Hierarchical petascale simulation framework for stress corrosion cracking

Priya Vashishta¹, Rajiv K Kalia¹, Aiichiro Nakano¹, Efthimios Kaxiras², Ananth Grama³, Gang Lu⁴, Stephan Eidenbenz⁵, Arthur F Voter⁵, Randy Q Hood⁶, John A Moriarty⁶ and Lin H Yang⁶

¹University of Southern California, Los Angeles, CA 90089-0373, USA
²Harvard University, Cambridge MA 02138, USA
³Purdue University, West Lafayette, IN 47907, USA
⁴California State University Northridge, Northridge, CA 91330, USA
⁵Los Alamos National Laboratory, Los Alamos, NM 87545, USA
⁶Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

E-mail: priyav@usc.edu

Abstract. We are developing a scalable parallel and distributed computational framework consisting of methods, algorithms, and integrated software tools for multi-terascal-to-petascale simulations of stress corrosion cracking (SCC) with quantum-level accuracy. We have performed multimillion- to billion-atom molecular dynamics (MD) simulations of deformation, flow, and fracture in amorphous silica with interatomic potentials and forces validated by density functional theory (DFT) calculations. Optimized potentials have been developed to study sulfur embrittlement of nickel with multimillion-to-multibillion atom MD simulations based on DFT and temperature dependent model generalized pseudopotential theory. We have also developed a quasi-continuum method embedded with quantum simulations based on DFT to reach macroscopic length scales and an accelerated molecular dynamics scheme to reach macroscopic time scales in simulations of solid-fluid interfaces that are relevant to SCC. A hybrid MD and mesoscale lattice Boltzmann simulation algorithm is being designed to study fluid flow through cracks.

1. Introduction

Corrosion is an enormously complex technological and economic problem with an annual cost of about 3% of the U.S. gross domestic product. The basic requirements for the operation of structural systems exposed to corroding conditions under stress loads are safety and reliability. Such safe and reliable operation is endangered by the uncertainties in stress corrosion cracking (SCC). To prevent SCC and to predict the lifetime beyond which SCC may cause failure requires that we understand the atomistic mechanisms underlying SCC; that is the conditions influencing initiation, dynamics, and growth rates of SCC.

The science and engineering of SCC provide a rich and challenging set of applications involving simultaneous chemical, physical, and material processes. To achieve the sound atomistic/mechanistic basis that would allow designers to optimize the performance of structures and systems in chemically aggressive environments, we must develop first-principles models for all aspects of SCC, including the role of pH, electrochemical potential, material microstructure, local temperature, and local stress.

2. Scalable and adaptive algorithms for hierarchical simulations

We are developing scalable parallel algorithms for quantum molecular dynamics (QMD), large-scale atomistic simulations – namely, molecular dynamics (MD) based on quantum-based model generalized
pseudopotential theory (MGPT) and reactive force fields (F-ReaxFF) – and for accelerated MD simulations. The algorithms are based on our embedded divide-and-conquer (EDC) algorithmic framework combined with adaptive multigrids. Scalability has been achieved on $10^5$ processors through linear-scaling algorithms and performance-optimization techniques. For example, we have developed a highly efficient, modular, and effective reactive MD simulation code employing state-of-the-art data structures, algorithms, and numerical methods. This code reduces the memory footprint by a factor of up to 3 and improves speed by a factor of up to 4, compared to other reactive codes. The code employs dynamic compressed octrees that minimize storage and time for fast neighborhood computations. The terms are themselves computed through composite lookup (the entire potential function is indexed into a dynamic table). Since the arguments to these potential functions tend to be highly clustered (bond lengths, angles, and torsion terms), the use of dynamic lookups results in significant speedups, while being memory efficient. Charge equilibration is achieved using an efficient predictor-corrector generalized minimal residual (GMRES) iterative scheme. This scheme is shown to achieve excellent solution times and convergence rates, while being memory efficient (small Krylov subspace). We have demonstrated 201 billion-atom MD, 1.59 billion-atom reactive MD, and 17.7 million-atom (1.56 trillion grid points) quantum-mechanical MD in the framework of divide-and-conquer density functional theory on adaptive multigrids with the parallel efficiency as high as 0.99 on 196,608 Blue Gene/L processors.

