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ScienceDirect
Acta Materialia 55 (2007) 467–471
Acta MATERIALIA
www.actamat-journals.com

Properties and determination of the interface stiffness

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Received 27 June 2006; received in revised form 18 August 2006; accepted 18 August 2006
Available online 25 October 2006

Abstract

The chemical potential of a curved interface contains a term that is proportional to the product of the interface curvature and the interface stiffness. In crystalline materials, the interface stiffness is a tensor. This paper examines several basic issues related to the properties of the interface stiffness, especially the determination of the interface stiffness in particular directions (i.e. the commonly used scalar form of the interface stiffness). Of the five parameters that describe an arbitrary grain boundary, only those describing the inclination are crucial for the scalar stiffness. We also examine the influence of crystal symmetry on the stiffness tensor for both free surfaces and grain boundaries. This results in substantial simplifications for cases in which interfaces possess mirror or rotational symmetries. An efficient method for determining the interface stiffness tensor using atomistic simulations is proposed.

Keywords: Interface migration; Interface stiffness; Surface energy; Grain boundary migration

1. Introduction

The interface stiffness is the coefficient of the interface curvature in the description of the capillarity contribution to the chemical potential. In curvature-driven interface migration, the interface velocity is proportional to the interface stiffness, mobility and curvature. As a result, the interface stiffness is the key material property that relates interface curvature to interface thermodynamics and kinetics. The determination of interface stiffness is, however, extremely difficult. In the past several years, there have been several attempts to determine the stiffness using atomistic simulation methods (e.g. Ref. [1] is a pseudo-three-dimensional study of a grain boundary and Ref. [2] is a pseudo-three-dimensional study of a liquidsolid interface based on two-dimensional stiffness). Recently, the thermal fluctuation-based method [2] for liquid–solid interface stiffness was generalized to study the interface stiffness of grain boundaries in 3D and showed a relatively mild anisotropy for a boundary in Ni [3]. The interface stiffness depends not only on interface orientation but also the direction of the curvature. In fact, the interface stiffness in three dimensions is a 2×2 tensor whose components vary with all of the parameters that specify the interface crystallography (for grain boundaries, there are five such parameters – including inclination and misorientation). For the special case of a special $\Sigma 7[1\,1\,1]$ – tilt asymmetric grain boundary, it was observed that the interface stiffness had a twofold symmetry and could be fitted with a simple trigonometric function [3,4].

In this note, we examine several basic issues regarding interface stiffness and describe a practical approach for determining it. In particular, we examine the essential difference between the stiffness and the stiffness tensor, and provide an analytical form that relates the two. The relationship demonstrates that the trigonometric dependence of the stiffness upon the direction of curvature [3] found in the atomistic simulation of a special Σ asymmetric grain boundary has a fundamental basis and is a common feature of general anisotropic interfaces. Based on this relationship, we describe a method for efficiently determining

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1359-6454/$30.00
doi:10.1016/j.actamat.2006.08.038

the stiffness tensor from atomistic simulations. Finally, we examine the influence of crystal symmetry on the stiffness tensor for both free surfaces and grain boundaries. The results were found to be consistent with the distribution of grain boundary types in polycrystalline materials.

2. Free surface stiffness tensor

Consider a solid surface at which the solid is in contact with a vacuum, vapor or liquid. If the only driving force for surface evolution is capillarity and the only operative evolution mechanism is evaporation/condensation [5], the surface velocity in two-dimensions (i.e. a one-dimensional surface) is

$$V = -M(\gamma + \gamma'')\kappa = -M\Gamma\kappa \tag{1}$$

where M is mobility, γ is the surface free energy, κ is the curvature, the double prime indicates the second derivative with respect to the orientation of the surface normal and the surface stiffness is $\Gamma = (\gamma + \gamma'')$.

In three dimensions (i.e. a two-dimensional surface), the surface energy γ is a function of the surface normal $\mathbf{n}$. In this case, the surface evolves under evaporation/condensation kinetics with the curvature as

$$V = -M\boldsymbol{\Gamma} : \boldsymbol{\kappa} = -M[(\gamma(\mathbf{n})\mathbf{1} + \nabla_{\mathbf{n}}\nabla_{\mathbf{n}}\gamma(\mathbf{n})) : \boldsymbol{\kappa}] \tag{2}$$

where $\nabla_{\mathbf{n}}$ is the surface gradient on the unit sphere of interface normal $\mathbf{n}$,

$$\boldsymbol{\Gamma}(\mathbf{n}) = (\gamma\mathbf{1} + \nabla_{\mathbf{n}}\nabla_{\mathbf{n}}\gamma) \tag{3}$$

is the stiffness tensor, $\boldsymbol{\kappa} = \nabla_{\mathbf{n}}$ is the curvature tensor and $\mathbf{A}{:}\mathbf{B} = A_{ij}B_{ij}$.

