Structure and Energy of the 90° Partial Dislocation in Diamond: A Combined *Ab Initio* and Elasticity Theory Analysis

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The core structure and stability of the 90° partial dislocation in diamond is studied within isotropic elasticity theory and *ab initio* total energy calculations. The double-period reconstruction is found to be more stable than the single-period reconstruction for a broad range of stress states. The analysis of the *ab initio* results shows further that elasticity theory is valid for dislocation spacings as small as 10–20 Å, thus allowing *ab initio* calculations to provide reliable parameters for continuum theory analysis.

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The ability to predict the large scale mechanical properties of materials remains an outstanding challenge to materials physicists. Mechanical properties are linked to the properties of the dislocations in a material. Discerning the dislocation properties and their subsequent impact on mechanical properties is complicated by the long-ranged elastic and short-ranged contact forces between dislocations. True prediction of mechanical properties, therefore, is a formidable "many-body" problem.

Currently, computational resources have advanced to the point where one can consider simulating the dynamics of a large number of dislocations. Typical continuum dislocation dynamics simulations [1] rely on elasticity theory to describe interactions between dislocations. However, it is well known that the elastic self-energy of a dislocation (even in a finite medium) diverges. This divergence stems from the failure of a continuum description when applied to lengths smaller than the average distance between atoms. Within simulations (and elasticity theory), this divergence is removed through the introduction of a small scale cutoff, defined to be the core radius of the dislocation r_c [2]. The isotropic continuum expression for the total energy per unit length of an infinite edge dislocation may be written as

$$E_{\mathrm{tot}} = E_c + \frac{\mu b^2}{4\pi(1-\nu)} \log\frac{R_{\max}}{r_c}, \qquad (1)$$

where E_c is the dislocation core energy, μ is the shear modulus of the solid, ν is Poisson's ratio, b is the magnitude of the Burgers vector, and $R_{\max}$ is a large scale cutoff. In *lieu* of a better description of the dislocation core, Hirth and Lothe [2] suggest that r_c be chosen to minimize the absolute value of E_c. In essence, the core radius is chosen so that the second term on the right-hand side of Eq. (1) suffices as a description of the total energy. This choice provides the best possible representation of the total energy of the dislocation within isotropic elasticity theory, assuming that E_c is independent of stress.

Presently, it is possible to study the cores of dislocations using *ab initio* calculations. From these studies one expects to obtain (at a minimum) two types of information. First, the stable core structure should be identified. Second, one would like to extract a set of parameters which can be used to describe the long-ranged interactions and self-stresses of the dislocation. The present paper demonstrates that one may use relatively small unit cells and periodic boundary conditions to identify the stable core structure, begin to explore the stress dependence of that stable core structure, and extract parameters relevant to larger scale computations.

Atomic scale studies of dislocation cores are complicated by the long-ranged elastic interactions mentioned above. In particular, the choice of boundary conditions becomes an integral part of the problem being solved. Two approaches are common in the literature. The first approach is to study a "cluster" of atoms imposing the displacements expected from elasticity theory at the boundaries [3–7]. A second approach is to impose periodic boundary conditions [8–10]. Each unit cell considered, however, must have a net Burgers vector equal to zero. Otherwise, the logarithmic divergence of the energy apparent in Eq. (1) poses difficulties.

If one uses simple empirical potentials, it is possible to calculate the total energies of collections of thousands or even millions of atoms. Empirical techniques, however, often suffer from the approximations one makes in constructing the potentials, and hence may be inadequate for the study of some properties. *Ab initio* techniques provide more reliable estimates of total energies, but one is forced to address a much smaller number of atoms. This may lead to unusual and extreme stress states, particularly in the calculations performed using periodic boundary conditions.

The influence of these unusual stresses on the relative energies of different dislocation core structures is controversial. Bennetto and co-workers [9] recently proposed a double-period (DP) reconstruction of the 90° partial in

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Si that is lower in energy than the previously assumed single-period (SP) structure (see Fig. 1). Lehto and Öberg [5] countered that the relative stability of the two structures is influenced by the periodic arrangement of dislocations, and presented cluster calculations indicating that the energy difference between the two structures is smaller than that reported by Bennetto *et al.* and may even change sign. Valladares *et al.* [11] reported that the free energy difference between the two structures decreases with increasing temperature, and argued that, at an elevated temperature, both core structures should be present.

