mathbf{s}}$ be normal to a planar element of the boundary surface, and let its magnitude, denoted by \sqrt{g} , be equal to the area of the element. With γ depending on the surface normal $\bar{\mathbf{s}}/\sqrt{\bar{\mathbf{s}} \cdot \bar{\mathbf{s}}}$ (Thus, on $\bar{\mathbf{s}}$), the capillarity vector $\bar{\boldsymbol{\xi}}$ is defined by

$$d(\gamma\sqrt{g}) = \bar{\boldsymbol{\xi}} \cdot d\bar{\mathbf{s}}.$$

The surface tension can be expressed via the capillarity vector: Let $\bar{\mathbf{t}}$ be a unit vector tangent to an edge of unit length. The shift of the edge by an infinitesimal vector $d\bar{\mathbf{x}}$ corresponds to the surface elements $d\bar{\mathbf{s}} = \bar{\mathbf{t}} \times d\bar{\mathbf{x}}$. The surface tension $\bar{\boldsymbol{\sigma}} = \bar{\boldsymbol{\sigma}}(\bar{\mathbf{t}})$ at the edge, and the change of potential $d(\gamma\sqrt{g})$ caused by the shift, are related by $d(\gamma\sqrt{g}) = \bar{\boldsymbol{\sigma}} \cdot d\bar{\mathbf{x}}$. On the other hand, $d(\gamma\sqrt{g}) = \bar{\boldsymbol{\xi}} \cdot d\bar{\mathbf{s}} = (\bar{\boldsymbol{\xi}} \times \bar{\mathbf{t}}) \cdot d\bar{\mathbf{x}}$. Hence, due to arbitrariness of $d\bar{\mathbf{x}}$, the surface tension can be expressed as

$$\bar{\boldsymbol{\sigma}} = \bar{\boldsymbol{\xi}} \times \bar{\mathbf{t}}. \quad (3)$$

Readers are referred to the original papers [14, 15] and to Appendix B for more on the capillarity vector.

2. RECONSTRUCTION METHOD

Let the capillarity vectors $\bar{\boldsymbol{\xi}}_1$, $\bar{\boldsymbol{\xi}}_2$ and $\bar{\boldsymbol{\xi}}_3$ correspond to three boundaries of which a triple junction is built. By assumption, tensions at the junction are equilibrated. Because of (3), this means that the component of $\bar{\boldsymbol{\xi}}_1 + \bar{\boldsymbol{\xi}}_2 + \bar{\boldsymbol{\xi}}_3$ perpendicular to the junction vanishes, i.e.

† For a discussion of more general surfaces see Taylor [20, 21].

$$(\bar{\xi}_1 + \bar{\xi}_2 + \bar{\xi}_3) \times \bar{\mathbf{t}} = 0, \quad (4)$$

where $\bar{\mathbf{t}}$ is tangent to the junction [14]. All vectors in (4) must be specified in one coordinate system; it is assumed to be the one referred to the sample. On the other hand, one wants to calculate the free energy with respect to the system of the crystal, and there are three crystals involved in the above relation. Thus, in order to make use of (4), the vectors $\bar{\xi}_s$ ($s = 1, 2, 3$) must be expressed via components of $\xi = \xi(\mathbf{b})$ given in the crystal coordinate system.

Before giving that relation, we need to list the triple junction data obtained directly from the experiment; these are: vector $\bar{\mathbf{t}}$, vectors normal to grain boundaries $\bar{\mathbf{n}}_s$, and special orthogonal matrices $\bar{\mathbf{o}}^s$ representing orientations of the grains at the junction. Grain misorientations are calculated from orientations by $\mathbf{m}^1 = \bar{\mathbf{o}}^1(\bar{\mathbf{o}}^2)^T$, $\mathbf{m}^2 = \bar{\mathbf{o}}^2(\bar{\mathbf{o}}^3)^T$ and $\mathbf{m}^3 = \bar{\mathbf{o}}^3(\bar{\mathbf{o}}^1)^T$. The normals in the crystal coordinate system are $\mathbf{n}_s = \bar{\mathbf{o}}^s \bar{\mathbf{n}}_{(s)}$. Now, with $\mathbf{b}_s = (\mathbf{m}^s, \mathbf{n}_s)$, the components of the capillarity vector in the crystal coordinate system $\xi_s(\mathbf{b}_s)$ and those in the sample coordinate system $\bar{\xi}_s$ are related by $\xi_s(\mathbf{b}_s) = \bar{\mathbf{o}}^s \bar{\xi}_s$. Hence, the equilibrium condition (4), written with the explicit use of Cartesian coordinates, takes the form[†]