In two dimensions, the stiffness $\Gamma(\mathbf{n})$ is a scalar function and in three dimensions the stiffness tensor $\boldsymbol{\Gamma}(\mathbf{n})$ is a second rank, symmetric tensor function of the surface normal $\mathbf{n}$. The value of the stiffness at a point depends on the direction the surface is curved at that point. If $\mathbf{t}$ is the tangent direction in which the surface is curved, then $\mathbf{T}$ is the space of all such tangent vectors perpendicular with normal $\mathbf{n}$, i.e.

$$\mathbf{T}(\mathbf{n}) = \{\mathbf{t} | \mathbf{t}\cdot\mathbf{n} = 0,\ |\mathbf{t}| = 1\} \tag{4}$$

Choosing fixed orthogonal unit reference vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ in the tangent plane at $\mathbf{n}$, the tangent vector set $\mathbf{T}$ can be parameterized by

$$\mathbf{T}(\mathbf{n}) = \{\mathbf{t} | \mathbf{t}(\theta) = \cos\theta\mathbf{e}_1 + \sin\theta\mathbf{e}_2,\ \theta \in [0, 2\pi]\} \tag{5}$$

where θ is the angle between the tangent vector $\mathbf{t}$ and $\mathbf{e}_1$.

We now relate the general stiffness tensor to the value of the stiffness at a particular point P on a surface which is curved in a particular direction along $\mathbf{t}(\theta)$. Since we are only concerned about this one curvature direction, we focus on the case where the other principal curvature (the principle curvature directions are orthogonal to each other) has zero magnitude. Then, the curvature tensor is

$$\boldsymbol{\kappa} = \kappa\mathbf{t}(\theta) \otimes \mathbf{t}(\theta) \tag{6}$$

where $(\mathbf{A} \otimes \mathbf{B})_{ij} = A_iB_j$. Substituting this relation into Eq. (2), the stiffness $\Gamma(\theta)$ in the tangent orientation $\mathbf{t}(\theta)$ is

$$\Gamma(\theta;\mathbf{n}) = \mathbf{t}(\theta)\cdot\boldsymbol{\Gamma}(\mathbf{n})\cdot\mathbf{t}(\theta). \tag{7}$$

We can rewrite this general form for the stiffness explicitly as

$$\Gamma(\theta;\mathbf{n}) = \Gamma_{11}\cos^2\theta + \Gamma_{22}\sin^2\theta + \Gamma_{12}\sin 2\theta \tag{8}$$

$$= \Gamma_{11}\frac{1+\cos 2\theta}{2} + \Gamma_{22}\frac{1-\cos 2\theta}{2} + \Gamma_{12}\sin 2\theta \tag{9}$$

$$= \frac{\Gamma_{11}+\Gamma_{22}}{2} + \frac{\Gamma_{11}-\Gamma_{22}}{2}\cos 2\theta + \Gamma_{12}\sin 2\theta, \tag{10}$$

where Γ_{11}, Γ_{22} and Γ_{12} are all three unique components of the symmetric stiffness tensor $\boldsymbol{\Gamma}(\mathbf{n})$, measured with respect to the reference orthogonal unit vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ in the tangent plane at $\mathbf{n}$. Therefore, only three parameters are required to determine the stiffness tensor and the dependence of the stiffness on the tangent orientation at each surface normal orientation $\mathbf{n}$.

Examination of Eq. (10) shows that the stiffness $\Gamma(\theta;\mathbf{n})$ possesses a twofold rotational symmetry in the tangent space at $\mathbf{n}$. This is not surprising, since $\boldsymbol{\Gamma}(\mathbf{n})$ is a 2nd rank tensor. Interestingly, this twofold rotational symmetry is present even if the underlying material possesses no such symmetry.

Note that, although we have a stiffness tensor for the three-dimensional case (i.e. the stiffness is a function of both surface orientation $\mathbf{n}$ and tangent orientation $\mathbf{t}(\theta)$ in the tangent space at $\mathbf{n}$), the mobility M for evaporation/condensation in Eq. (2) is a scalar and is a function of surface orientation $\mathbf{n}$ only.