The availability of a large number of experimental results and the technological importance of silicon (Si) based devices have triggered efforts to understand the structure and stability of dislocations and related kinks in bulk Si [5,8,9,12–14]. Comparatively, much less attention has been directed towards the study of dislocations in diamond (though some initial work has been reported [15,16]). Clearly, the properties of the dislocations in diamond are at the heart of the extreme hardness of diamond, and it is thus of significant fundamental interest to understand the structure and stability of the dislocations in diamond.

Dislocations in diamond are commonly thought to be similar to those in Si. For example, it is assumed that the 60° dislocations in diamond dissociate into 30° and 90° partials. This expectation is borne out by microscopy experiments on thin films [17,18]. This Letter addresses the structure and stability of the 90° partial in diamond.

Following the work of Bennetto *et al.* [9], the difference in energy between the DP and SP structures is studied within a density functional theory-pseudopotential approach [19,20]. The calculations are performed within the local density approximation [21,22]. A standard nonlocal pseudopotential [23,24] for carbon is employed, and the plane-wave expansion of the wave functions is performed with an energy cutoff of 36 Ry. The Brillouin zone is sampled by four **k** points along the dislocation line in the SP case and by the two equivalent **k** points in the DP case. Test studies at larger cutoff and higher numbers of **k** points show that differences of energy are well converged with these running parameters.

Several basic unit cells are employed in the calculations. The "small" cells are chosen to be identical to those described in Ref. [9], containing 96 atoms in the SP structure and 192 in the DP structure. By adopting the notations of Ref. [5] to describe the unit cells (see Fig. 2), one finds for the small cell that $L = 4|\mathbf{a}|$ and $D = 2|\mathbf{b}|$, where $(\mathbf{a}, \mathbf{b})$ are the unit vectors in the (110) plane of the perfect diamond 12-atom orthorhombic cell [9]. In addition, larger cells characterized by $L = 6|\mathbf{a}|$ or $D = 3|\mathbf{b}|$ are examined. (L and D will hereafter be expressed as integers, with the unit vectors **a** and **b** understood.) Various values of w/L are considered, and T/L is chosen to be either 0 (the "dipolar" configuration) or $1/2$ (the "quadrupolar" configuration). (The strain introduced by the presence of the dislocations is used to adjust the offset T, as proposed in Ref. [5].) Within isotropic elasticity theory, the stresses and their gradients depend sensitively on the choice of unit cell parameters. Since the stress field from an edge dislocation is inversion antisymmetric, the unit cells in which the dislocation lattice is inversion symmetric will place no net stress on the dislocations. Hence, for $w/L = 1/2$, the net stress felt by each dislocation is identically zero. In contrast, for $w/L = 1/4$, the shear stress at each core may be large. (For diamond, it is demonstrated below that the periodic cells employed here exert shear stresses of 10–20 GPa.)

Table I contains the results calculated from the eight configurations considered here. In this and the following table, energies refer to the most stable SP structure [see Ref. [9] and Fig. 1(a)]. The small cell results for the quadrupolar case ($T/L = 1/2$) agree with those of Ref. [16], in which calculations indicate that the DP structure is more stable than the most stable SP structure by ~172 meV/Å.

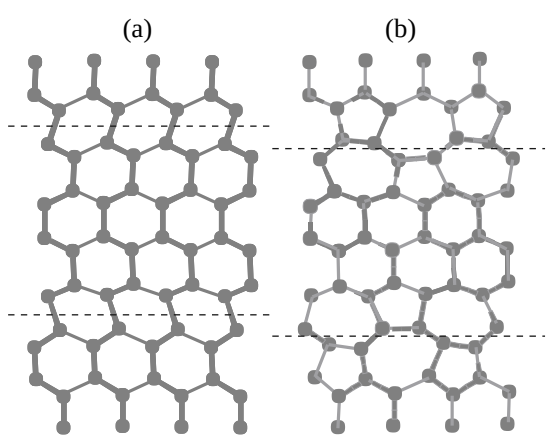

FIG. 1. Symbolic ball-and-stick representation of the 90° partial in diamond: the (a) SP and (b) DP reconstructions. The dotted lines indicate the positions of the dislocation cores.