$$\varepsilon_{ijk} \bar{\mathbf{t}}^k \bar{\mathbf{o}}_{ij}^s \xi^l(\mathbf{b}_s) = 0, \quad (5)$$

where ε denotes the Levi–Civita permutation symbol. This relation is our basis for determining an approximation of the sought field $\xi = \xi(\mathbf{b})$.

To proceed with numerical calculations, the space of boundary parameters is discretized by a tessellation into cells. The cells are enumerated by an index β . Each point \mathbf{b} belongs to a certain cell, and a certain index corresponds to it. Within the cell, the field $\xi(\mathbf{b})$ is approximated by a vector ξ_β assigned to the cell. The relation (5) can be written as $A_{il}^\beta \xi_\beta^l = 0$, where $A_{il}^\beta = W \varepsilon_{ijk} \bar{\mathbf{t}}^k \bar{\mathbf{o}}_{ij}^s$ if \mathbf{b}_s is a point of the cell β , and $A_{il}^\beta = 0$ otherwise; the constant W is chosen in such a way that $A_{(i)l}^\beta A_{(i)l}^\beta = 1$ (no summation over i). The measurement is designed to provide a large number ($\sim 10^6$) of triple junctions, and a set of relations (5) corresponds to each triple junction. Therefore, we add to A an index J ($J = 1, \dots, J_{\max}$) enumerating the junctions, so we have

$$A_{Jil}^\beta \xi_\beta^l = 0. \quad (6)$$

This is a system of $3J_{\max}$ linear equations with respect to ξ_β^l . It is solved by a iteration method

which does not require the transposition of the matrix of the system.[‡] In the k th iteration step, the unknown ξ_β^l is denoted by $\xi_{\beta[k]}^l$. The initial form of ξ_β is given by $\xi_{\beta[0]} = P_2(\mathbf{b})$, where \mathbf{b} is a point of the cell β . For the k th step approximation, the quantity

$$\delta_{J[k]} = A_{Jil}^\beta \xi_{\beta[k]}^l \quad (7)$$

represents the deviation of the left-hand side of (6) from zero. The capillarity vector is modified by

$$\xi_{\beta[k]}^l = \xi_{\beta[k-1]}^l - \omega A_{Jil}^\beta \delta_{J[k-1]}, \quad (8)$$

where ω is a relaxation parameter. Because the system (6) is homogeneous, ξ_β^l can be determined only up to a constant factor. That factor is established by the following normalization procedure: in each step, $\xi_{\beta[k]}^l$ obtained from (8) is replaced by $N_{[k]} \xi_{\beta[k]}^l$, where $N_{[k]}$ is defined by $N_{[k]} (\xi_{\beta[k]}^l \xi_{\beta[k]}^l)^{1/2} = (\xi_{\beta[0]}^l \xi_{\beta[0]}^l)^{1/2}$.

Once the capillarity vector is known, the energy distribution γ is determined from $\gamma = \xi \cdot \mathbf{n}$. More precisely, $\gamma(\mathbf{b})$ is approximated by $\gamma(\mathbf{b}) = \xi_{\beta[K]}^l n^l$, where β corresponds to the cell containing \mathbf{b} , K is the last iteration step, and the vector \mathbf{n} is given by $\mathbf{n} = P_2(\mathbf{b})$.

Finally, there is an important additional element to the above construction which must be taken into account, namely the presence of symmetries. As we already mentioned, it manifests itself by the fact that numerous different sets of boundary parameters (or points in different cells) may correspond to physically identical boundaries. There are a number of possible approaches to deal with symmetry. First, one can determine the field ξ in the complete five parameter space, with the condition that the vectors in symmetrically equivalent locations are related. The second, more economic method, is to determine the field ξ in the asymmetric domain, i.e. in the sub-domain of the space in which each physically distinct boundary is represented only once. The third option, which is applied in our test, is to use a proper sub-domain larger than the asymmetric domain; this is analogous to the method employed earlier [23]. To relate ξ at symmetrically equivalent locations, we use (5) not only for \mathbf{b}_s but also for all points $S_q(\mathbf{b}_s)$ located in the sub-domain. This means that for each set of equations (5) a group of equivalent equations is created. When calculating $\delta_{J[k]}$ in (7) the average of all deviations in that group is taken.