3. Interface stiffness tensor

For general interfaces, such as grain boundaries in polycrystalline materials, the situation is further complicated by the larger number of degrees of freedom that grain boundaries possess. It is important to unify the language used to determine grain boundary geometry and that used to determine interface stiffness.

Consider a boundary separating two grains, I and II (i.e. the grain boundary in a bicrystal). Five parameters are necessary to fully describe the bicrystallography of such a boundary. These five parameters can be divided into two sets. The first set S_1 indicates misorientation; three independent parameters are required to specify the rotation of grain II with respect to grain I. The second set S_2 indicates the inclination of the interface normal $\mathbf{n}$; two independent parameters are required to specify the normal direction.

Thus the grain boundary energy is parameterized by

$$\gamma = \gamma(\mathbf{n}; S_1) \tag{11}$$

The grain boundary stiffness tensor is

$$\boldsymbol{\Gamma}(\mathbf{n}; S_1) = (\gamma(\mathbf{n}; S_1)\mathbf{1} + \nabla_{\mathbf{n}}\nabla_{\mathbf{n}}\gamma(\mathbf{n}; S_1)) \tag{12}$$

where, similar to the free surface interface discussed previously, $\nabla_{\mathbf{n}}$ is the surface gradient on the unit sphere of grain boundary normal $\mathbf{n}$. Conceptually, in order to determine the stiffness tensor, we first fix the misorientation S_1

between the two grains and write the grain boundary energy as $\gamma_{S_1}(\mathbf{n}) = \gamma(\mathbf{n}; S_1)$. Thus the stiffness for each tangent orientation $\Gamma_{\mathbf{n};S_1}(\theta)$ is related to the stiffness tensor $\mathbf{\Gamma}(\mathbf{n}; S_1)$ through a similar relationship as for the free surface

$$\Gamma_{\mathbf{n};S_1}(\theta) = \frac{\Gamma_{11}+\Gamma_{22}}{2} + \frac{\Gamma_{11}-\Gamma_{22}}{2}\cos 2\theta + \Gamma_{12}\sin 2\theta \qquad (13)$$

Here, Γ_{11}, Γ_{22} and Γ_{12} are components of $\mathbf{\Gamma}(\mathbf{n}; S_1)$ with respect to the orthogonal reference unit vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ in the tangent plane at $\mathbf{n}$ for misorientation S_1. We emphasize that how the stiffness depends on the direction in which the boundary curves is completely characterized by the stiffness tensor.

4. Determination of the interface stiffness tensor

It is possible to determine the interface stiffness directly from molecular dynamics simulations, as shown by Ref. [2] using quasi-two-dimensional simulations. Due to its complexity, few efforts were devoted to determine stiffness tensors. For a weak anisotropic interface (such as a solid–liquid interface near melting temperature), it is possible to determine interface energy directly using lower order harmonic expansion together with a thermal fluctuation-based method [2]. For mild or strong anisotropy, harmonic expansion involves many terms. However, it is still possible to determine the grain boundary stiffness tensor directly from molecular dynamics simulations with three-dimensional configurations, as shown by Ref. [3], using the thermal fluctuation method. Due to the three-dimensional nature of the simulations, it is necessary to employ a very large simulation cell in all directions to allow sufficient freedom for the boundary profile to fluctuate in all directions. This requires more simulation efforts than quasi-two-dimensional simulations.

However, based on the previous analysis, we can devise a scheme that requires no more than three traditional quasi-two-dimensional simulations to determine the full stiffness tensor $\mathbf{\Gamma}(\mathbf{n}; S_1)$ and thus the dependence of the stiffness on the orientation of the tangent direction in which the boundary curves. In such quasi-two-dimensional simulations, the simulation cell would be long in one direction parallel to the nominal boundary plane and very thin in the orthogonal direction (i.e. orthogonal to this direction and the boundary normal). Using this elongated simulation cell, it is possible to determine the stiffness in the long direction (i.e. the long direction is parallel to the tangent orientation $\mathbf{t}(\theta)$). If we do three simulations with the long axis of the simulation cell oriented in three different directions, it is possible to extract the full boundary stiffness tensor for any set of $\mathbf{n}$ and S_1. Such an approach would be much more efficient that performing such a simulation on a large three-dimensional simulation cell.

