Multi-paradigm modeling of dynamical crack propagation in silicon using the ReaxFF reactive force field

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We report a study of dynamic cracking in a silicon single crystal in which the ReaxFF reactive force field is used for several thousand atoms near the crack tip while more than 100,000 atoms of the model system are described with a simple nonreactive force field. The ReaxFF is completely derived from quantum mechanical calculations of simple silicon systems without any empirical parameters. Our results reproduce experimental observations of fracture in silicon including differences in crack dynamics for loading in the [110] or [100] orientations and dynamical instabilities with increasing crack velocity. We also observe formation of secondary microcracks ahead of the moving mother crack.

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I. INTRODUCTION

Brittle fracture is characterized by breaking of atomic bonds leading to formation of two new materials surfaces. Most existing atomistic models of fracture assume an empirical relationship between bond stretch and force. However, breaking of bonds in real materials is an extremely complicated process that could previously only be captured with sufficient accuracy only by using quantum mechanical (QM) methods, which are limited to 100 atoms. In this paper we present a new theoretical concept based on building a multi-scale simulation model completely derived from QM principles, while being computationally efficient and capable of treating thousands of atoms with QM accuracy. This opens a new subdomain in materials modeling enabling a seamless integration of chemistry and mechanics.

Fracture of silicon has received tremendous attention due to its complexity of bond breaking and due to interesting failure dynamics observed experimentally [1–7]. These experimental efforts led to critical insight into deformation modes, such as the mirror-mist-hackle transition and orientational dependence of crack dynamics in silicon single crystals [6].

Atomistic modeling fracture of silicon has been the subject of several studies using empirical force fields [8–11]. In contrast to many metals, where fracture and deformation can be described reasonably well using embedded atom (EAM) potentials [12–17], a proper description of fracture in silicon has proved to be far more difficult, as many models did not agree with experimental observations. This suggested that silicon requires a different, more accurate treatment of the atomic interactions. There have been several previous attempts to describe fracture of silicon using atomistic methods (see, for example [4, 8–10, 17–29]). Early attempts to model fracture in silicon used Tersoff’s classical potential [30] (in the following referred to as “Tersoff potential”) and similar formulations such as the Stillinger-Weber potential [31]) or the EDIP potential [32]. Simulations carried out with those potentials were not able to reproduce experimentally observed brittle fracture of silicon [3]. It has been suggested that the reason for these discrepancies between computation and experiment is that the description of the atomic bonding at large stretch obtained by empirical potentials deviates significantly from the more accurate, quantum mechanical solution [3].

It is thus believed that in order to develop models of crack dynamics in silicon that agree with experimental observations, the accuracy of QM for atoms near the propagating crack tip is necessary. This allows to describe the large, potentially plastic strains as chemical bonds are broken. This has been successfully demonstrated in earlier work discussing fracture in silicon, for example in the MAAD approach [9] by coupling QM regions to empirical potentials. Due to computational limitations of QM methods, the number of atoms treated with QM accuracy is limited to approximately one hundred atoms. However, the zone near a crack tip in which bonds are stretched and broken often comprises of several thousand atoms.

Baskes and coworkers used their modified EAM formulation (MEAM) to describe crack motion in silicon [10] and to investigate the critical load for fracture initiation [11]. Even though this model leads to improved results compared to Tersoff-type potentials, the MEAM formulation cannot describe bond formation and breaking of silicon with other elements such as oxygen.

Here we present the results for an alternative approach utilizing the ReaxFF reactive force field developed to reproduce the barriers and structures for reactive processes from QM, but at a computational cost many orders of magnitude smaller. The challenge of modeling the physics of fracture is that bond breaking processes must be simulated, while allowing the heat generated to be dissipated properly to the remaining system. At the same time we present the results for an alternative approach utilizing the ReaxFF reactive force field developed to reproduce the barriers and structures for reactive processes from QM, but at a computational cost many orders of magnitude smaller. The challenge of modeling the physics of fracture is that bond breaking processes must be simulated, while allowing the heat generated to be dissipated properly to the remaining system. At the same time...
time, models need to describe the flux of energy towards a moving crack tip. Time scales of microseconds to milliseconds may be needed to follow the crack propagation across grains to various surfaces. Such calculations have not previously been possible. Here we describe the first simulation treating the silicon system with this level of accuracy. We use a hybrid simulation technique in which the ReaxFF reactive potential for silicon [33, 34] is used for a modest region of a few thousand atoms close to the crack tip while a computationally inexpensive but unreactive Tersoff potential [30] is used to describe the other 100,000 more distant atoms needed to include their elastic constraints on the propagating tip. Tersoff-type potential and ReaxFF lead to similar materials behavior or equation of state for small strains, but deviate strongly at large strains as demonstrated previously [33]. The fact that both descriptions overlap for small strains enable a smooth handshake between the two methods.