3. TEST OF THE RECONSTRUCTION PROCEDURE

The simplest method of testing the computational side of the procedure is by creating a valid[§] model of the energy distribution, and then reconstructing it from computer generated triple junction data, with geometrical parameters of the junctions based

[†] Summation over all indices which appear twice in the formula, including s . There will be no summation over indices taken in parentheses or squares brackets.

[‡] The transposition would be computationally awkward because of the size of A .

[§] That is, satisfying the symmetry conditions (2).

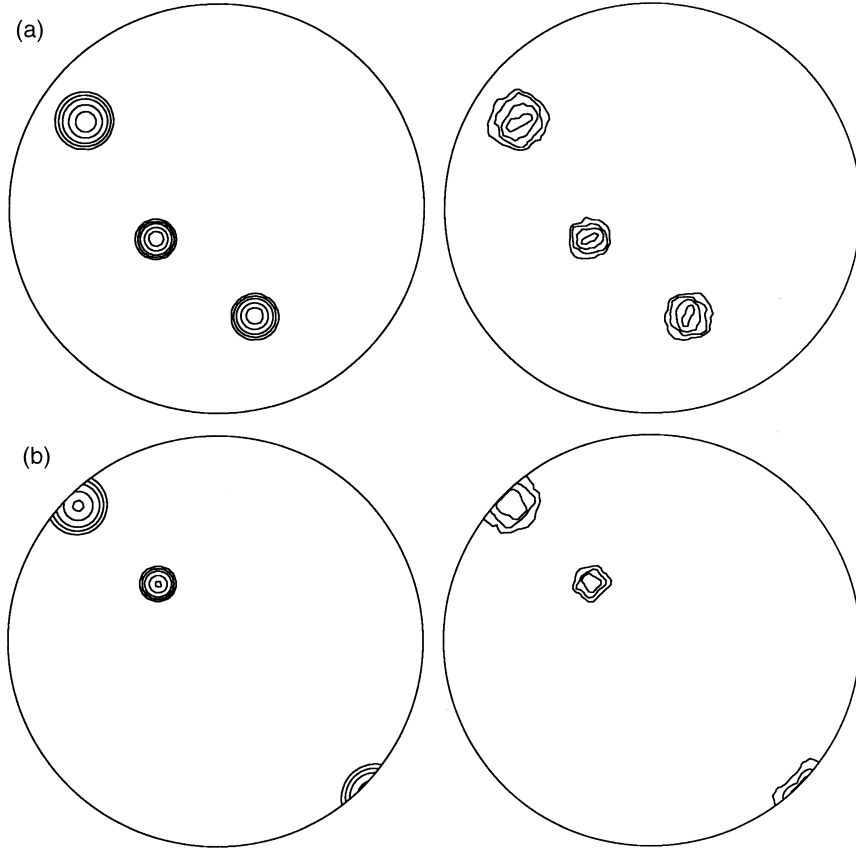


Fig. 1. Sections through the model (left) and reconstructed (right) energy distribution. Figures (a) and (b) are stereographic projections of one hemisphere of the γ -plots corresponding to the misorientations of $([111], 38.21^\circ) \approx \Sigma 7$ and $([110], 50.48^\circ) \approx \Sigma 11$, respectively. (That is, for the fixed misorientations, the dependence of γ on boundary inclination is plotted.) For all figures, the isolines 1.00, 0.97, 0.93, 0.85 and 0.75 were chosen. The value of 1.00 corresponds to the outer contour; the values assigned to other contours sequentially decrease towards centers of the cusps.

on the assumed model. From the numerical viewpoint, the task of generating equilibrated junctions is considerably more complicated than the reconstruction itself. Details concerning the construction of the model function and the generation of junction geometry are given in Appendix A.

We wrote simple programs for the generation of junctions and for the reconstruction of the energy distribution. One of the programming difficulties is how to deal with the size of the five parameter space. Moreover, with our programs, the generation of junction geometry, as well as the reconstruction of the relative energy are lengthy processes. The results of reconstruction, however, are reasonably good.

