# Simulations of strain relief at the crack tip in silicon

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**Abstract**
The mechanism of strain relief for a tensile strained diamond-structure silicon-
atom system containing an initial cut is considered theoretically. Molecular
dynamics and molecular mechanics simulations were employed as simulation
methods. Loading under finite-temperature conditions starts cleavage crack
initiation. Simulations made using tight-binding density functional molecular
dynamics favour the traditional mechanism of brittle crack initiation. In
this process, bonds are broken entirely at the tip of the cut. Under specific
conditions, molecular dynamics simulation can lead to the formation of new
stable structures. This transformation is associated with bond switching. The
results for the bond-bending force from the energy models are compared and
its influence on the results of the simulations is discussed.

## 1. Introduction

The large range of technological applications of covalently bonded silicon material calls for
a deeper understanding of the extreme mechanical properties. Tensile stress relief is one of
the basic issues which is connected to circumstances of fracture, cutting and bonding [1]. In
spite of the developments of atomic resolution microscopy, the microscopic mechanism of
stress relief is not completely clear [2]. One theoretical method that can give insight into these
problems is atomistic molecular dynamics simulation. In particular, approximate approaches
based on semiempirical potential energy models and also tight-binding approaches offer a way
to simulate corresponding collective large deformations of atom systems without too much
computational effort. In our approach to strain relief we are interested in bonding of atoms in
a crystalline environment and what kind of deformation dependence may be associated with
this. We study mechanisms that lead to easy fracture and also ones which do not.

We will consider the strain relief that occurs because of the influence of both externally
applied strain and thermal vibrations in an idealized crystalline system containing an initial cut.
Two different mechanisms of cleavage of the diamond-structure system, in which an initial
cut is aligned perpendicular to the cleavage plane, were considered. Dynamics and relaxation

simulations were carried out by using the two-centre *ab initio* tight-binding method and the more approximative atomic coordination-dependent semiempirical potential energy model.

In our previous paper [3] dynamical simulations were done by using a semiempirical potential energy model (we shall term this approach here MD), applied at low temperature. The new methodology, most importantly the tight-binding molecular dynamics (TBMD) and the new cleavage mechanism, seems to give clearer results when compared against experimental knowledge of the properties of silicon. Simulations support a traditional perfect brittle crack-initiation mechanism with a perfectly sharp crack tip at finite temperatures. This finding is in agreement with other recent computer simulations of stable crack propagation in silicon [4] and pseudopotential calculations of the stability of brittle cracks in silicon [5]. As we indicated [3], strain may alternatively be relieved by the formation of opened stable intermediate structures. We will explain an obvious mechanism for the formation and evolution of this structure. We point out that deformation contributions can have significant effects on microscopic properties of crystalline structures.

This paper is organized as follows. We start the discussion of the simulation methodology by giving an overview of the applied MD and TB simulation methods and interaction models in section 2. We continue to the discussion of bond-bending analysis and molecular dynamics simulations in section 3. Conclusions are given in section 4.

## 2. Simulation technique

It can be assumed that classical mechanics can approach realistic dynamics at high kinetic temperatures since pure quantum effects are less significant there [6, 7]. This effect may be even more pronounced for highly stressed systems [8]. These factors provide arguments for the use of the molecular dynamics simulation method discussed in more detail elsewhere [3]. Since silicon has a ductile phase at higher temperatures and the models that we employ are not well fitted for these temperatures, we limit the simulation temperatures to below 500 K. The fact that high enough temperatures can cause structural changes and create new fracture surfaces in sufficiently strained atom systems offered the possibility of approaching also very low-rate deformation conditions.

In molecular dynamics simulations atoms are moved to new positions by repeatedly updating the position $r_i$ (of atom $i$) by solving the classical equation of motion. The interatomic forces needed are simply of the form

$$F_{ij} = -\frac{\partial E_{tot}}{\partial r_{ij}} \tag{1}$$

were $E_{tot}$ is the total energy of the system. In order to generate thermal vibrations in the system, the dynamics was slightly modified by thermostat methods. In the case of MD, a Nose–Hoover thermostat [9] was employed, while in the case of TBMD, temperature scaling was used [10]. These choices were made so as not to limit collective fluctuations of the much smaller TBMD system. Thermostats were used also to approximately maintain temperature constancy. The strain was applied to the system by moving atoms in the opposite end planes apart. To introduce a shear loading component, the opposite end planes are pulled apart in opposite directions parallel to the end planes.