The ReaxFF reactive potentials [33, 34] have been developed to describe combinations of many different elements across the periodic table, including first row elements (C, O, H, N), metals (Cu, Al, Mg, Ni, Pt) and semiconductors (Si) [33–38]. Thus, the methodology described here could potentially be a valuable tool for describing plasticity and fracture for some materials, where certain details of the bond breaking process are necessary to model crack propagation. Here we focus on modeling fracture in pure silicon and the interactions of silicon with oxygen competing with crack extension.

II. HYBRID ATOMIC MODELING OF CRACKING IN SILICON

The Computational Materials Design Facility (CMDF) is a Python [39] based simulation framework allowing multi-paradigm multi-scale simulations of complex materials phenomena operating on disparate length- and time scales [40, 41]. Individual computational engines are wrapped using the “Simplified Wrapper and Interface Generator” (SWIG) for rapid integration of low-level codes with scripting languages [42]. This framework enables complex multi-scale simulation tasks encompassing a variety of simulation paradigms, such as quantum mechanics, reactive force fields, nonreactive force fields, coarse grain mesoscale, and continuum descriptions of materials. The CMDF framework enables the combination of ReaxFF to capture the QM description of reactants and products describing the partial bond orders, energies, and charges [33], ReaxFF is 1-2 orders of magnitudes more expensive than the Tersoff potential but several orders of magnitude faster than QM.

We use a simple general approach to describe the transition region between two paradigms, described using two parameters, $R_{\text{trans}}$ for the size of the transition region, and $R_{\text{buf}}$ for the size of the ghost atom region. A schematic of this approach is shown in Figure 1. In the examples discussed here, we model a reactive region $\Omega_{\text{rx}}$ embedded into a nonreactive domain $\Omega_{\text{nr}}$. The reactive region is updated every $N_u = 10$ steps during the integration. We choose $R_{\text{trans}} = 6$ Å and $R_{\text{buf}} = 5$ Å. We have chosen these parameters by trial and error to make sure that the crack dynamics is not affected by changing these parameters. The shape and size of the reactive region surrounding the moving crack is based on the strain energy density of each atom. All atoms with a strain energy larger than $E_{\text{crit}} = -3.5$ eV are embedded in a cylindrical reactive region of $R = 10$ Å. The critical strain filters atoms at the tip of cracks and atoms in the vicinity of cracks whose bonds are stretched significantly. The union of all cylindrical regions yields the total reactive region, allowing representation of arbitrary shapes. The final reactive region is typically not circular, as can be clearly seen in Figure 4 (red regions) and Figure 5 (yellowish regions). Initially, the systems contain several hundred reactive atoms, which corresponds to a small reactive region at the crack tip. This initial
size of the reactive region may increase during the simulations approaching several thousand atoms because of crack branching or due to formation of microcracks.

When oxygen atoms are present in the system, a similar procedure is applied and in addition to the criterion based on the strain energy density, each oxygen atom is embedded in a cylindrical reactive region of $R = 10$ Å.

The force and energy contribution from different simulation engines is weighted as shown in Fig. 1. Each computational engine $i$ has a specific weight $w_i$ associated with it. For each atom in the system, the weight of $N$ computational engines add up to unity.

The force contribution from different computational engines is obtained as

$$\vec{F}_j = \sum_{i=0}^{N} \vec{F}_{j,i} w_i,$$

where $\vec{F}_{j,i}$ is the force contribution on atom $j$ due to computational engine $i$ and $\vec{F}_j$ is the resulting force vector on atoms $j$.