In the test we use as an example, $J_{\max} = 2 \times 10^5$ triple junctions (i.e. sets of $\bar{\mathbf{t}}, \bar{\mathbf{o}}^s$ and $\bar{\mathbf{n}}_s$, $s = 1, 2, 3$) were generated using the procedure described in Appendix A. The assumed crystal symmetry was cubic. The model energy distribution was uniform except some cusps. We chose the cusps to be located at the misorientations defined by coincidence lattice relationships of the f.c.c. structure with

Σ in the range from 1 to 13b. The relationships are enumerated in the standard order as Σ_n with $n = 0, 1, \dots, 8$, i.e. $\Sigma_0 = 1, \Sigma_1 = 3, \dots, \Sigma_8 = 13$. The cusp at $\Sigma_0 = 1$ is independent of boundary inclination. In the remaining cases, the centers of the cusps had inclinations of the densest lattice planes for particular misorientations. The half-widths of the cusps are given by the criterion $w_n = (\pi/12)\Sigma_n^{-1/2}$, and their depths are determined by $a_n = \Sigma_n^{-1/2}$.

The iteration process of reconstruction converges; though we stopped it arbitrarily after $K = 15$ iterations, in the future a reasonable termination criterion is needed. Figure 1 contains some sections through the model and reconstructed distributions.

4. CONCLUDING REMARKS

Although, the program we used was only provisional and some of its elements must be improved, it shows that the numerical part of the energy reconstruction can be performed using simple algebraic tools. A number of aspects of the reconstruction remain to be investigated. One of them is to

determine the level of robustness of the procedure with respect to experimental errors, and to include it in the error analysis of the whole measurement. There is also a problem of a practical nature: how to deal with the vast amount of information contained in a function of five variables. An analogous function is applied for descriptions of orientational correlations of molecules in molecular fluids, but only some sections are approached numerically; see, e.g. Lazaridis and Karplus [24].

An alternative approach to the reconstruction would be to apply the series expansion similar to that used by Gale *et al.* [25] for determination of surface energy anisotropy. Details of such a procedure for the five parameter boundary energy distribution remain to be explored.

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APPENDIX A

Three distinct steps in the generation of the geometry of triple junctions are described in some detail below.

Model of γ function

The model we use is based on the uniform energy distribution with cusps. The cusps are shaped in analogy to Read–Shockley's [26] expression for energy of low angle boundaries $\gamma \propto x(1 - \ln(x))$. We use a function f defined as

$$f(x, a) = ax(1 - \ln(x)) + (1 - a) \quad \text{for } 0 < x \leq 1,$$

$$f(0, a) = 1 - a \quad \text{and} \quad f(x, a) = 1 \quad \text{otherwise,}$$

where x determines a “distance” from the center of a cusp, and a ($0 \leq a \leq 1$) corresponds to its depth. To proceed further a definition of the distance in the space of boundary parameters is needed. The distance χ between boundaries \mathbf{b} and \mathbf{b}' can be defined by $\chi^2(\mathbf{b}, \mathbf{b}') = \|\mathbf{b} - \mathbf{b}'\|^2/2$, where the norm $\|\cdot\|$ of a matrix \mathbf{X} is given by $\|\mathbf{X}\| = (\text{tr}(\mathbf{X}^T\mathbf{X}))^{1/2}$, [22]. Assuming that $\mathbf{b} \doteq (\mathbf{m}, \mathbf{n})$ and $\mathbf{b}' \doteq (\mathbf{m}', \mathbf{n}')$, the quantity χ^2 can be expressed as

$$5 - \text{tr}(\mathbf{m}^T\mathbf{m}') - \mathbf{n} \cdot \mathbf{n}' - (\mathbf{m}^T\mathbf{n}) \cdot (\mathbf{m}'^T\mathbf{n}'). \quad (\text{A1})$$

Moreover, it has to be taken into account that symmetries affect the metric properties of the space. In the symmetric case, the distance χ^S between two boundaries is given by the smallest of all values of χ for all representative of the equivalency classes to which the boundaries belong. Formally, one has $\chi^S(\mathbf{b}, \mathbf{b}') = \min_q \{\chi(\mathbf{b}, S_q(\mathbf{b}'))\}$, where $S_q(\mathbf{b}')$ denotes the q th point symmetrically equivalent to \mathbf{b}' .