The highest-deformation-rate MD simulations, with tensile strain rate 3 m s$^{-1}$, were used as a starting point for lower-rate deformation simulations with a minimum rate of 0.01 m s$^{-1}$ for MD and 2 m s$^{-1}$ for TBMD simulations. Also a few experiments were performed in order to explore slower deformation rates. In these experiments, only temperature up-scaling started bond-breaking events in systems which were initially strained and equilibrated close to the

point of fracture. However, the results of these simulations did not seem to show any deviation if reasonable temperatures were used. In the simulations, strain was applied along the [111] crystal direction and the initial crack was made by cutting bonds between the widely spaced shuffle planes (shown also in figure 2—see later). We chose the crack line to lie either along the [$\bar{1}\bar{1}2$] or alternatively along the [$\bar{1}10$] crystal direction. The first orientation corresponds to a low density of bonds along the crack line and thus easy crack propagation in practice [11]. Along the crack line, the systems were in all cases periodic and were composed of 4 to 18 atomic planes. In the MD simulations a large simulation box with two sides of size 180 Å was used. In order to study the role of different contributions and to eliminate the possibility of statistical errors, tens of simulation runs were performed.

### 2.1. Potential energy model

The MD method was useful for getting an overview of the atomistic fracture under different simulation conditions, and for generating atom configurations for tight-binding simulations. It is expected that MD could give qualitatively correct behaviour of an sp$^3$-coordinated system [3] and also take into account well the associated collective motions of atoms due to their large number.

For MD simulations we implemented a model based on the environment-dependent interatomic potential (EDIP) model described in detail by Bazant, Justo and Kaxiras [12]. This model is reasonably well developed for integer-coordinated structures like diamond, and graphitic and some metallic systems. The model was modified to give qualitatively a correct bond-breaking behaviour of sp$^3$-hybridized bonds in a crystalline atomic environment [3]. This was achieved by minimally limiting the flexibility of the potential to model structures other than crystalline ones. The total potential energy of the system can be written in the form

$$E_{tot} = \sum_i E_i$$
$$E_i = \sum_{i \neq j} V_2(r_{ij}, Z_i) + \sum_{j,k \neq i; k > j} V_3(\boldsymbol{r}_{ij}, \boldsymbol{r}_{ik}). \tag{2}$$

Here $\boldsymbol{r}_{ij}$ is the vector between atoms $i$ and $j$. The two- and three-body terms read as follows:

$$V_2(r, Z_i) = A \left[ \left( \frac{B}{r} \right)^\rho - e^{-\beta Z_i^2} \right] \exp\left( \frac{\sigma}{r - a} \right) \tag{3}$$

$$V_3(\boldsymbol{r}_{ij}, \boldsymbol{r}_{ik}) = g(r_{ij})g(r_{ik})h(l_{ijk}) \tag{4}$$

where $g(r)$ is an exponentially decreasing function and $h(l_{ijk})$ is the angular part of the potential which depends on the angular variable

$$l_{ijk} = \boldsymbol{r}_{ij} \cdot \boldsymbol{r}_{ik} / r_{ij} r_{ik}.$$

The local coordination number $Z_i$ can vary from one atom to the other and it is defined as $Z_i = \sum_{m \neq i} f(R_{im})$, where $f$ is a cut-off function that depends on the distance to nearest-neighbouring atoms. The minimum value of the coordination number was limited to a value corresponding to crystalline structure (i.e. equal to four). The connection to the constant value was implemented to maintain continuity of forces. The form of the three-body term in equation (4) is similar to one used in the more well known potential of Stillinger and Weber [13].

### 2.2. The tight-binding simulation method

The properties of the energy model system introduced above can depend considerably on the functional fitting. In particular, the energy model is not assumed to model low-coordinated

structures correctly and it can overestimate short-range interactions. These are some of the arguments for simulating systems by using other methods that are more directly based on density functional theory. We applied a nonorthogonal tight-binding method of Frauenheim and Porezag [14, 15].

