Multiscale Materials Simulations: A Hybrid Quantum-Classical Approach

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A hybrid simulation approach is developed to study chemical reactions coupled with long-range mechanical phenomena in materials. The finite element method for continuum mechanics is coupled with the molecular dynamics method for an atomic system that embeds a cluster of atoms described quantum-mechanically with the electronic density-functional method based on real-space multigrids. The hybrid simulation approach is implemented on parallel computers using both task and spatial decompositions. Hybrid simulation runs for a cracked-Si model under tension (mode-I opening) with multiple H_2O molecules around the crack-front are performed, to investigate possible effects of the environmental molecules on fracture initiation in Si.

Key words: multiscale simulation, hybrid simulation, density-functional theory, molecular dynamics, environment effects on fracture

1. INTRODUCTION

Various kinds of nanosystems [1,2] such as nanoparticles, thin films, and nanophase materials have drawn attention due to their improved electronical, physical, and chemical properties [3] resulting from their nanometer-size phases [1,3]. Understanding such physicochemical unique properties requires dynamic simulations of chemically reacting atoms in these materials. Highly accurate simulations based on energy density-functional theory (DFT) [4,5] for electronic structures have been used extensively to study chemical reactions in clusters of Despite its considerable progress, current atoms. DFT-based dynamic simulations are still limited to systems containing less than a few hundred atoms due to long computation times [6,7].

We have recently developed a hybrid quantummechanical/molecular-dynamics (QM/MD) approach [8] to dynamic simulation of materials on parallel computers. Computation can be made less when we partition a simulation system into different regions that are modeled with varying degrees of approximation. In the hybrid QM/MD approach, a QM system described by DFT based on real-space multigrids [8] is embedded in a classical system of atoms interacting via an empirical interatomic potential. Handshake atoms are introduced to couple the quantum and the classical systems dynamically based on the scaled position method [8]. The hybrid QM/MD approach enables dynamic simulations of material processes involving chemical reactions such as oxidation [8].

There exists growing demand for large-scale

materials simulations involving chemical reactions, e.g., to study the interplay between stress fields and chemical reactions. Stress in materials is longranged [2,3]. Stress fields, which depend on the size and the overall shape of the system, may affect local atomic diffusion rates and hence chemical reactions. Large-scale dynamic simulations with realistic stress fields are expected to play a key role in understanding atomistic mechanisms of these processes. Another example that requires large-scale simulations involving chemical reactions is found for microelectro-mechanical systems (MEMS) [9], in which feature sizes are submicrons. Lifetime prediction of MEMS is currently impractical since constitutive relations and scaling laws [2] in engineering mechanics have not been validated at such small length scales. Large-scale simulations involving chemical reactions should contribute significantly in this area by providing atomistic understanding of environmental effects on fracture and fatigue processes in MEMS.

Recent progresses in algorithms and parallel computers have enabled MD simulations [10] involving 10^8 - 10^9 atoms with system sizes exceeding 0.1 micrometer [11,12]. With the hybrid QM/MD approach [8], systems with similar sizes can be simulated in which 10^3 - 10^4 atoms are treated quantummechanically, using scalable DFT algorithms [7]. To simulate entire MEMS and device structures (> 1 micrometer), however, it is necessary to coarse-grain atomic details in the peripheral region of the system. The coarse-graining can be achieved with the finite element (FE) method [13], in which a material is regarded as a continuum and is decomposed into a mesh of finite elements.

In this paper, we develop a hybrid FE/MD/QM approach to materials simulations on parallel computers by combining the FE method with our hybrid QM/MD method [8]. The hybrid code is applied to a cracked-Si model under tension (mode-I opening) with multiple H_2O molecules around the crack-front, to investigate possible effects of the environmental molecules on fracture initiation in Si.

2. HYBRID SIMULATION SCHEME

In the present hybrid scheme, a simulation system is decomposed into FE, MD, and QM regions. The QM region is surrounded by the MD region, while the MD region connects with the FD region. In the FE method, the system is regarded as a continuum and is decomposed into a mesh of finite elements. In the handshake (HS) region between the FE and the MD regions, the FE mesh is refined down to the atomic scale in such a way that each FE node coincides with an MD atom [8]. The FE calculations apply to the FE and the FE/MD-HS regions, whereas the MD calculations apply to the MD and the FE/MD-HS regions. The OM atoms as well as the HS atoms between the QM and the MD regions are treated with the DFT calculations. Virtual hydrogen atoms are introduced in the DFT calculations to terminate dangling bonds of the QM atoms. Details of the termination scheme are described in Ref. 8.