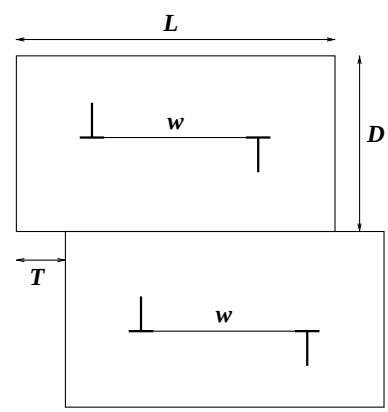

FIG. 2. Symbolic representation of the unit cell. The figure contains two unit cells. L is the width of the unit cell, D is the height, and w is the distance between dislocations in the unit cell. The displacement T is also shown.

TABLE I. Difference of energy $\Delta E = E_{\mathrm{DP}} - E_{\mathrm{SP}}$ (in meV/Å) between the double-period and single-period structures as a function of cell size and geometry. A negative number indicates that the DP structure is more stable. The lengths L and D are given in units of the underlying 12-atom orthorhombic cell ($\mathbf{a}, \mathbf{b}$) unit vectors (see text). The stresses σ_{xy}, σ_{xx}, and σ_{yy} on a dislocation, in units of $10^{-3}\mu$, are determined using isotropic elasticity theory.

L	D	w/L	σ_{xy}	σ_{xx}	σ_{yy}	ΔE
	$T/L = 0$					
4	2	1/2	0	0	0	−121
6	2	1/2	0	0	0	−128
6	2	1/3	6.69	−0.63	1.88	−120
6	2	1/4	16.2	−0.74	1.92	−69, −110[a]
4	3	1/2	0	0	0	−141
	$T/L = 1/2$					
4	2	1/2	0	0	0	−169
6	2	1/2	0	0	0	−198
6	2	1/3	27.7	0.63	−1.88	−161

[a]For this set of parameters, two different unit cells for the DP structure are possible, depending on how the 5- and 7-membered rings are aligned with respect to each other (see Fig. 1).

Table I reveals clearly that the energy difference between the cores is dependent on the dislocation configurations. For the dipolar case (i.e., $T/L = 0$), $\Delta E = E_{\mathrm{DP}} - E_{\mathrm{SP}}$ decreases only slightly upon increasing L. However, for $T/L = 1/2$, which corresponds to the quadrupolar structure suggested by Bigger *et al.* [8], the decrease in ΔE jumps to ≈30 meV/Å. Table I also demonstrates the sensitivity of the energy difference to the choice of w/L. For a particular value of T/L, the configurations for which ΔE has the smallest absolute value correspond to those for which $w/L \neq 1/2$, i.e., those which impose a net shear stress on the dislocation. These stresses can be quite large; for $L = 6$ and $w/L = 1/3$ in the quadrupolar configuration, the shear stress σ_{xy} is determined to be 0.028μ, or almost 15 GPa. The diagonal stresses, σ_{xx} and σ_{yy}, though smaller than the shear stress by about an order of magnitude, are nonetheless significant and may also affect the stable core structure.

These calculations suggest then that the energy difference between the two core structures is a sensitive function of the stress state. This leads to the possibility that the stable core structure is, in fact, *dependent on the applied stress*. The implication is that the kink *structures*, and hence the dislocation dynamics, may depend strongly on the applied stress, even if the energy scales are not much altered. If true, this observation is of significant importance to those desiring to model the mechanical properties of materials from the atomic scale.

Arias and Joannopoulos [14] in their study of the spontaneous annihilation of two screw dislocations in Si extracted a core energy by calculating the elastic energy using isotropic elasticity theory and comparing with *ab initio* results. They correctly noted that the summation appearing in the expression for the elastic energy is similar to a Madelung sum, and hence must be treated with caution. Bulatov has made similar observations [25]. The summation is performed here by making use of analytical results for tilt boundaries available in the literature.

The periodic arrangements considered here can be thought of as a 1D stack of tilt boundaries. The total elastic energy of an isolated tilt boundary can be calculated explicitly [2]. Further, the stress field of a tilt boundary is known to decay exponentially with distance from the boundary. The total elastic energy per unit cell is calculated as a sum of the self-energy of each tilt boundary plus the elastic work performed in assembling the tilt boundaries into the studied configuration. The energy, when calculated in this fashion, converges very rapidly. The elastic self-energy of a tilt boundary depends on μ and r_c, and the work needed to construct the stack depends directly on the shear modulus μ.