3. Damage, flow, and fracture in amorphous silica

We have performed large-scale MD simulations to investigate shear-induced void deformation and nanoductility and defect nucleation and migration in nanoindentation of a-SiO$_2$. The simulations are based on an interatomic potential, which incorporates ionic and covalent effects through a combination of two-body and three-body terms. The interatomic potential was validated by comparing the MD simulation results for structural and mechanical properties of a-SiO$_2$ with experimental measurements and quantum mechanical calculations based on density functional theory performed by our SciDAC team member Lin Yang at LLNL.

3.1 Damage and cracking in shearing silica glass

One set of SCC simulations is focused on shear-induced deformation and breakup of nanovoids with and without water in silica glass. The simulations involve up to 633 million atoms. The initial diameter of the void ranges between 3 and 50 nm, which covers nearly the entire range of void sizes observed in the damage zone in dynamic fracture simulations [1] and quasi-static stress corrosion cracking experiments [2] on silica glass.

Figure 1 shows the degree of deformation for a void in silica glass at room temperature. The initial diameter of the void is 10 nm. As time evolves, the void shape changes to ellipsoidal and damage in the form of nanocracks nucleates on the void surface at the two ends of the short axis of the ellipsoid; see the snapshot in figure 1(a). The same kind of deformation and damage are also observed for voids of initial diameters 3 nm and 50 nm. Stress calculations reveal that nanocracks form along the direction of maximum tensile stress.
Figure 1. (a) Shear deformation of a spherical void of diameter 10nm to an ellipsoid after 15 ps; (b) time variation of the deformation parameter, $D$, for voids of initial diameters 3 nm (blue circles), 10 nm (red squares), and 50 nm (green triangles). Shear rate = $10^{12}$ s$^{-1}$.

Figure 1(b) shows the time variation of the deformation parameter, $D$, for initially spherical voids of diameters 3 nm (blue), 10 nm (red), and 50 nm (green). The deformation parameter is defined as $D = (L-B)/(L+B)$, where $L$ and $B$ are the major and minor axes of the ellipsoid, respectively. In all three cases $D$ increases linearly with time up to 15 ps, which is an indication that the void deformation is elastic up to a shear strain of 15%. To distinguish between elastic and plastic void deformations, we switch off the shear strain rate at a certain value of the strain and let the system relax without shear. We find that if the shear strain rate is dropped to zero before the strain reaches 15%, voids recover their initial spherical shapes and sizes. This situation confirms that the void deformation is elastic so long as the strain is below 15%. Plastic deformation in shearing silica glass appears after 15 ps (strain > 15%) as the deformation parameter begins to increase non-linearly with time. Figures 2(a) and 3(b) are snapshots showing long, thin voids with nanocracks on the surfaces near the middle of the long axis. Initially, these were spherical voids of diameters 3 nm and 50 nm. In both cases, the voids become threadlike before breakup, which occurs above a strain of 40%. Figure 2(c) shows plastic deformation of a void, which was initially a sphere of diameter 10 nm. The snapshot taken at 35ps shows a long, thin void with ends deformed roughly like an $S$ shape. There are nanocracks on the surface and near the ends of the void. As time evolves, nanocracks grow and the void becomes more elongated, and at 40 ps the void fragments; see figure 2(d).
Figure 2. Panels (a) and (b) show plastic deformations of voids of initial diameters 3 nm and 50 nm, respectively. Panel (c) shows a plastically deformed void that was initially a sphere of diameter 10 nm; and panel (d) shows its breakup at 40 ps.