We also need a special cusp at $\mathbf{m} = \mathbf{I}_3 = \text{identity}$; that cusp is independent of the boundary inclination. Let the distance between orientations \mathbf{m} and \mathbf{m}' be given as $\chi_{\bullet}^2 = \|\mathbf{m} - \mathbf{m}'\|^2/2$. Analogously to χ^S , the distance χ_{\bullet}^S is defined by $\chi_{\bullet}^S(\mathbf{m},$

$\mathbf{m}' = \min_q \{\chi_s(\mathbf{m}, S_q^*(\mathbf{m}'))\}$, where misorientations $S_q^*(\mathbf{m})$ symmetrically equivalent to \mathbf{m} are $\mathbf{c}_i \mathbf{m} \mathbf{c}_j$ and $\mathbf{c}_i \mathbf{m}^T \mathbf{c}_j$, for all \mathbf{c}_i and \mathbf{c}_j .

Finally, the energy distribution is assumed to have the form of the product

$$\gamma(\mathbf{b}) \propto F_0(\mathbf{b}) \prod_k F_k(\mathbf{b}), \quad (\text{A2})$$

where $F_0(\mathbf{b}) = f(\chi_s^S(P_1(\mathbf{b}), \mathbf{I}_3)/w_0, a_0)$, $F_k(\mathbf{b}) = f(\chi^S(\mathbf{b}, \mathbf{b}_{(k)})/w_{(k)}, a_{(k)})$, \mathbf{b}_k determines the location of the k th cusp, w_k is its half-width, and a_k corresponds to its depth. It may look involved, but it is quite simple. Function f equals 1 everywhere except a cusp. Thus, the product of such functions equals 1 everywhere except a number of cusps. Complicated arguments of particular factors f just specify locations and shapes of the cusps.

Determination of ξ from the model γ function

Let $\mathbf{b} \doteq (\mathbf{m}, \mathbf{n})$. For a fixed misorientation \mathbf{m} , with components n^j treated as independent variables, one can write

$$\xi^i = \frac{\partial g}{\partial n^j} (\delta_{ij} - n^i n^j) + n^i \gamma.$$

To get ξ , the derivatives $\partial \gamma / \partial n^i$ are needed. Based on (A2), they can be expressed as

$$\frac{\partial \gamma}{\partial n^j} = F_0 \sum_l \frac{\partial F_l}{\partial n^j} \prod_{k(k \neq l)} F_k.$$

Taking into account that (for $x \leq 1$) $\partial f(x, a) / \partial x = -a \ln(x)$ and using (A1) one has

$$\frac{\partial F_k}{\partial n^j} = a_{(k)} \ln(\chi^S(\mathbf{b},$$

$$\mathbf{b}_{(k)})/w_{(k)})(n_{(k_q)}^j + m_{ji} m_{ii}^{(k_q)} n_{(k_q)}^i) / (2w_{(k)} \chi^S(\mathbf{b}, \mathbf{b}_{(k)})),$$

where $(\mathbf{m}^{k_q}, \mathbf{n}_{k_q}) \doteq S_q(\mathbf{b}_k)$ corresponds to a point closest to \mathbf{b} among those symmetrically equivalent to \mathbf{b}_k . The above sequence of relations (in reverse order) allows us to determine ξ from the model of γ for all of its domain except some isolated points (e.g. centers of the cusps). In practical terms, the presence of those points is immaterial due to the numerical and statistical nature of the procedure.

Generation of triple junctions' geometry

The first step in the construction of an equilibrated triple junction is to generate three random grain orientations $\bar{\mathbf{o}}^s$ ($s = 1, 2, 3$), and to calculate the misorientations $\mathbf{m}^1 = \bar{\mathbf{o}}^1 (\bar{\mathbf{o}}^2)^T$, $\mathbf{m}^2 = \bar{\mathbf{o}}^2 (\bar{\mathbf{o}}^3)^T$, $\mathbf{m}^3 = \bar{\mathbf{o}}^3 (\bar{\mathbf{o}}^1)^T$. Moreover, a random unit vector is taken as the direction $\bar{\mathbf{t}}$ of the triple line.

