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#### Multiscale modeling approach for calculating grain-boundary energies from first principles

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A multiscale modeling approach is proposed for calculating energies of tilt-grain boundaries in covalent materials from first principles over an entire misorientation range for given tilt axes. The method uses energies from density-functional calculations for a few key structures as input into a disclination structural-units model. This approach is demonstrated by calculating energies of  $\langle 001 \rangle$ -symmetrical tilt-grain boundaries in diamond. [S0163-1829(98)50806-5]

Predicting brittle fracture strengths of polycrystalline materials requires detailed knowledge of energetic stabilities and stress concentrations at grain boundaries and related defects such as triple junctions. In principle, structures and energies of grain boundaries can be accurately calculated at the atomic scale using density-functional methods.<sup>1</sup> In practice, however, first-principles calculations can be extremely computationally intensive, especially for systems having long-range stress fields that require a large number of atoms. Alternatively, grain boundaries can be modeled at the atomic scale using empirical and semiempirical potentials.<sup>2</sup> While much larger systems can be treated with this approach, results produced by analytic potentials vary widely in reliability.<sup>3</sup> This limits their use for predicting quantitative properties of grain boundaries.

One approach in which system size limitations can be overcome is through the use of multiscale modeling in which different length scales are treated with different methods. Gumbsch and co-workers,<sup>4</sup> for example, have developed a method in which local defect structures are treated with an atomic model, and long-range stresses are calculated using a finite element approach. The key to this type of multiscale

modeling is the development of methods that satisfactorily couple the atomic-level and finite-element techniques.

In this paper, a multiscale modeling approach is introduced for predicting energetics of grain boundaries with arbitrary misorientation angles for low index tilt axes. This scheme combines atomic-scale first principles (FP) calculations with a mesoscopic-scale disclination-structural units model (DSUM). The central idea of this FP-DSUM multiscale modeling approach is to construct properties of related grain boundaries from a few key structures carefully chosen so that they are accessible to accurate first-principles methods. This allows first-principles predictions of the energies of not only short-period, coincidence-site-lattice grain boundaries, but also grain boundaries with long periods having large reciprocal coincidence site densities,  $\Sigma$ .

The idea of constructing properties of grain boundaries (GBs) with low-index tilt axes from a subset of structures is not new. Sutton and Vitek, for example, proposed a structural units model (on which our technique is based) for tilt-grain boundaries in metals over a decade ago.<sup>5</sup> Similarly, a disclination description of grain boundaries was developed by Shih and Li in the 1970s,<sup>6</sup> and density-functional calcu-

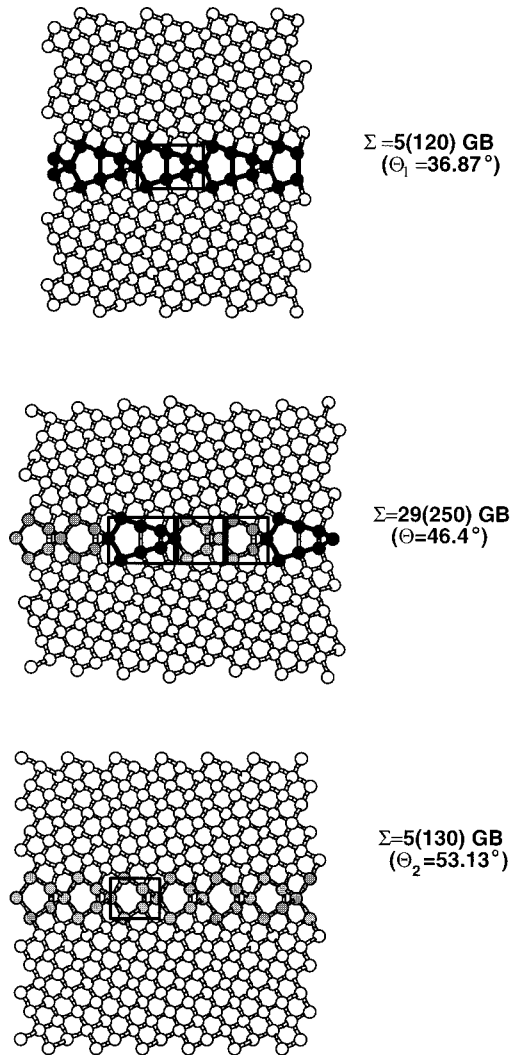


FIG. 1. The grain boundaries illustrated at the top and bottom of the figure each contain a single structural unit indicated by the superimposed boxes. The center structure, which represents a grain boundary at an intermediate angle, is composed of a mix of the structural units from the two delimiting grain-boundary structures.

lations on selected grain boundaries (usually short-period coincident site structures) in covalent materials have been reported by a number of researchers.<sup>1</sup> The combination of these techniques, however, is a unique aspect of our approach which provides a powerful synergy for materials modeling.