Analyses of elastic-to-plastic void deformation and crack initiation and growth reveal a novel mechanism involving strain-enhanced defect transport. In the unstrained α-SiO$_2$, each Si atom (yellow) is connected to four O atoms (red) in the form of a SiO$_4$ tetrahedron, and these tetrahedra are linked into nanometer size –Si-O-Si-O– rings through corner-sharing O atoms. In figure 3(a), green and blue regions represent 6- and 9-member rings, respectively, at a strain of 5%. The magenta atom is a bridging O, and the blue atom is a threefold coordinated Si atom in the 9-member ring. Figure 3(b) shows that at a strain of 8% the magenta O atom becomes nonbridging while the blue Si atom remains undercoordinated. The grey ring with these Si and O defects is a 13-member ring. At a strain of 10%, the green Si and magenta O atoms become fully coordinated by bonding with each other. The blue Si is still undercoordinated but now belongs to a 14-member ring (yellow). Nonbridging oxygen and threefold coordinated silicon atoms play pivotal roles in the nucleation of cracks through the enlargement of –Si-O-Si-O– rings and in void deformation and shear flow in silica glass.

We have also investigated changes in the void shape and elastic-to-plastic transition in silica glass at 1200K. In contrast to the case at room temperature, the voids are partially filled with atoms released from the void surfaces and the density of these atoms inside the voids increases with time. The voids still undergo spherical-to-ellipsoidal shape transformation, but the time variation of the deformation parameter is slightly less than that at room temperature. Nanocracks appear on void surfaces with the onset of plasticity. Voids deform into long ellipsoidal shapes with pointed ends, and their breakup is again preceded by threadlike structures just as at room temperature.

Taken together, MD simulations reveal that shear-induced void deformation, damage, and flow in silica glass have the same underlying mechanism involving Si-O bond breaking and the migration of threefold coordinated silicon and non-bridging oxygen defects on –Si-O-Si-O– rings. The density of these defects remains small and nearly constant in the elastic deformation regime. With the onset of plasticity at a shear

Figure 3. Defects responsible for shear deformation and flow in silica glass.
strain of 15%, the defect density increases and reaches a plateau soon after a void breaks up. Despite the enormous differences in spatio-temporal scales, the observed shape changes and fragmentation of voids in silica glass are remarkably similar to the deformation and breakup of macroscopic inviscid drops at high shear rates.

3.2 Defect migration and recombination in nanoindentation of silica glass
Multimillion-atom MD simulations are performed to investigate plasticity and flow mechanisms in nanoindentation of amorphous silica [3]. The simulations reveal migration of nonbridging oxygens and their recombination with undercoordinated silicons in the densified plastic region under and the material pileup region around the indenter. The migration involves chains of defects switching bonds in string-like processes. These defects were postulated by Mott to explain shear flow in silica glass.

Figure 4(a) shows a snapshot of the system at the maximum indentation depth. The amorphous film contains 40 million atoms and has dimensions 100×100×60 nm³. The indenter, a square-based rigid pyramid with an apical angle of 90°, interacts with the substrate through a repulsive potential. We have used two kinds of indenters to study the effect of the indenter curvature: an atomistically sharp indenter and an indenter whose end is spherical with a diameter of 10 nm. Figure 4(b) displays the applied load in the MD simulation as a function of the penetration depth of the indenter. From the load and residual indentation impression, we obtain the hardness, $H$, of a-SiO$_2$. In the case of an atomistically sharp indenter, $H = 7.2$ GPa, and for the slightly blunt indenter $H = 8.0$ GPa. The AFM indentation experiment on fused silica yields a hardness value of 10 GPa.

![Figure 4](image_url)

**Figure 4.** (a) Pileup around the indenter at the maximum indentation depth. Indentation causes localized damage creating high-temperature area underneath the indenter, which facilitates pile-up through plastic flow. The colors represent temperature. (b) Load versus displacement during loading and unloading phases of indentation.