The finite elements, which are either prismatic or rectangular, occupy the whole FE and FE/MD-HS regions by sharing their corners or edges [8]. Total number of nodes in the finite element varies between 8 and 20 [8]. Twenty-node elements are used in the FE region far from the FE/MD-HS region, while eight-node elements are used close to the FE/MD-HS region. Side length of the finite element scales down to the atomic spacing in the FE/MD-HS region.

We denote positions of the FE nodes, MD atoms, and QM atoms as $\{\vec{r}_{FE}(i)\}$, $\{\vec{r}_{MD}(i)\}$, and $\{\vec{r}_{QM}(i)\}$, respectively. Similarly, $\{\vec{r}_{FE/MD}^{-HS}(i)\}$ represents the FE/MD-HS atoms, and $\{\vec{r}_{QM/MD}^{-HS}(i)\}$ the QM/MD-HS atoms. The dynamics of the system is determined by the Hamiltonian

$$\begin{split} H &= H_{\text{FE/MD}}^{\text{system}}(\vec{R}_{\text{all}}, \vec{R}_{\text{all}}) \\ &+ E_{\text{CM}}^{\text{cluster}}(\{\vec{r}_{\text{QM}}\}, \{\vec{r}_{\text{QM/MD}}^{\text{HS}}\}), \end{split} \tag{1} \\ &- E_{\text{MD}}^{\text{cluster}}(\{\vec{r}_{\text{QM}}\}, \{\vec{r}_{\text{QM/MD}}^{\text{HS}}\}) \end{split}$$

where \vec{R}_{all} denotes all the positions of atoms and nodes, and $\vec{R}_{all} = d\vec{R}_{all}/dt$. The $H_{FE/MD}^{system}$ in Eq. (1) is the FE/MD Hamiltonian (see Sec. 2.1) of the total system (including the FE, MD, and QM regions). The last two terms on the right hand side of Eq. (1) represent the QM correction to the MD potential energy for the cluster of atoms in the QM region [8,14,15]. The gradient of H with respect to the position \vec{r}_i of the *i*-th atom gives the force \vec{F}_i on the atom as a summation of three partial forces corresponding to the three terms of H in Eq. (1): $\vec{F}_i = -\partial H / \partial \vec{r}_i = \vec{F}_{\text{FE}/\text{MD},i}^{\text{system}} + \vec{F}_{\text{QM},i}^{\text{cluster}} - \vec{F}_{\text{MD},i}^{\text{cluster}}$. We note that $\vec{F}_{\text{QM},i}^{\text{cluster}} = \vec{F}_{\text{MD},i}^{\text{cluster}} = 0$ for those atoms which are neither the QM nor QM/MD-HS atoms

2.1 FE-MD coupling

Following linear elasticity theory for continua, we may write the potential energy of the finite elements as [16]

$$\sum_{m}^{\text{elements}} \int_{\text{element}(m)} d\vec{r} \frac{1}{2} \sum_{i,j \ k \ l}^{3} \varepsilon_{ij}(\vec{r}) \ C_{ijkl} \varepsilon_{kl}(\vec{r}) \quad (2)$$

with the strain tensor field given by

$$\varepsilon_{ij}(\vec{r}) = \frac{\partial u_i(\vec{r})}{\partial r_j} + \frac{\partial u_j(\vec{r})}{\partial r_i}, \qquad (3)$$

where $\vec{u}(\vec{r})$ is the displacement field and the elastic matrix C_{ijkl} of the material is either obtained experimentally or calculated theoretically. We perform each integral in Eq. (2) by interpolating $\vec{u}(\vec{r})$ between the FE nodes using a linear (for the 8-node elements) or quadratic (for the 20-node elements) function of \vec{r} [16]. Denoting the total number of FE nodes for element-*l* as n_{node} (*l*), Eq. (2) reduces to

$$\sum_{l}^{\text{elements}} \sum_{\mu,\nu}^{\eta_{\text{hode}}} \frac{l}{2} \vec{u}_{\mu} \cdot \vec{K}_{\mu,\nu}^{l} \cdot \vec{u}_{\nu} , \qquad (4)$$

where $\vec{K}_{\mu,\nu}^{l}$ is the stiffness matrix [16] for element-*l*. We employ the lumped-mass approximation [16] for the kinetic energy of the finite elements, *i.e.*, each FE node-*a* is assigned a mass m_a calculated with the mass density ρ_{mass} of the material:

$$m_a = \sum_{l}^{\text{chemicals}} \sum_{i}^{\text{node}} \langle v_i \rangle_{a,i} / n_{\text{node}} (l), \text{ where } V_l \text{ is}$$

the volume of element-*l*, and $\delta_{ai}=1$ if node-*a* coincides with node-*i* of element-*l* and $\delta_{ai}=0$ otherwise. The FE mass reduces to the atomic mass m_i in the FE/MD-HS region.