The overlap matrix elements $S_{sp\sigma}$, $S_{pp\sigma}$, $S_{ss\sigma}$ and $S_{pp\pi}$ and the Hamiltonian matrix elements $H_{sp\sigma}$, $H_{pp\sigma}$, $H_{ss\sigma}$ and $H_{pp\pi}$ depend on interatomic separations. The matrix elements are calculated in advance by using Slater-type orbitals that are self-consistent solutions of modified Kohn–Sham equations.

In simulations, the eigenvalue problem

$$\sum_\nu C_{\nu i}(H_{\mu\nu} - \varepsilon_i S_{\mu\nu}) = 0 \tag{5}$$

is solved to get the one-particle energies $\varepsilon_i$ and the eigenstate expansion coefficients $C_{\nu i}$. The total energy is then a sum of the band-structure energy and a repulsive two-body interaction term $V_{rep}$:

$$E_{tot} = \sum_i n_i \varepsilon_i(\boldsymbol{r}_k) + \sum_k \sum_{<l} V_{rep}(|\boldsymbol{r}_l - \boldsymbol{r}_k|) \tag{6}$$

where $n_i$ is the occupation number of orbital $i$.

The conditions of the TBMD simulations were made to correspond to the conditions of the MD simulations. A small Si cluster containing 200–300 Si atoms was taken around the crack tip of the MD atom system and hydrogen atoms were added to the free surfaces. Slightly different equilibrium bond lengths were taken into account by scaling the system along the periodic direction. The hydrogen atoms were relaxed to equilibrium positions. Silicon atoms that had a hydrogen nearest neighbour were fixed in the way as represented in figure 2—see later. In simulation runs, hydrogen atoms were made to follow rigidly their nearest silicon atoms to allow larger time steps of order 3–4 fs. The initial cut was made both allowing and not allowing the opposite atoms to interact with each other. Since the fixing of atoms can inhibit displacements of other atoms, different fixing and freeing conditions of boundary atoms were studied, but no significant effect on the results was found. Also some relaxation simulations were performed using a double-size system along the crack line (containing 18 atomic planes) to rule out the possibility that the stable structures observed were influenced by the size of the system being too small.

## 2.3. Bond-bending force

Large deformations lead us to study various distortions in the crystal, where many approaches are possible [16–18]. Since the bond-breaking force is expected to be qualitatively correct [3] we will consider bending of bonds in an ideal crystalline environment by comparing the interactions discussed above.

Figure 1 illustrates the function of the three-body term $V_3$ of equation (4). The curve corresponds to the bond-bending force that opposite atoms (indexes $j$ and $k$) experience because of the $V_3$-term as the angle ($\arccos l_{ijk}$) to the common third-neighbouring atom (index $i$) is changed. The distances were set to $r_{ij} = r_{ik} = 2.35$ Å. Because of the definition of equation (4), all atoms are in a sort of stable crystalline environment. Clearly, a bond-bending force that is of relatively low magnitude sustains the crystalline structure. In simulations, it turned out that, if this force is made larger as shown in figure 1, ideal brittle initiation occurs. But if some other $V_3$-term with less bending force is chosen, systems tend to form distorted crack tip structures. In this way the properties of the system can depend significantly on the bond-bending force at large bond-bending angles.
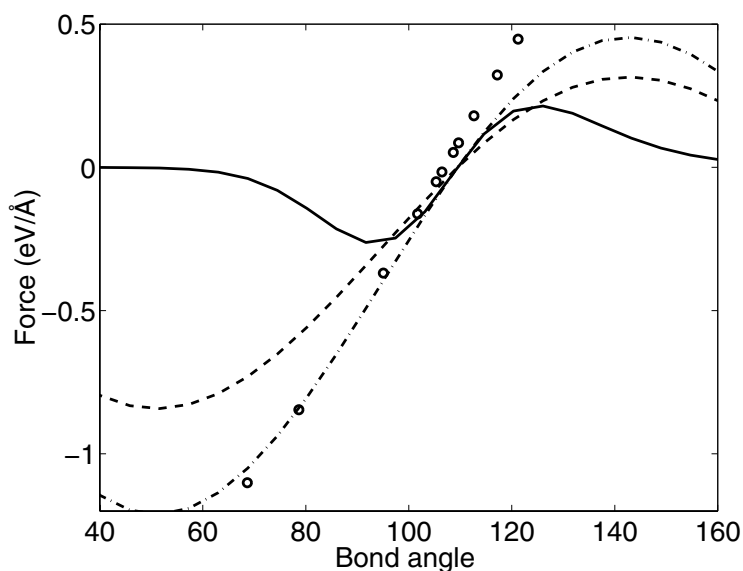
**Figure 1.** Bond-bending force as a function of bond angle in the stable $sp^3$-coordinated atomic environment of the EDIP (black line) and Stillinger–Weber (dashed line) potential energy models. The corresponding force of the system with pure brittle properties is also shown (dash–dot line). Open circles correspond to bending forces calculated by using the tight-binding method.