Figure 5 shows snapshots of the indented silica film at indentations depths (a) $h = 11$ nm and (b) 32 nm. For clarity, only a slice of the system without the indenter is shown here. At low indentation depths (e.g., $h = 11$nm), the material close to the bottom of the indenter densifies but there is no material pile-up around the indenter. At the maximum indentation depth of 32 nm, we observe significant pileup and a 20% increase in the mass density of a-SiO$_2$ beneath the indenter relative to the mass density of bulk silica glass under ambient conditions (2.2 g/cc). In the pileup region shown in panel (b), the density is 18% lower (1.8 g/cc) than in the bulk system. During the unloading phase of the simulation, the silica substrate exhibits slight elastic recovery and a decrease in the density under the indenter. Panel (c) is a snapshot of a slice of the system after the indenter is pulled out of the substrate. Here the density just beneath the indenter goes back to the normal bulk a-SiO$_2$ density (2.2 g/cc), but there is still a considerable pileup around the indenter.
Detailed analyses of atomistic configurations reveal how plastic deformation and pileup occur in the nanoindentation of a-SiO₂. In the normal SiO₂ glass, each Si atom is bonded to 4 O in the form of a tetrahedron and each O bonds with two Si atoms to connect neighboring SiO₄ tetrahedra. These corner-sharing tetrahedra form closed –O–Si–O–Si–O– rings of various sizes, with a peak in the distribution around 6-member rings, that is, 6 Si–O connected pairs. According to Mott, undercoordinated Si and nonbridging O point defects diffusing on –Si-O-Si-O– rings are responsible for plastic flow in silica glass. These point defects in the silica network glass play a central role in the plastic deformation and pileup we observe in both nanoindentation simulations. The defects are involved in bond-switching events, where either a silicon or an oxygen atom severs its bond with one of its neighbors and shortly thereafter (~ 10 ps in simulation 1) forms a new bond with a different neighbor atom. Figures 6 (a)–(c) show how a bond-switching event occurs in the case of a nonbridging oxygen defect. The three atoms involved in this event are labeled as O1 (initial oxygen defect), Si2 (bond switching silicon) and O3 (the final oxygen defect). Initially, O1 is a nonbridging oxygen, whereas Si2 and O3 have normal coordinations (4 O neighbors for Si2 and 2 Si neighbors for O3). At the transition state, the Si2-O3 bond breaks, and these two atoms become undercoordinated. Subsequently, Si2 forms a new bond with O1, and they both become fully coordinated, whereas the oxygen labeled O3 remains a defect.

Another bond-switching event we observe involves the annihilation of a nonbonded pair of undercoordinated silicon and oxygen atoms. Figures 6 (d)-(f) show this pair-annihilation event. The four atoms involved in this event are labeled as Si1 (an undercoordinated silicon), O2 (bond-switching oxygen), Si3 (bond-switching silicon), and O4 (a non-bridging oxygen). Initially, O2 is bonded with Si3 and they both have normal coordinations of 2 and 4, respectively. In the transition state, O2-Si3 bond breaks, and they both become undercoordinated. In the final state, Si1 forms a bond with O2 and Si3 with O4 and now these four atoms have normal coordinations.

Our simulations also reveal a defect transport mechanism in which a defect migrates a considerable distance via a chain of bond-switching events. This is an important mechanism in the plastic flow of silica glass. Panels (a) and (b) in figure 7 and show two examples of a bond-switching chain event. In panel (a), an undercoordinated silicon migrates via a bond-switching chain involving seven atoms and in panel (b) the annihilation of a defect pair is mediated by a bond-switching chain of six atoms. Here
yellow and red spheres represent positions of silicon and oxygen atoms, respectively, after each multiatom bond-switching event. In the transport event for a silicon defect, the defect effectively migrates about 1 nm in 10 ps.

**Figure 7.** Snapshots of defect migration pathways ((a) and (b)) in a ball-and-stick representation. Yellow and red spheres represent silicon and oxygen atoms. Black dotted lines indicate covalent bonds before defect migration. Blue and red arrows represent initial and final positions of defect atoms, respectively. (a) Migration of a silicon defect. (b) Annihilation of a pair of silicon and oxygen defects. Panels (c) and (d) show the length of the string-like defect motion as a function of the number of migration events during loading and unloading, respectively. Mechanical loading by the indenter induces longer migration pathways.