We consider MD interatomic potentials that are composed of two-body $(\phi_2(i, j))$ and three-body $(\phi_3(i, j,k))$ terms as in Stillinger-Weber (SW) potential [17] for Si. To link the FE and the MD regions in a seamless manner, we introduce a weight function w for the MD atoms and the FE nodes [8]. We assign w = 1 for the MD atoms in the MD region, and w = 0 for the FE nodes in the FE region. In the FE/MD-HS region, all MD atoms in an atomic layer are assigned a single w value, and the value of w varies from 1 to 0 layer-by-layer in a stepwise manner. Similarly, w for the FE nodes in the FE/MD-HS region is graded element-by-element. Using the weight function, $H_{\text{FE/MD}}^{\text{system}}$ in Eq. (1) is written as

$$H_{\text{FE/MD}}^{\text{system}} \approx \sum_{i}^{\text{atoms} \ell \text{ elements}} \frac{1}{2} m_{i} v_{i}^{2}$$

$$+ \frac{1}{2!} \sum_{i,j}^{\text{atoms}} w(i)\phi_{2}(i, j) + \frac{1}{3!} \sum_{i,j,k}^{\text{atoms}} w(i)\phi_{3}(i, j, k) \quad (5)$$

$$+ \frac{1}{2!} \sum_{i}^{\text{elements}} n_{\text{nods}}^{(l)} [1 - w(\mu)] \vec{u}_{\mu} \cdot \vec{K}_{\mu,\nu}^{l} \cdot \vec{u}_{\nu}$$

where $\{\vec{v}_i\}$ are velocities of the atoms and the FE nodes.

2.2 DFT-MD coupling

We consider an insulator such as ceramics or semiconductors, whose bonding pairs are known. Stabilizing atomic configuration of the cluster requires termination of its dangling bonds by hydrogen (H) atoms. The positions of the termination H atoms are determined from those of the QM/MD-HS. Let $\vec{r}_{i(i)}$ and $n_{\rm c}(i)$ be the positions of the QM atoms bonding to a QM/MD-HS atom at \vec{r}_i and the number of different j for each i, respectively. A termination H is placed at $\vec{x}_{i,j}^{H} = \beta \vec{r}_i + (1-\beta)\vec{r}_{j(i)}$ for each (i, j) pair with a control parameter β [8]. The DFT calculations of the H-terminated atomic cluster are performed with free boundary conditions to obtain $E_{\rm QM}^{\rm cluster}$ and the corresponding forces on the QM and the QM/MD-HS atoms. Value of β is determined to minimize mean square displacements of the QM atoms caused by cluster formation.

In the Kohn-Sham (KS) formulation of DFT [4-6], total energy of a cluster of atoms located at $\{\vec{r_k}\}$ is written as

$$E_{QM}^{\text{cluster}}(\{\vec{r}_{k}\}) = 2 \sum_{i=1}^{\infty} \psi_{i}^{*} \left(-\frac{\nabla^{2}}{2}\right) \psi_{i} d\vec{x}$$
$$+ \frac{1}{2} \iint \frac{\rho(\vec{x})\rho(\vec{x}')}{|\vec{x} - \vec{x}'|} d\vec{x} d\vec{x}' \qquad (6)$$
$$+ \int V_{\text{ion}}(\vec{x})\rho(\vec{x}) d\vec{x} + E_{\text{xc}}(\rho) + E_{\text{ion}}(\{\vec{r}_{k}\})$$

with the KS electronic wave functions $\{\psi_i\}$ and the

charge density
$$\rho(x) = 2\sum_{i=1}^{N} |\psi_i(\vec{x})|^2$$
. The V_{ion} in

Eq. (6) is the pseudopotential for valence electrons; $E_{\rm xc}$ and $E_{\rm ion}$ are the exchange-correlation energy and the interaction energy between ion cores, respectively [4-6]. We may obtain $\{\psi_i\}$ as solutions to the KS nonlinear differential equations [5-7].

We use real-space multigrids for DFT calculations [7,8], in which $\{\psi_i\}$ and the Hartree potential V_{Hartree} are represented on a uniform real-space mesh in Cartesian coordinates with an auxiliary set of coarser meshes. Details of the method are explained in Refs. 7 and 8. We use norm-conserving pseudopotentials for V_{ion} with the generalized

gradient correction. The second derivative of $\{\psi_i\}$ in Eqs. (6) and (7) is calculated by the sixth-order finite difference method [18]. The $\{\psi_i\}$ are solved by repeating the self-consistent field (SCF) iteration cycle [7,8]. Convergence of both the Hartree potential and the KS equation is accelerated with the multigrid method [7,8].