The main task is to determine the three normals to the boundary planes in such a way that the equilibrium condition is satisfied. The vector $\bar{\mathbf{n}}_1$, normal to the first boundary, is chosen randomly with a condition that it is perpendicular to the junction ($\bar{\mathbf{n}}_1 \cdot \bar{\mathbf{t}} = 0$). As for the normals $\bar{\mathbf{n}}_2$ and $\bar{\mathbf{n}}_3$, they are calculated by minimizing $F = \zeta \cdot \zeta$, where $\zeta = (\bar{\xi}_1 + \bar{\xi}_2 + \bar{\xi}_3) \times \bar{\mathbf{t}}$ and $\bar{\xi}_s$ are the capillarity vectors for particular boundaries. The vectors $\bar{\xi}_s$ are given by $\bar{\xi}_s = (\bar{\mathbf{o}}^{(s)})^T \xi(\mathbf{b}_{(s)})$, where ξ at the point $\mathbf{b}_s \doteq (\mathbf{m}^s, \mathbf{n}_s) = (\mathbf{m}^s, \bar{\mathbf{o}}^{(s)} \bar{\mathbf{n}}_{(s)})$ is obtainable directly from the model of γ in a way described in the previous subsection. With fixed $\bar{\mathbf{o}}^s$, $\bar{\mathbf{t}}$ and $\bar{\mathbf{n}}_1$, the quantity F is a function of $\bar{\mathbf{n}}_2$ and $\bar{\mathbf{n}}_3$; the latter are requested to satisfy the conditions $\bar{\mathbf{n}}_2 \cdot \bar{\mathbf{t}} = 0 = \bar{\mathbf{n}}_3 \cdot \bar{\mathbf{t}}$. A standard numerical procedure is used to determine $\bar{\mathbf{n}}_2$ and $\bar{\mathbf{n}}_3$ which minimize F . If the minimum of F does not reach a sufficiently small value, the junction is rejected and new $\bar{\mathbf{t}}$ and $\bar{\mathbf{n}}_1$ are generated.

The described procedure does not simulate a microstructure; it is limited to generating *individual* equilibrated triple junctions. Moreover, the vector $\bar{\mathbf{n}}_1$ is generated randomly, which means that we allow all crystallographic planes as the boundary plane \mathbf{n}_1 . Nevertheless, the generated junctions are considered to be sufficiently good for testing the reconstruction method.

APPENDIX B

This appendix introduces the capillarity vector via the classical variational technique. We begin with a reminder of some simple facts from the elementary differential geometry of surfaces. (See, e.g. Goetz [27].) Let a surface Σ be parameterized by (u^1, u^2) , and let $x^i = x^i(u^\alpha)$ ($i = 1, 2, 3$, $\alpha = 1, 2$) denote Cartesian coordinates of a point of the surface. It is assumed that the functions $x^i(u^\alpha)$ are of class C_2 . The dot will be used to denote derivatives with respect to u^α , e.g. $\dot{x}_\alpha^i = \partial x^i / \partial u^\alpha$. The first fundamental form (metric tensor) of the surface is defined as $g_{\alpha\beta} = \dot{x}_\alpha^i \dot{x}_\beta^i$. The relation $g_{\alpha\beta} g^{\beta\mu} = \delta_\alpha^\mu$ defines the contravariant form $g^{\beta\mu}$ of the metric tensor. The vector product s^i of tangent vector \dot{x}_1^i and \dot{x}_2^i can be expressed as

$$s^i = \varepsilon_{ijk} \varepsilon^{\alpha\beta} \dot{x}_\alpha^j \dot{x}_\beta^k / 2.$$

The vector s^i is normal to the surface and satisfies $s^i s^i = \det(g_{\alpha\beta})$. We use \sqrt{g} to denote $\sqrt{\det(g_{\alpha\beta})}$. It is assumed that there are no singular points, i.e. for each point of the surface $\sqrt{g} \neq 0$. Vector $n^i = s^i / \sqrt{g}$ is a unit vector normal to the surface. Both \sqrt{g} and n^i depend on \dot{x}_α^i via dependence on s^i , e.g. $n^i = n^i(s^i(\dot{x}_\alpha^i))$. Later on, we will use the following relations involving derivatives of s^k :

$$(a) \quad \frac{\partial s^k}{\partial \dot{x}_\alpha^i} \dot{x}_\beta^i = \delta_\beta^\alpha s^k, \quad (b)$$

$$\frac{\partial s^k}{\partial \dot{x}_\alpha^i} \dot{n}^i = -\sqrt{g} \dot{x}_\beta^k g^{\alpha\beta} \quad \text{and} \quad (c) \quad (A3)$$

$$\frac{d}{du^\alpha} \left(\frac{\partial s^k}{\partial \dot{x}_\alpha^i} \right) = 0.$$

The second fundamental form is defined as $b_{\alpha\beta} = -\dot{x}_\alpha^i \dot{n}_\beta^i$. It is directly related to the mean curvature H via $2H = g^{\alpha\beta} b_{\alpha\beta} = b_\alpha^\alpha$.