The length of the chain of bond-switching events varies with mechanical loading. Panels (c) and (d) in figure 7 show the dependence of the number of bond-switching events $N_{\text{chain}}$ on the chain length $l$ at several indentation depths. In the loading phase, longer bond-switching chains appear as the indentation depth increases. Note that the slopes at the three indentation depths are almost constant in the semi-log plot, which implies exponential distributions $N_{\text{chain}} \propto \exp(-l/l_0)$ with nearly the same characteristic length $l_0$. The slopes differ significantly before ($h = 31$ nm) and after ($h = 16$ and 21 nm) the indenter is pulled out of the substrate, which shortens the chain length.
4. Hybrid atomistic/mesoscale simulations of fluid flow through cracks

We are designing an algorithm to interface MD with a mesoscale approach to fluid flow simulation, namely, the lattice Boltzmann (LB) method, which solves a minimal form of the Boltzmann kinetic equation ignoring all details of molecular motion except those needed to recover hydrodynamic behavior at the macroscopic scale. For hierarchical fluid flow simulations, we have developed an extensible LB computational framework for terascale-to-petascale parallel/distributed platforms. The LB framework includes scalable algorithms and tools as well as capabilities for handling, analyzing, and visualizing petabyte simulation datasets. It allows collaborative construction and execution of complex, multi-component, computationally demanding hybrid numerical simulations of fluid flow. We have achieved scalability beyond $10^5$ processors through linear-scaling algorithms and performance-optimization techniques. Recently, we have performed LB simulations of fluid flow through a network of cracks in amorphous silica on a cluster of PlayStation3 consoles (figure 8).

Currently, we are developing an automated model transitioning to embed higher fidelity MD simulations concurrently inside LB simulations only when and where they are required (figure 10). We are using a domain decomposition algorithm based on Schwartz alternating method to implement hybrid MD-LB simulations. In this scheme, the system is decomposed into (1) a purely atomistic region described by MD, (2) a continuum region described solely by LB, and (3) an overlapping MD-LB region. Since the MD region is open and particles move out of the MD into the LB region, it is necessary to design an efficient algorithm to insert particles back into the MD region to keep the average particle density constant. This is a challenging task, especially in the case of a dense fluid.

We are using a highly efficient algorithm called USHER to introduce particles effectively even in a dense fluid. The attractive features of USHER are as follows:

1) If the initial random position of the inserted particle is too close to an existing particle, USHER solves this problem in one update.
2) The displacement in each step is bounded by an upper limit.
3) The final energy of the inserted particle is close to the average energy per particle in the system.

5. Optimized potentials for MD simulations based on DFT and temperature-dependent model generalized pseudopotential theory

The LLNL group is tasked with providing the capability to perform ultrascale atomistic simulations to study SCC in materials with quantum-mechanical accuracy. To this end, they are developing a new hybrid QMD-MD/MGPT simulation algorithm for materials properties to be used in SCC applications. This algorithm directly links first-principles DFT quantum simulations, namely, quantum molecular dynamics (QMD) [4], with large-scale atomistic simulations, namely, molecular dynamics with quantum-based model generalized pseudopotential theory (MGPT) interatomic potentials [5-7]. By developing this capability for small systems in the solid and in the liquid, one can dramatically extend the effective QMD time scale and harvest optimized temperature-dependent MGPT potentials in the long time limit, as shown
schematically in figure 10. In this process, there will be a real-time information feedback loop between the alternate QMD and MD/MGPT segments of the simulation, with both snapshot and accumulated QMD information being used to achieve optimization of the potentials. The optimized potentials can then be reused in ultra-large linear-scaling MD/MGPT atomistic simulations of materials properties. The initial goal is to simulate one billion atoms at high temperature in prototype systems (e.g., Mo, Ni) via MD/MGPT with the accuracy to a direct QMD simulation on one hundred atoms.

Figure 10. Schematic representation of the hybrid QMD-MD/MGPT simulation algorithm. A real-time information feedback loop between the alternate QMD and MD/MGPT segments of the simulation will allow optimized and reusable MGPT potentials.