Firstly, we choose two orthogonal reference orientations $\mathbf{e}_1$ and $\mathbf{e}_2$ in the tangent plane at $\mathbf{n}$ for misorientation S_1. Next, we run simulations for three quasi-two-dimensional cells (as described above) with the long axis parallel to three orientations $\mathbf{t}(\theta)$ with $\theta = 0$, $\frac{\pi}{4}$ and $\frac{\pi}{2}$, respectively, where θ is the angle between $\mathbf{t}$ and $\mathbf{e}_1$. Using the thermal fluctuation method, this will yield three values of stiffness: $\Gamma_{\mathbf{n};S_1}(0)$, $\Gamma_{\mathbf{n};S_1}(\frac{\pi}{4})$ and $\Gamma_{\mathbf{n};S_1}(\frac{\pi}{2})$. Using Eq. (13), we have

$$\Gamma_{\mathbf{n};S_1}(0) = \Gamma_{11} \qquad (14)$$

$$\Gamma_{\mathbf{n};S_1}\left(\frac{\pi}{4}\right) = \frac{\Gamma_{11}+\Gamma_{22}}{2} + \Gamma_{12} \qquad (15)$$

$$\Gamma_{\mathbf{n};S_1}\left(\frac{\pi}{2}\right) = \Gamma_{22} \qquad (16)$$

Solving this set of equations for Γ_{11}, Γ_{22} and Γ_{12} gives

$$\Gamma_{11} = \Gamma_{\mathbf{n};S_1}(0) \qquad (17)$$

$$\Gamma_{22} = \Gamma_{\mathbf{n};S_1}\left(\frac{\pi}{2}\right) \qquad (18)$$

$$\Gamma_{12} = \Gamma_{\mathbf{n};S_1}\left(\frac{\pi}{4}\right) - \frac{\Gamma_{\mathbf{n};S_1}(0) + \Gamma_{\mathbf{n};S_1}\left(\frac{\pi}{2}\right)}{2} \qquad (19)$$

We expect that this approach is at least seven times more efficient than the straightforward three-dimensional approach.

5. Interface symmetries

While the discussion presented above was completely general, crystalline materials necessarily exhibit certain symmetries that decrease the relevant parameter space. Most interfacial properties (e.g. grain boundary energy, surface energy) exhibit extrema (often cusps) for particular high symmetry orientations (misorientations, inclinations). Therefore, it is reasonable to assume that crystal symmetry may play an important role in interface stiffness as well. In this section, we examine the effects of crystal symmetry operations on the stiffness tensor and see how symmetry can reduce the number of unknowns.

Firstly, if there is a mirror plane orthogonal to the interface, then we can choose $\mathbf{e}_1$ such that it is the intersection of the interface and the mirror plane. In this case, the interface tensor must be an even function of θ in Eq. (13) and, therefore, $\Gamma_{12} = 0$, where $\mathbf{e}_2$ is orthogonal to $\mathbf{e}_1$ and both are principal directions of the stiffness tensor (i.e. the stiffness tensor is diagonal). When there is a mirror plane perpendicular to an interface, only two simulations are necessary to determine the stiffness tensor. All free surfaces that are perpendicular to a mirror plane of the bulk crystal possess a mirror symmetry. Table 1 shows a complete list of such surfaces in common cubic and hexagonal materials.

For grain boundaries, the symmetry is determined by the common symmetries of grains on both sides of the interface. For grain boundaries, the condition for mirror symmetry is more restricted. In order to possess a mirror symmetry, the interface must be perpendicular to a special plane which is a mirror plane of the bulk crystals of both grains I and II. Thus there are three classes of possible misorientations: (a) pure tilt boundaries with a tilt axis corresponding to the normal to a mirror plane common to both grains (valid for any misorientation (Σ or non-Σ) and any

Table 1
All of the surfaces and grain boundaries in cubic and hexagonal crystals that exhibit a mirror plane perpendicular to the interface

Crystal class	Free surface	Grain boundary
Cubic		[001] or [110] tilt axes
	$(hk0)$; (001) mirror plane	90° twist about $[1\bar{1}0]$; mirror planes (001) and(110)
	$(h\bar{h}k)$; (110) mirror plane	60° twist about [111]; mirror planes $(1\bar{1}0)$ and $(\bar{1}01)$
		45° twist about [100]; mirror planes (001) and (011)
HCP		[0001] or $[1\bar{1}00]$ tilt axes
	$(hkl0)$; (0001) mirror plane	60° twist about [0001]
	$(\frac{h}{2}\frac{h}{2}\bar{h}n)$; $(1\bar{1}00)$ mirror plane	90° twist about [1210]

inclination angle); (b) pure twist boundaries with a twist axis corresponding to the intersection of two mirror planes in the underlying crystal and with a twist angle equal to the angle between these two mirror planes; and (c) mixed tilt/twist boundaries, provided that the twist component is as described in (b) followed by a tilt with the tilt axis perpendicular to the mirror plane. A complete list of pure tilt and pure twist grain boundaries in cubic and hexagonal materials that have mirror symmetries is provided in Table 1. For boundaries in other crystal classes, the symmetry can be obtained by removing symmetry elements from one of these two classes.