Although the tight-binding model has a longer range of interactions, we may examine what kind of bond-bending properties the tight-binding model implies in a similar test case. We shall consider the following simple test set-up. Three neighbouring silicon atoms were chosen from a silicon cluster that was relaxed to its equilibrium, and only bond angles between the three atoms were changed. All of the distances between atoms were held fixed. This procedure was implemented by changing the position vectors which are needed in the calculation of $S$- and $H$-matrix elements in equation (5). As a result of the calculation of the forces, two points become evident. As shown in figure 1, the tight-binding model predicts a closely similar force when compared with potential energy models. Large bending force implies strong resistance to structural changes to structures other than crystalline ones. The second observation was that forces along bonds that were bent were insignificant, unless the bond angle was set to values smaller than $90°$. In this case the interaction also attempts to reduce the bond lengths.

## 3. Molecular dynamics simulations

Our simulations indicated the possibility of defining bond-breaking events as occurring in a brittle form, in the sense that the crack tip is atomistically sharp. Typical features of ductile-phase materials, like propagation of defect structures away from the crack tip, formation of twin structures and unconfined blunting of the crack tip, were not observed. However, experimental results [19] suggest that a crack propagation in silicon can also have properties other than perfectly ideal ones.

In seems that the simulated system relieves strain by sharing it with nearest adjacent cleavage planes as much as possible. In a case of suitable nonsymmetry, as discussed in more detail below, opened structures may be formed as strain is increased. This behaviour is in principle similar to that observed in other idealized lattice systems like trigonal ones [20]. At

larger strain values, after some bonds have broken, some silicon atoms can gain high kinetic energy. The binding energy is however about 1 eV larger than the kinetic energy and ejection of atoms from the system does not occur. As the rapid nonstable crack initiation starts, the (111) cleavage plane can change to another similar (111) cleavage plane.