According to the Sutton-Vitek model, for a given tilt axis there are short-period grain-boundary structures consisting of a single type of structural unit from which all related grain boundaries at misorientation angles in the range delimited by these structures can be constructed (see Fig. 1 as an example). Based on this principle, Sutton and Vitek developed a structural-units-grain-boundary dislocation model in which the minority structural units are dislocation cores.<sup>5</sup> Using this model and an extension of the Read-Shockley equation,<sup>7</sup> Wang and Vitek<sup>8</sup> predicted energy versus misorientation angle curves for  $\langle 001 \rangle$  and  $\langle 111 \rangle$  tilt-grain boundaries in copper from atomistic calculations using an analytic pair potential. While proving the validity of the structural-units model, their calculations required not only energies of single-structural-unit grain boundaries, but also energies for

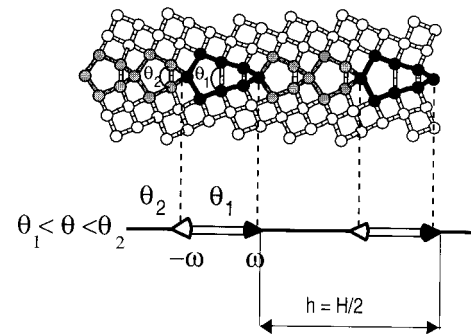


FIG. 2. Illustration of the disclination dipole wall formed by the structural units within the grain boundary shown in the center of Fig. 1.

additional grain boundaries between the single-structural-unit delimiting structures. This required, for example, calculations on a total of 11 tilt angles for the  $\langle 001 \rangle$  tilt axis. This is a consequence of using dislocations as structural units, and results from limitations of the Read-Shockley formula for defining the elastic energy of dense dislocation walls and the need to determine a dislocation core radius for each subinterval over which the Read-Shockley formula is used. The single-structural-unit grain boundaries have short repeat units and stress fields that tend to be more localized than other structures; therefore smaller systems can be used to satisfactorily model these structures at the atomic scale. Structures at intervening angles, however, have longer repeat cells and less localized stress fields. While calculating energies for these structures is not difficult with analytic potentials, they can be prohibitively large for first-principles calculations.

When the structural units are taken as disclination dipoles, a new structural parameter, namely, the separation of disclinations in a dipole, is introduced in the elastic energy. This overcomes the limitation of the Read-Shockley formula. As a result, the elastic energy term [see Eq. (2) below] is well defined at any separation of disclination dipoles. In addition, part of the dislocation core energy becomes included in the elastic energy. The result is that the disclination model requires a single parameter (discussed below) associated with the disclination cores to define the energy for the entire misorientation range to complete the disclination core energy calculations.

As illustrated in Fig. 2, the junctions where different types of structural units meet can be described by disclinations of strength  $\pm\omega = \pm(\theta_2 - \theta_1)$ , where  $\theta_1$  and  $\theta_2$  are the misorientation angles of the delimiting single-structural-unit grain boundaries. Thus, the minority structural units can be represented as dipoles of disclinations. This leads to the structure of an intermediate grain boundary being described as a disclination dipole wall with a total energy given<sup>9</sup> as a weighted sum of the energy of the individual structural units,

$$\frac{md_1e_1 + nd_2e_2}{h}, \quad (1)$$

the elastic energy of the disclination dipole wall,

$$\frac{G\omega^2h}{32\pi^3(1-\nu)} \left\{ f(\lambda) + \sum_{i=1}^{n-1} \sum_{j=i+1}^n [f(\tilde{y}_j - \tilde{y}_i + \lambda) - 2f(\tilde{y}_j - \tilde{y}_i)] \right\}$$