Extraction of numerical values for μ and r_c is accomplished as follows. A number of *ab initio* calculations are performed and the total energies compiled. The considered configurations (all are chosen to be SP structures) and the relevant elastic energies, corrected for the presence of the stacking fault, are contained in Table II. (The stacking fault energy is calculated to be 17 meV/Å^2, in good agreement with the experimental results of 17.4 and 18.1 ± 2.5 meV/Å^2 reported in Refs. [17,18]. The stacking fault energy is subtracted from the total energy of the unit cell, measured relative to bulk diamond, and the results are reported in Table II as E_{atom}.)

TABLE II. Comparison of atomic scale results (for the single-period structure) and isotropic elasticity theory analysis. E_{atom} is the *ab initio* energy per unit length of the dislocation, corrected for the stacking fault energy. E_{fitted} is the same quantity calculated using elasticity theory and the fitted parameters. Lengths are given in terms of the unit cell vectors ($\mathbf{a}, \mathbf{b}$) and energies are in eV/Å.

L	D	T/L	E_{atom}	E_{fitted}
	$w/L = 1/2$			
4	2	0	1.47	1.49
4	2	1/2	1.68	1.68
6	2	0	1.54	1.56
6	2	1/6	1.82	1.78
6	2	1/2	2.01	2.05
4	3	0	1.61	1.57
	$w/L = 1/3$			
6	2	0	1.54	1.52
6	2	1/2	1.92	1.90
	$w/L = 1/4$			
6	2	0	1.43	1.46
6	2	1/6	1.59	1.59
6	2	1/2	1.70	1.71

The values of E_{atom} are fitted to the expression for elastic energy discussed above, with μ and r_c as fitting parameters. [The elastic energy of a tilt boundary composed of edge dislocations depends on $\mu/(1-\nu)$, where ν is Poisson's ratio. For simplicity, the experimental value for ν for diamond cubic carbon quoted in Hirth and Lothe [2], 0.068, is used; however, the results should be considered as fits to the prefactor $\mu/(1-\nu)$ and not μ alone.] Table II lists these results as E_{fitted}. The shear modulus deduced from the fitting procedure is $\mu = 545 \pm 20$ GPa [26], in good agreement with the experimental value of 536 GPa quoted in Hirth and Lothe [2].

The core radius deduced from the fit is $r_c = 0.41 \pm 0.04$. Nandedkar and Narayan [6], using Tersoff potentials and cylindrical boundary conditions, find $r_c \approx 3$ Å and $E_c = 4.69$ eV/Å. By contrast, the fitting procedure repeated above, assuming $r_c = 3.0$ Å and allowing for nonzero E_c, yields $E_c = 1.26$ eV/Å. The precise origin of the large difference in core energies is unknown. Perhaps the difference stems from errors in the total energy as described by Tersoff potentials. It is also possible that the core energies obtained from the periodic unit cells are influenced by the proximity of the nearby dislocations, though it seems unlikely to the present authors that this could lead to energy differences of over 3 eV/Å. Nonetheless, the value $r_c = 0.41$ Å, about $b/3.5$, is consistent with general expectations for the magnitudes of core radii [2] and not far from the value $r_c \approx b/4$ found by Trinczek and Teichler [7] for the 90° partial dislocation in Si and Ge.

While the use of anisotropic elasticity theory might improve the overall fit, it is evident from the table that simple isotropic elasticity theory does an excellent job of describing the energetics of the considered arrangement of dislocations. The largest discrepancy between the fitted values and the *ab initio* calculations is about 0.04 eV/Å, which translates into an uncertainty of about 0.6 MPa in the stress required to bow a dislocation of length 1 μm to its critical configuration. Thus, the parameters μ and r_c obtained are certainly adequate for inclusion into larger scale simulations.

In conclusion, this paper addresses the energetics and core structure of the 90° partial dislocation in diamond. It is demonstrated that the double-period core reconstruction is the lowest energy state for a wide range of stresses. It is also noted that the energy difference between the two core structures decreases with increasing shear stress, suggesting that the stable core structure may, in fact, be stress dependent. Finally, it is shown that the energy changes for a dislocation placed in various periodic environments can be reproduced accurately using isotropic elasticity theory, even in the limit of dislocation spacings as small as ≈10 Å. One may thus use *ab initio* total energy techniques on relatively small systems to extract with excellent accuracy the parameters for larger scale simulations.

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