Having explained the overview of the deformation, we shall now consider the case with the [1$\bar{1}$2]-oriented crack line (i.e. where the crack is on the ($\bar{1}$10) surface of the crystal). As strain increases, bonds along the initial tip break and corresponding atoms move further, approaching other atoms and forming new bonds with them. The new structures formed during this event were not found to stabilize significantly in any of the simulations. Before and after the first bond-breaking events, closely equivalently strained bonds (within one per cent of the bond length) exist in the three adjacent cleavage planes (see figure 2). Therefore crack initiation may in a more fluctuating environment proceed by using one of these three planes. In
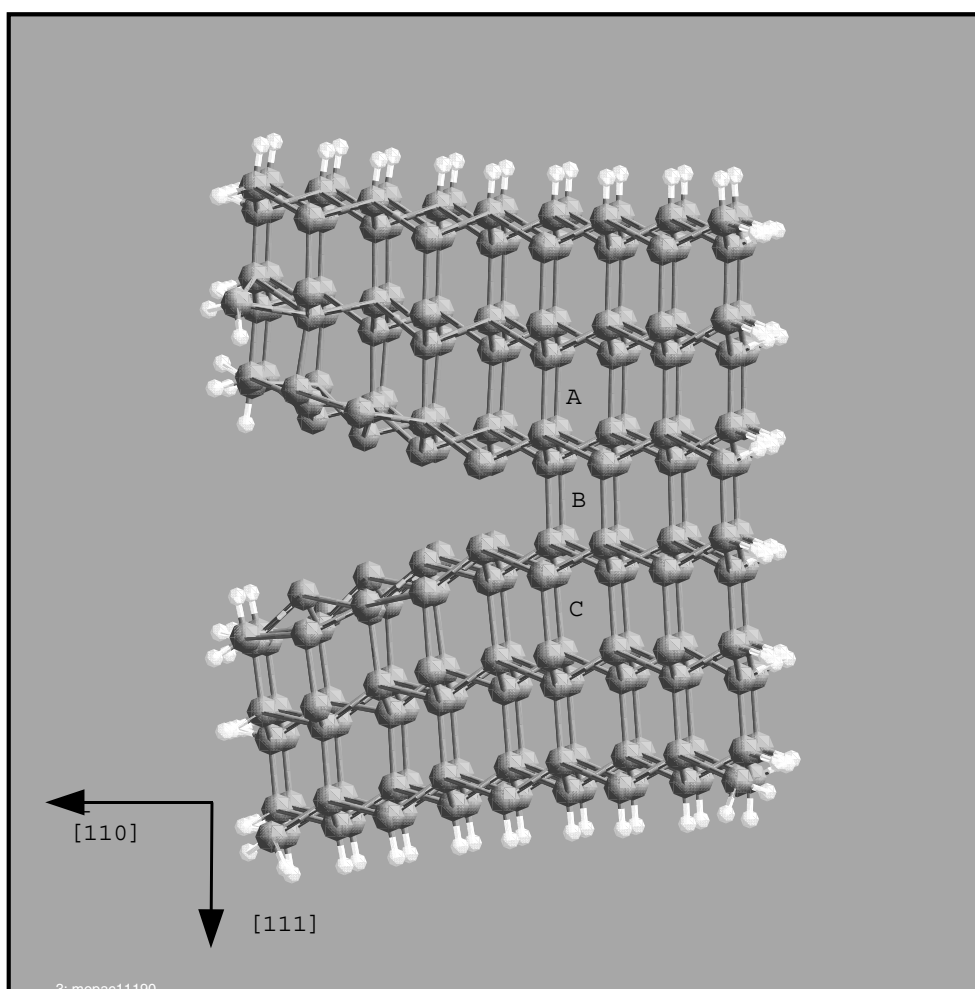


**Figure 2.** The atomic configuration after the first bond-breaking events. Three closely equivalently strained bonds A, B and C relieve strain at the crack tip. Hydrogen atoms (smaller circles) are rigidly connected to nearest silicon atoms. On the right and left surfaces, these pairs are allowed to move along the strain direction.

agreement with this finding, in MD simulations, the cleavage plane changes easily to another nearby cleavage plane during rapid crack initiation.