One wants to minimize the total energy which is given by $\Gamma = \int_\Sigma \gamma dS = \int_\Sigma \gamma \sqrt{g} du^1 du^2$, where γ depends on n^i , $\gamma(n^i) > 0$, and $dS = \sqrt{g} du^1 du^2$. For a particle of fixed volume V (bounded by a closed surface), one additionally has $3V = 3 \int_V dV = \int_V (\partial x^i / \partial x^i) dV = \int_\Sigma x^i s^i du^1 du^2$. Taking that condition into account, the Lagrangian $L = L(x^i, \dot{x}_\alpha^j)$ is given by

$$L = \gamma \sqrt{g} - \lambda x^i s^i. \quad (A4)$$

The case of the surface stretched on a fixed frame corresponds to $\lambda=0$. When the particle is considered, λ is a constant related to its volume.

The necessary condition for the integral $\int L(x^i, \dot{x}_\alpha^j) du^1 du^2$ to assume a minimum is $(\partial^2 L / \partial \dot{x}_\alpha^i \partial \dot{x}_\beta^j) \delta_\alpha \delta_\beta d^i d^j \geq 0$ for all δ_α and d^i (e.g. [28]). For L given by (A4), that condition is equivalent to the convexity of $\gamma \sqrt{g}$ as a function of s^i . This requirement seriously limits the scope of our analysis, but it does not affect the properties of the capillarity vector which are given below.

With $p_i^\alpha = \partial L / \partial \dot{x}_\alpha^i$ and $E^i = dp_i^\alpha / du^\alpha - \partial L / \partial x^i$, the surface minimizing the energy of the system is governed by the parameter invariance conditions $p_i^\alpha \dot{x}_\beta^i = \delta_\beta^\alpha L$, and by the Euler–Lagrange equations $E^i = 0$. (See, e.g. [28].)

The Hoffman–Cahn capillarity vector ξ is defined by

$$\xi^i = \frac{\partial}{\partial s^i} (\gamma \sqrt{g}).$$

Using ξ the moments p_i^α can be expressed as $p_i^\alpha = (\xi^k - \lambda x^k) \partial s^k / \partial \dot{x}_\alpha^i$. Due to equation (A3), one has $p_i^\alpha \dot{x}_\beta^i = \delta_\beta^\alpha (\xi^k - \lambda x^k) s^k$. Thus, the parameter invariance conditions lead to

$$\xi^k n^k = \gamma, \quad (A5)$$

which is the first of the Hoffman–Cahn relations concerning the capillarity vector. Using (A3c), E^i can be written as

$$E^i = (\xi_\alpha^k - \lambda \dot{x}_\alpha^k) \frac{\partial s^k}{\partial \dot{x}_\alpha^i} + \lambda s^i. \quad (A6)$$

For L which does not explicitly depend on u^α , there occurs $E^i \dot{x}_\mu^i = 0$ (cf. [28]). Multiplying (A6) by \dot{x}_β^i and using (A3), one gets $E^i \dot{x}_\beta^i = (\xi_\alpha^k -$

$\lambda \dot{x}_\alpha^k) \delta_\beta^\alpha s^k = \xi_\beta^k s^k$, and therefore,

$$\xi_\beta^k s^k = 0. \quad (A7)$$

From the above relation and from $\dot{\gamma}_\alpha = \xi_\alpha^k n^k + \zeta^k \dot{n}_\alpha^k$, one obtains

$$\dot{\gamma}_\alpha = \zeta^k \dot{n}_\alpha^k,$$

which is the second of the relations emphasized by Hoffman and Cahn [14].