For the calculations of $E_{\text{MD}}^{\text{cluster}}$ in Eq. (1), we similarly introduce classical termination atoms by displacing the QM/MD-HS atoms to minimize surface effects on atomic forces on the QM atoms [8]. Position $\bar{x}_{i,\{j\}}$ of the termination atom-*i* is $\bar{x}_{i,\{j\}} = \alpha \bar{r}_i + (1 - \alpha) \langle \bar{r}_{j,\{i\}} \rangle_j$, where α is a parameter and $\langle \cdots \rangle_j$ denotes taking average over different *j*. If a surface atom in the atomic cluster interacts only with its first nearest-neighbor atoms in the empirical interatomic potential, as in the SW potential for Si, we may set $\alpha = 1$. Value of $E_{\text{MD}}^{\text{cluster}}$ is obtained as the MD potential energy of the terminated atomic cluster.

3. APPLICATION

Α hybrid quantum-mechanical/moleculardynamics simulation is performed for a cracked-Si model under tension (mode-I opening) with three H₂O molecules around the crack-front, to investigate possible effects of the environmental molecules on fracture initiation in Si. The crack surfaces of the model are set parallel to Si (110). Electronic structures of atoms near the crack-front are calculated with the density-functional theory. Those atoms are embedded in a system of classical Si-atoms. Neighboring three atomic clusters (i.e., QM clusters) containing atoms around the crack-front are selected from the MD atoms. Atomic configurations at the initial are same between the OM clusters. Centers of the QM clusters align along the crack-front line. Numbers of the QM atoms are, in total, 108 for Si and 120 for termination-H. There exist four dangling bonds in each QM cluster on the crack surfaces. Relating to the change in Hamiltonian from the purely classical one to the hybrid one further relaxation is required to stabilize the hybrid system. Hybrid simulation runs are performed for those systems with the stress-intensity factor K = 0.4MPa $\cdot \sqrt{m}$ and 0.5MPa \cdot m, in which the velocity scaling-factor is 0.95 at every time step of 2.0 fs, until the largest temperature of atom becomes less than 0.01K. The smallest grid-size used in DFT calculation is 0.21a.u. in real space.

To investigate possible effects of H_2O molecules on fracture initiation we add a H_2O molecule in each QM region, with zero velocity and random orientation, at a position separated by 4.0 Å in the $\langle 001 \rangle$ direction from the central Si atom at the crack-front. Initial configuration of the present hybrid simulation for the environment effects of H_2O molecules is depicted in Fig. 1 in Ref. 19. The time step is 1.0 fs in the simulation. Hybrid QMMD simulation runs for K = 0.4MPa $\cdot \sqrt{m}$ and 0.5MPa $\cdot \sqrt{m}$ are performed on parallel computers. A single computer-node is assigned to the MD computation, while 16 computer-nodes are assigned to computation for each QM cluster; in total, 49 computer-nodes are used for the present hybrid simulation. The simulation runs are performed for \sim 500 fs until the system reaches equilibration.

Through the simulation runs we find that chemical reactions of three H2O molecules with Si atoms at the crack tip may be grouped into three different processes. In the K = 0.4 MPa \cdot m run, two of the three H₂O molecules dissociate into H and OH and adhere to dangling-bond sites on the crack surface (chemisorption). Other single H₂O molecule dissociates into 2H and O. Then two H-atoms adhere to two dangling-bond sites on the crack surface, while O inserts between a Si-Si pair at the crack-front (oxidation). In the K = 0.5MPa \cdot m run, two H₂O molecules dissociate into 2H and O and oxidization process follows. One H₂O molecule dissociates into H and OH. The H adheres to a dangling-bond site, while OH breaks the Si-Si bond at the crack-front (bond breakage). In both runs, chemical reaction of the H₂O molecules with Si atoms at the crack-font does not initiate fracture in agreement with experimental observations.

In the present study we have considered only (110) crack-surface of pure Si (i.e., with no surface saturation-atoms) to study the environment effects of H_2O molecules. In experiments, depending on preparation procedures, crack surfaces can be partially saturated by H or other elements. Separate hybrid simulation runs are in progress to study the environment effects for different crack-planes with varying surface conditions.

4. ACKNOWLEGEMENT

Present simulation runs are performed on SGI2800 in ISSP (University of Tokyo), T3E in NAVO, and PC-clusters in CCLMS (LSU) and Yamaguchi University. This research is supported by ACT-JST.

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(Received March 8, 2002; Accepted April 30, 2002)