$$\left. + f(\tilde{y}_j - \tilde{y}_i - \lambda) \right\}, \quad (2)$$

and the energy of the disclination cores,

$$\alpha \frac{Ga_0^2 \omega^2 n}{32\pi^3(1-\nu)h}. \quad (3)$$

In Eqs. (1)–(3)  $m$  and  $n$  are the numbers of the first and second types of structural unit in a disclination dipole wall with period  $h$ ,  $d_1$  and  $d_2$  are their lengths,  $e_1$  and  $e_2$  are the energies of the delimiting grain boundaries composed of these units,  $\tilde{y}_i = \pi y_i / h$ ,  $\lambda = \pi d_2 / h$ , where  $y_i$  are the coordinates of disclination dipoles,  $G$  and  $\nu$  are the shear modulus and Poisson ratio of the bulk material, respectively,  $a_0$  is the lattice parameter, and  $\alpha$  is a parameter discussed below. The function  $f(t)$ , which was derived by Shih and Li,<sup>6</sup> is given by

$$f(t) = -16 \int_0^t (t-v) \ln[2 \sin(v)] dv. \quad (4)$$

The period  $h$  of a disclination dipole wall is one-half of the period of the grain-boundary atomic structure for centered boundaries (the period of a centered grain boundary contains two equivalent cells shifted along the tilt axis<sup>5</sup>) (Fig. 2), and one period for noncentered grain boundaries.

With the exception of the parameter  $\alpha$ , all of the contributions to the energy of a grain boundary are well defined by the bulk elastic properties of the material and the energies of the delimiting grain boundaries. An assumption has been made<sup>9</sup> that the value of the parameter  $\alpha$  in the core energy contributions depends only on the disclination line and will be different for different tilt axes for a given material. The results of our calculations with empirical potential confirm this assumption. For a given tilt axis, this parameter can be conveniently obtained by fitting to the energy of a single misorientation angle containing a mix of structural units.

The approach outlined above is powerful for several reasons. First, it reduces the *number* of calculations needed to obtain energies for a large number of related grain-boundary structures. Second, by using the disclination dipoles as structural units, the inner cutoff radius associated with dislocations, which depends on their Burgers vector and therefore on the subinterval to be fitted, is replaced by a parameter  $\alpha$ . This parameter is valid over the entire range of misorientation and can therefore be evaluated from a single calculation, because core radii do not depend on disclination strength. Finally, the key structures used in the calculations have short repeat units and stress fields that are highly localized near the interface; this minimizes the *size* of the systems required for an accurate calculation. This feature facilitates the use of first-principles methods to estimate energies.

To demonstrate the accuracy of this multiscale modeling approach for a covalent material, energies obtained directly from a many-body analytic potential for  $\langle 001 \rangle$  symmetrical tilt grain boundaries at 12 misorientation angles are compared to values predicted by our multiscale method. The simulated grain-boundary structures were derived from a coincident-site lattice model proposed previously for group IV materials in which each atom is fourfold coordinated.<sup>10,11</sup> The initial structures were formed by rotating two crystals

TABLE I. Properties of diamond given by the analytic bond-order potential, the density-functional local-density approximation (DF/LDA) calculations, and experiments.

Property	Analytic Potential	DF/LDA	Experiment
Lattice constant (Å)	3.566	3.52	3.566 <sup>a</sup>
Bulk modulus (Mbar)	4.45	4.62	4.44 <sup>a</sup>
Shear modulus (Mbar)	5.4	5.23	5.0–5.5 <sup>b</sup>
$C_{11}$ (Mbar)	10.78	11.11	10.81 <sup>a</sup>
$C_{12}$ (Mbar)	1.31	1.38	1.25 <sup>a</sup>
$C_{44}$ (Mbar)	6.8	5.95	5.79 <sup>a</sup>
Stacking fault energy (J/m <sup>2</sup> )	0.0	0.224	0.279 <sup>b</sup>

<sup>a</sup>From Ref. 14.

<sup>b</sup>From Ref. 15.

around a common  $\langle 001 \rangle$  axes at an angle  $\theta$  with a median  $(110)$  plane. The resulting interface structures contain a mix of five-, six-, and seven-membered rings. The structures illustrated in Fig. 1 are examples of this model. Studies in our group of a large number of other possible candidate structures, some of which include  $\pi$  bonding, suggest that the fully coordinated structures are likely the lowest-energy structures for the interface in diamond. A possible exception that is being explored are two-phase grain boundaries containing small regions of graphite.<sup>12</sup> Nevertheless, these two-phase GBs may also be described by our multiscale approach. Generally, the model easily incorporates any possible structures of the basic grain boundaries, since the change of local atomic structure of the structural units affects the additive surface energy but does not change the other parts of the grain boundary energy.