We will next consider the other orientation, with the [$\bar{1}$10]-oriented crack line. As strain increases, atoms can become displaced to positions where, instead of complete bond breaking occurring, bonds can switch to other atoms. Figure 3 shows the atomic arrangement after the first such switching events have taken place. In figure 3, not all of the switching events have ended yet, because of the small strain. But as strain increases, these events cease and an ordered open sevenfold ring structure is formed. In MD simulations this structure is formed at temperatures up to 500 K. In TBMD simulations, we found it useful to perform straining by applying both tensile and also shear loading components (see figure 3) in order to move atoms closer so that the switching of their bonds becomes more likely at lower strain. Strain could be increased further to observe successive bond switchings and open structures, but this process is not found to stabilize.
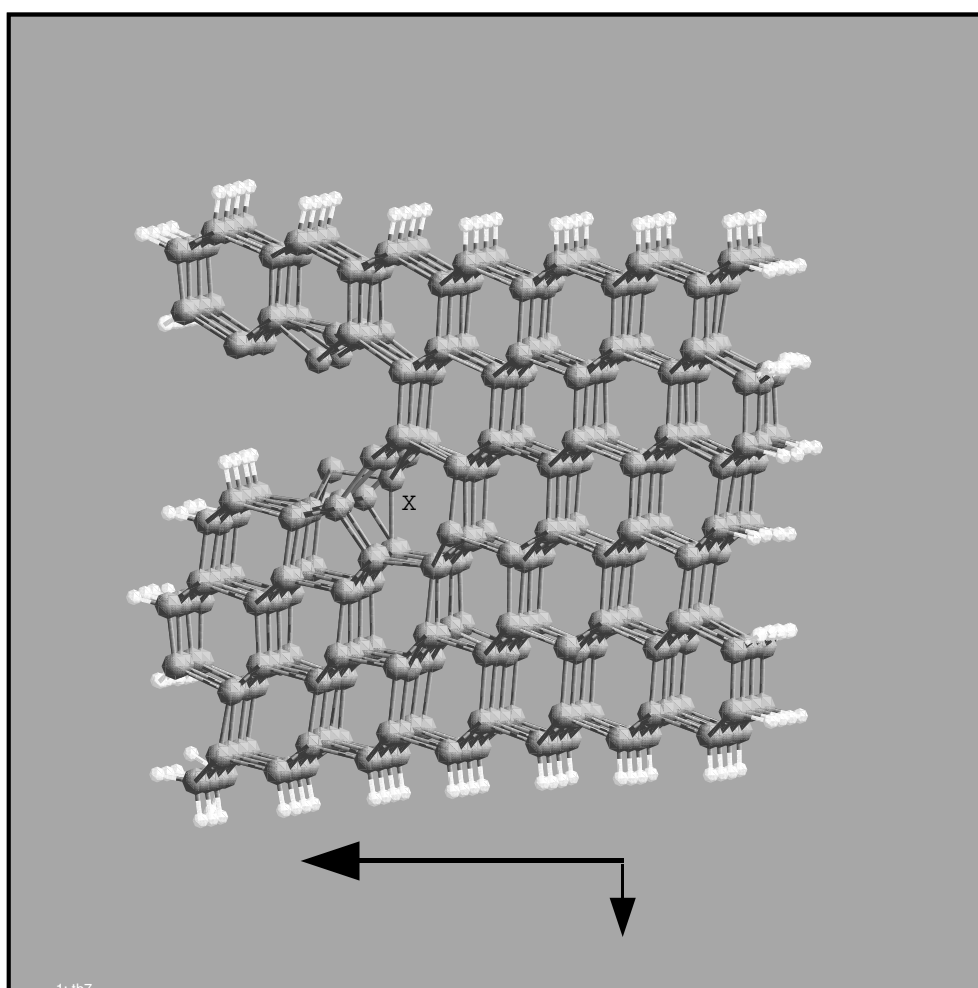


**Figure 3.** The atomic configuration after three bond-switching events have taken place. The bond labelled X has not yet switched. The arrows indicate applied tensile and shear strain components.

## 4. Discussions and conclusions

Since a very large number of time steps and complex deformations are associated, the results of the simulations are considerably dependent upon the methods applied. Therefore the tight-binding method was applied to provide an effective understanding from the level of an electron eigenvalue problem. From the present point of the view, it seems that the two different methods, the tight-binding method and that based on the more approximate semiempirical potential energy model, can together give a coherent view of a crack tip strain relief process. The use of the finite-temperature condition is significant in these simulations in having a dependence on the natural fluctuations in the strained system. We show that a simple bond-bending experiment, that was performed also for the tight-binding system, may be useful for comparing interactions. It can also give qualitative information on the expected deformation. The similar behaviour of the MD and TBMD systems may be partly explained by the similarity of the bond-bending forces.

In simulations, an almost perfect cleavage mode of crack initiation and strain relief is identified independently of the crack tip orientations considered. When compared with experimental knowledge of silicon crystals, this result seems to be in accordance, and clarifies the idea of microscopic strain relief in silicon. In particular, in the case of crack tip orientation along $[\bar{1}\bar{1}2]$ there were three closely identically strained bonds in different cleavage planes. For more complex deformation or under sufficiently nonequilibrium conditions, crack initiation may therefore switch to another cleavage plane. In the case of the crack tip orientation $[\bar{1}10]$, the bond-switching mechanism by which the intermediate sevenfold atomic ring structure may form is observed. An implication of this result for experimental loading conditions of crystalline silicon is that strain-induced bond-switching events may occur. Depending on how closely the structure and straining procedure corresponds to the idealization described, strain may therefore be relieved at crack tips. However, one should also note that the perpendicular orientation with the $[\bar{1}\bar{1}2]$ crack line is the direction in which the crack propagation may be expected. Thus we propose that if the crack tip is on the (111) cleavage plane, brittle crack initiation will proceed on this plane and may, because of instability, switch to another similar cleavage plane.

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