Figure 2 depicts our atomistic model. We consider a perfect crystal with an initial crack of length $a$ serving as the failure initiation point. The thickness of the system is one unit cell in the z-direction with periodic boundary conditions, corresponding to a plane strain case (size in z-direction $L_z \approx 5.43$ Å). This model is chosen due to computational limitations for keeping the reactive region small. We note that this choice of geometry may impose some constraints on the system, which may effect the possibility of dislocation nucleation. We strain the slab with strain $\varepsilon_{xx}$ in mode I prior to simulation similar as done in [24]. The boundaries are held fixed during the simulation so that the stress in the material can only be relieved by crack propagation. The crack starts to nucleate shortly after the simulation is started.

**III. SIMULATION RESULTS**

First we compare the dynamics of crack propagation described using pure Tersoff [30] to the results incorporating a region treated by ReaxFF close to the crack tip to demonstrate the importance of QM level accuracy at the crack tip to describe the bond breaking process. The crack direction is [110] with a (110) crack surface. We strain the system by 20 percent in mode I loading and then minimize the potential energy. We consider two cases, one in which a small region around the crack tip is treated using ReaxFF embedded in a Tersoff region, and the other case in which all atoms are described using Tersoff. The results of these computational experiments are shown in Figure 3. We observe that with pure Tersoff, the crack does not propagate. Instead the crack becomes blunt (Figure 3(a)) and eventual amorphizes as the loading is increased sufficiently. This incorrect description of brittle fracture has been observed in previous studies with Tersoff-type potentials [4, 11], and is in sharp contrast to experimental results [6]. Experiment clearly suggest a highly brittle behavior of silicon, in particular when initial cracks have (110) faces. In agreement with experiment, the hybrid treatment leads directly to a correct description of the fracture process (Figure 3(b)) [1, 3, 4, 6]. For [100] crack direction with (100) crack surface, similar behavior is observed: The pure Tersoff model leads to amorphization at the crack tip, in contrast to the hybrid model that leads to initiation of brittle fracture.

Figure 4 (a) shows various snapshots of a crack propagating in a silicon crystal strained by 10 percent with the temperature controlled to be around $T \approx 300$ K. The crack propagates through the material in a perfectly brittle manner. The crack approaches a speed of 3.41 km/sec, which is about 75 percent of the Rayleigh-wave speed, the limiting speed predicted by continuum theory [46] ($c_{R, Si} \approx 4.5$ km/sec [47]). Figure 4 (b) depicts the results for the same system but strained by 20 percent. Here we observe an initial phase of mirror-like cleavage, followed by a regime in which the crack leaves a rougher surface, setting in at about 1/3 of the Rayleigh-wave speed (1.5 km/sec). Eventually, the crack surface becomes highly coarsened (hackle regime). These observations from our hybrid simulations, in particular the onset of the rough surface at 1/3 of the Rayleigh-wave speed or 1.5 km/sec, agree with experimental studies of cracks propagating along the same crystalllographic planes [6]. Our observations for silicon seem to resemble the universal behavior of dynamical cracks in homogeneous materials showing a mirror-mist-hackle transition, as has been confirmed experimentally for a variety of materials, such as polymers (PMMA), silica glass, and crystalline materials [6, 48, 49]. Further, we observe that fracture dynamics in this case of large loading and elevated temperature leads to a mechanism of continuous formation of secondary microcracks ahead of the primary mother crack that coalesce with the mother crack as the crack moves forward (sec, for example in Figure 4 (b)). This mechanism is similar to the experimental observations made by Wu and Xu [50] and also are consistent with theoretical analyses [51].

Figure 4 (c) shows crack dynamics for an initial crack oriented into the [100] direction. Experiment shows that the crack branches into multiple (110) surface directions.
FIG. 3: Crack propagation with a pure Tersoff potential (subplot (a)) and the hybrid ReaxFF-Tersoff model (subplot (b)) along the [110] direction (energy minimization scheme). The blue regions are Tersoff atoms, whereas the red regions are reactive atoms. The systems contain 28,000 atoms and \( L_x \approx 270 \text{ Å} \times L_y \approx 460 \text{ Å} \). Subplot (c) shows the difference in large-strain elasticity between the Tersoff potential and ReaxFF, while both descriptions coincide at small strain. This result demonstrates the importance of large-strain properties close to breaking of atomic bonds [28, 44, 45].