The computational cells used in these calculations were periodic in the plane of the grain boundary, with hydrogen-terminated free surfaces in the direction perpendicular to the grain-boundary plane. Minimum energy structures for the coincident-site lattice model at 12 misorientation angles were obtained using an analytic many-body bond-order potential.<sup>13</sup> This function, which has been described previously,<sup>13</sup> reproduces a relatively large data base of solid-state and molecular properties of carbon, including the lattice constant, cohesive energy, and bulk elastic properties of diamond. A subset of these properties is given in Table I.

Energies for the grain boundaries given by the full atomistic calculations using the analytic potential versus misorientation angle are indicated by the circles in Fig. 3. The energies appear in three regions separated by energy cusps at misorientation angles of  $0^\circ$ ,  $36.87^\circ$ ,  $53.13^\circ$ , and  $90^\circ$ . The grain boundaries corresponding to the four cusps were chosen as the delimiting structures containing a single structural unit. Therefore these energies together with the elastic properties for the analytic potential given in the Table I and a value for the parameter  $\alpha$  can be used with Eqs. (1)–(4) to determine energies for any arbitrary misorientation angle between these cusps. A value for  $\alpha$  of 20 was determined by fitting the grain-boundary energy at a misorientation angle of  $28.07^\circ$ . This grain boundary contains two types of structural unit and has a relatively short period of 10.39 Å. The key structures (solid circles in Fig. 3) provided input for the calculation of the grain-boundary energies in the entire misori-

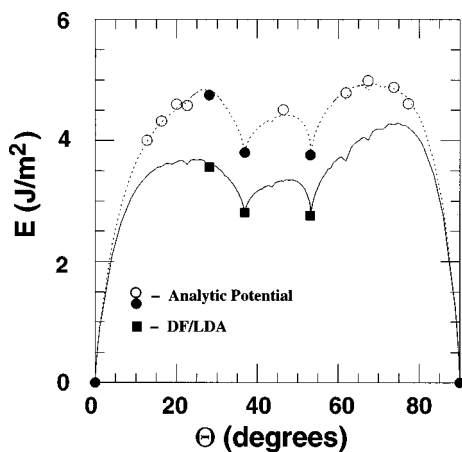


FIG. 3. Dependence of energy on angle for  $\langle 001 \rangle$  symmetrical tilt-grain boundaries in diamond.

entation range, which are represented by the dashed line in Fig. 3. The agreement between the atomistic calculations with the analytic potential (open circles) and the multiscale DSUM is excellent, where the maximum energy difference between the two methods is less than 3%.

Analysis of the stress distributions predicted by the analytic potential suggests that the strain fields surrounding the key structures are sufficiently localized that they decay to insignificant values within approximately one nanometer of the boundary. The largest of these key structures (at a  $28.07^\circ$  misorientation angle) therefore requires only 136 atoms to completely incorporate the stress field for a single grain boundary, or twice this number of atoms for a structure containing two grain boundaries and periodic boundary conditions in all directions. This system size is well within current capabilities of density-functional calculations, making energy estimates from the DSUM possible using only input from first principles. To obtain these values, minimum energies of the key structures were recalculated using density-functional calculations starting with the configurations predicted by the analytic potential. The Kohn-Sham equations were solved within a plane-wave-pseudopotential representa-

tion with a conjugate-gradient algorithm<sup>16</sup> and the grain-boundary structures were relaxed using Hellman-Feynman forces. Soft-core pseudopotentials<sup>17</sup> in separable form were used in conjunction with efficient sampling over the first Brillouin zone.<sup>18</sup> A basis-set energy cutoff of 60 Ry was used;<sup>17</sup> this produced a fully converged basis. The lattice constant, elastic properties for bulk diamond, and stacking fault energy predicted by the density-functional calculations are given in Table I.

The first-principles energies predicted for the key structures are given by the squares in Fig. 3. These energy values are approximately 0.75 times those given by the analytic potential. A value of 17 for  $\alpha$  was obtained from first-principles calculations using the  $28.07^\circ$  misorientation angle grain boundary. Energies in the entire misorientation range produced by the FP-DSUM using the values mentioned above and the data in Table I as input to Eqs. (1)–(4) are represented by the solid line. The accuracy of the density-functional method combined with the analysis using the analytic potential suggests that this curve is an accurate representation of the grain-boundary energy over the entire range of misorientation angle.

In summary, we have proposed a multiscale modeling method which combines first-principles density-functional calculations with a disclination structural units model. Using this method, energies were estimated for  $\langle 001 \rangle$  symmetrical tilt-grain boundaries in diamond over the entire misorientation range using only input from first-principles calculations. Based on data generated from an analytic potential, this approach appears to produce accurate energies while minimizing computational effort.

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