Because of $E^i \dot{x}_\beta^i = 0$ the Euler–Lagrange equations are reduced to one scalar condition $E^i n^i = 0$. For E^i given by (A6), using (A3b), one obtains $E^i n^i = \sqrt{g} (3\lambda - g^{\alpha\beta} \xi_\alpha^k \dot{x}_\beta^k)$. Hence, one has

$$g^{\alpha\beta} \xi_\alpha^k \dot{x}_\beta^k = 3\lambda. \quad (A8)$$

It can be shown that $E^i n^i$ can be equivalently expressed as $E^i n^i = \sqrt{g} (3\lambda + b^{\alpha\beta} \dot{x}_\alpha^i \dot{x}_\beta^j h_{ij})$, where $h_{ij} = \gamma \delta_{ij} + \sqrt{g}^2 (\partial^2 \gamma / \partial s^i \partial s^j)$. This is an invariant form of the formula first obtained by Herring [13] in relation to the chemical potential near the surface of a particle; see also [29] and [15]. For constant γ , one has $h_{ij} = \gamma \delta_{ij}$, and the Euler–Lagrange equations lead to $2H = b_\alpha^\alpha = -3\lambda/\gamma$, which means that the mean curvature is constant. If $\lambda=0$, one gets $H = 0$, i.e. the well-known fact that the mean curvature vanishes for minimal surfaces. As for $\lambda \neq 0$, a closed simple surface with constant H is a sphere [30].

Let us also notice that because $\partial \sqrt{g} / \partial s^k = n^k$, the vector ξ^k can be expressed as $\xi^k = \gamma n^k + \sqrt{g} \partial \gamma / \partial s^k$. Due to (A5), the second (“torque”) term is a linear combination of \dot{x}_α^k ($\alpha=1, 2$), i.e. one can write $\xi^k = \gamma n^k + \tau^\alpha \dot{x}_\alpha^k$. Using the relations of Gauss and Weingarten, one obtains $\xi_{;\alpha}^k = (\dot{\gamma}_\alpha + \tau^\beta b_{\alpha\beta}) n^k + (\tau_{;\alpha}^\beta - \gamma b_{\alpha}^\beta) \dot{x}_\beta^k$, where the semicolon denotes the covariant derivative. Because ξ_α^k is perpendicular to n^k [equation (A7)], there occurs

$$\dot{\gamma}_\alpha + b_{\alpha\beta} \tau^\beta = 0 \quad \text{and} \quad \xi_{;\alpha}^k = (\tau_{;\alpha}^\beta - \gamma b_{\alpha}^\beta) \dot{x}_\beta^k. \quad (A9)$$

Substitution of the second expression into (A8) leads to $\tau_{;\alpha}^\alpha = 3\lambda + 2H\gamma$. Thus, by the divergence theorem, for a surface stretched on a frame, the energy weighted average of the mean curvature $\int_\Sigma H \gamma dS$ is determined by the value of the torque term τ^α on the boundary Σ . For a closed surface, because of $\int_\Sigma \tau_{;\alpha}^\alpha dS = 0$, the integral $\int_\Sigma H \gamma dS$ is equal to $-3\lambda/2$ times the area of Σ .

Finally, let us concentrate on the case of a particle. Vector ξ_α^k is tangent to the surface, so it can be expressed as $\xi_\alpha^k = A_\alpha^\beta \dot{x}_\beta^k$; see equation (A9). The observation of Hoffman and Cahn [14] that $A_\alpha^\beta = \text{const} \cdot \delta_\alpha^\beta$ or $x^i = a \zeta^i + d^i$ (with constant a and d^i) allows one to relate the above considerations to the Wulff construction. A pedal of Σ with respect to a point c^i is composed of points $p^i = c^i + n^i n^k (x^k - c^k)$, [16]. For $c^i = d^i$ the translate

$p^i - c^i$ of the pedal is given by $p^i - c^i = n^i n^k (x^k - c^k) = a n^i n^k \xi^k = a n^i \gamma$. This leads to the Frank's [16] version of the Wulff theorem (limited by the convexity requirement mentioned above): for the surface minimizing Γ , there exists a point c^i such that the γ -plot is the scaled pedal of the surface with respect to

that point. The relation $x^i = a \xi^i + d^i$ also allows us to determine the constant λ . Equation (A8) leads to $a = 2/(3\lambda)$, and the substitution of x^i in the formula for volume $3V = \int x^i n^i dS$ and equation (A5) give $9\lambda V = 2\Gamma_{\min}$, where Γ_{\min} is the minimal value of Γ (attained for that surface).