For interfaces with threefold or higher rotational symmetries, the stiffness tensor is isotropic, i.e. the stiffness is independent of the direction(s) about which the interface is curved. In such cases, only one simulation is required to determine the stiffness tensor, i.e.

$$\Gamma_{11} = \Gamma_{22} = \Gamma, \quad \Gamma_{12} = 0. \tag{20}$$

Some examples of interfaces with three- and fourfold rotational symmetries are listed in Table 2. Note, in some hexagonal systems, the {0001} planes actually possess sixfold symmetry as induced by the isogonal symmetry. This, however, does not change the conclusion that the stiffness is isotropic.

6. Discussion

This paper focused on the relation between interface stiffness and the interface stiffness tensor. The stiffness is the increase in the energy of an interface resulting from curving the interface in one direction. The stiffness tensor measures the stiffness for curving in an arbitrary direction (this includes curving along one or two arbitrary axes). This relation is represented analytically in Eq. (13). The relationship demonstrates that the trigonometric dependence of the stiffness on the direction of the axis of curvature observed in atomistic simulations for a special Σ asymmetric grain boundary [3] is mandated by the mathematics and is a common feature of general anisotropic interface. Based on this general relationship, we propose an approach for measuring the full stiffness tensor that results in significantly more efficient simulations than previous efforts.

Table 2
Examples of surfaces and grain boundaries that have three- and fourfold rotation axes perpendicular to the interface

n-Fold rotational symmetry	Free surface	Grain boundary
3	{111} in cubic	(111)|⟨111⟩ twist in cubic
	{0001} in HCP	(0001)|⟨0001⟩ twist in hexagonal
4	{100} in cubic	(100)|⟨100⟩ twist in cubic

Symmetry considerations can be used to simplify the stiffness tensor, leading to a full description with fewer parameters. Two particular types of symmetry are noteworthy: mirror planes and *n*-fold rotational symmetries, with $n \geqslant 3$. We identified all of the surfaces and grain boundaries in cubic and hexagonal crystals for which such mirror symmetries may be present (see Table 1). For grain boundaries with mirror symmetry, the interface stiffness tensor has only two unique parameters. For grain boundaries containing threefold or higher rotational symmetries, the stiffness tensor is isotropic and therefore is fully described by a single parameter.

Recent experimental observations of the population of grain boundary planes in a polycrystalline, cubic aluminum was not random; nor was it determined by the density of coincident lattice points [6]. This study showed that (001), (110) and (111) boundary planes appear significantly more often than expected. Examination of Table 1 shows that these boundaries are special in the sense that they possess mirror symmetries. The experimental measurements of the boundary population in polycrystalline aluminum [6] indicate that (111)|⟨111⟩ and (100)|⟨100⟩ (boundary plane, rotation axis pairs) boundaries (i.e. pure twist) occur with a higher probability than other boundaries, regardless of the twist angle. Examination of Table 2 shows that (111)|⟨111⟩ and (100)|⟨100⟩ boundaries in a cubic material have three- and fourfold rotational symmetry, respectively. In particular, the 60° twist (111)|⟨111⟩ boundary was observed to have the largest population amongst all of the ⟨111⟩(111) boundaries [6]. The 60° (111)|⟨111⟩ twist boundary also possesses a mirror symmetry with a coincident site lattice density Σ3. This is the only grain boundary in a cubic system that has both a mirror symmetry and a threefold rotational symmetry. While we have not established the link between grain boundary stiffness and grain boundary population density, these observations do show that boundaries that are special from the point of view of stiffness are also special from the

point of view of population in a polycrystalline material. This suggests that when the grain boundary distribution is determined by grain growth (as in the aluminum experiments), the boundary stiffness is the key parameter that determines the grain boundary population. At this point, however, this remains conjecture.

Acknowledgements

The authors gratefully acknowledge the support of the US Department of Energy, Grant No. DE-FG02-99ER45797, and the Computational Materials Science Network.

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