FIG. 4: (a) Crack dynamics along the [110] direction at finite temperature \( (T \approx 300 \text{ K}) \), 10 percent strain applied. (b) Same crack orientation, but 20 percent strain applied. The results suggest a transition from a regime of mirror-like cleavage to a misty and hackle region. (c) Crack dynamics along the [100] direction at finite temperature \( (T \approx 300 \text{ K}, 10 \text{ percent strain applied}) \). Shortly after nucleation of the primary crack two major branches develop along [110] directions. The bond breaking region is fully embedded within the ReaxFF region in all cases. The systems contain about 64,000 atoms and \( L_x \approx 350 \text{ Å} \times L_y \approx 700 \text{ Å} \) with up to 3,000 atoms treated by ReaxFF.

stress intensity factor at the crack tip, while leading to formation of strong Si-O bonds, making this Si-O layer harder to break than pure silicon (see Figure 5 (a) versus Figure 5 (b)).

IV. DISCUSSION AND CONCLUSION

We have presented a new numerical method integrating the ReaxFF and Tersoff force fields to allow a physics-based description of the fracture mechanics of silicon. Our new scheme represents a new multi-scale approach of coupling the QM scale of chemistry and bond breaking and formation with the scale of mechanics of materials. Unlike previous attempts [4] in which empirical potentials were modified heuristically to yield brittle fracture of silicon, our method is completely based on first-principles, with no empirical parameters used for fitting of ReaxFF for silicon.

Our results (see Fig. 3(a) and (b)) underline the importance of large-strain properties at bond breaking for the dynamics of fracture, as suggested earlier by Gao [44] and one of the authors [28, 45]. Figure 3(c) shows...
FIG. 5: Crack dynamics in silicon without oxygen ($O_2$ molecules) (subplots (a) and (c)) and with oxygen molecules present (subplots (b) and (d)). Subplots (a) and (b) show the results for 5 percent applied strain, whereas subplots (c) and (d) show the results for 10 percent applied strain. The gray regions are Tersoff atoms, whereas the colored regions correspond to ReaxFF atoms. The systems contain about 13,000 atoms, with $L_x \approx 160 \text{\AA} \times L_y \approx 310 \text{\AA}$. This demonstrates the dramatic effect of oxygen in making Si brittle.

the large deviation between Tersoff and ReaxFF at large strains close to bond breaking by stretching the crystal in the [110]-direction. The Tersoff description leads to a sharp rise of the force close to rupture of bonds, which deviates significantly from the more accurate solution by ReaxFF.

Our model is further capable of reproducing key experimental observations including crack limiting speed, crack instabilities and directional dependence on crystal orientation (see Fig. 4(a-c)). Our studies lead to important insight into the atomistic details of the fracture processes, suggesting continuous formation of micro-cracks ahead of a propagating mother crack (see Fig. 4(b)). This has been debated in the literature and our simulations clearly corroborate this concept.

We find that ReaxFF reactive force field [33, 34] successfully models chemo-mechanical properties of materials as crack propagation. Since ReaxFF is capable of describing a wide heterogeneous range of materials [33–38], our approach may be a practical means to studying the coupling of complex chemical reactions to mechanical properties. This is shown in the studies depicted in Figure 5. In this Letter, we have demonstrated the effect of oxygen in changing the fracture behavior of silicon by effectively blunting the crack tip and thus making silicon more brittle, in agreement with experiment. Our hybrid method could enable studies of stress corrosion processes and other degradation and aging mechanisms.

We find that a few thousand atoms in the reactive region at the crack tip are sufficient to describe the crack dynamics correctly. Although such calculations are not practical with pure QM, ReaxFF provides QM accuracy for the reacting part of the system, while retaining speeds comparable to that of simple force fields. As demonstrated in the literature and in Figure 3, the Tersoff potential cannot describe fracture accurately [10, 11], but it is adequate for describing the elastic regions.

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