The research accomplishments for the past year have been primarily in three areas: (1) progress in developing the hybrid QMD-MD/MGPT simulation algorithm and optimized temperature-dependent MGPT potentials for a Mo prototype; (2) calculation of DFT data bases of fundamental materials properties for Ni and Ni$_3$S$_4$; and (3) development of preliminary $T = 0$ MGPT potentials for Ni using the DFT data base. We have been greatly aided in this work with a large LLNL Institutional Computing Grand Challenge allocation of dedicated high-performance computer time (140,000 CPU hours per week) on the new 44 Tflops Atlas parallel machine at LLNL. This past year we successfully competed a renewal proposal to continue this allocation for a second year (through May 2009) [8].

5.1 Hybrid QMD-MD/MGPT algorithm for optimized potentials
There are four main technical tasks in the development hybrid QMD-MD/MGPT simulation capability.

5.1.1 Development and testing of an operational QMD-MD/MGPT simulation code.
During the past year we have fully adapted our fast portable quantum simulation code FEQMD [9] to perform efficient hybrid QMD-MD/MGPT simulations on Atlas. The resulting parallel QMD-MD/MGPT code is now called $P^4$MD. In QMD mode, this code uses the well-established plane-wave pseudopotential method to solve the finite-temperature DFT quantum-mechanical equations for the valence and outer core electrons in the system at each time step in the simulation, thereby providing accurate instantaneous forces on the ions to advance the molecular dynamics. Efficient parallelization is obtained by distributing the plane-wave basis functions, electronic energy bands and reciprocal-space k points across a group of nodes in an optimum way. A custom parallel 3D fast Fourier transform (FFT) routine has been developed and used to transfer information between reciprocal space, where the DFT equations are solved, and real space, where the forces are needed. In MD/MGPT mode, $P^4$MD evaluates the real-space, finite-temperature, many-body MGPT potentials at each time step, including two-, three- and four-ion interactions, to provide corresponding quantum-based energies and forces. This is done using the fast matrix version of MGPT, which also provides the most general functional form of the potentials currently available based on noncanonical $d$ bands. In the QMD and MD/MGPT modes, the same molecular dynamics equations are solved, and only the input forces are different. In the hybrid QMD-MD/MGPT simulation, $P^4$MD performs constant-volume, constant-temperature molecular dynamics in a chosen fixed-
shape computational cell. Ion positions and velocities are passed forward from one segment of the simulation to the next to provide initial conditions. QMD snapshot and accumulated information is passed forward to test and refine the MGPT potentials at the beginning of each MD/MGPT simulation segment.

5.1.2 Development and application of a robust simulation algorithm to produce optimized MGPT potentials.

Developing an algorithm to produce optimized MGPT potentials involves two main considerations: (1) the functional form of the potentials and what quantities are allowed to be optimized; and (2) the specific QMD data to be used to optimize the potentials and how that data is introduced. At present we have adopted a provisional functional form based on first-principles theory and focused on developing an effective strategy for (2) in the context of a Mo prototype system. The potential form currently used is a finite-temperature generalization of the well-established DFT-derived $T=0$ form we successfully developed in previous research and includes the introduction of noncanonical $d$-band variables. The available QMD data base of information for that refinement is extremely rich and includes snapshot energies and forces for thousands of ion configurations and accumulated information on thermal energies and pressures, atomic structure (pair and bond-angle distribution functions), electronic densities of states, and electron density. In our first-generation algorithm, we have used as potential input data a blend of fixed basic properties in the bcc phase (calculated at the temperature of interest) and 20-30 random snapshot energies from the QMD simulations of the liquid. This scheme has produced an excellent set of derived Mo potentials over a range of volumes at temperatures of 5000 and 10,000 K. Figure 11 shows the calculated thermal energy and pressure obtained in the first two segments of a representative hybrid QMD-MD/MGPT simulation, demonstrating the smooth join across the interface and the rapid convergence of the derived potentials. Figure 12 shows the corresponding excellent predicted atomic structure of the liquid obtained from these potentials. In both figures we have contrasted the results obtained with the present temperature-dependent MGPT potentials with those obtained using existing $T=0$ potentials. The contrast is indeed striking and clearly demonstrates both the validity of our present algorithm and the importance of electron temperature to the calculated high-temperature physical properties.

5.1.3 Establishment of a QMD test database and corresponding test simulations on derived MGPT potentials.

An important additional test of the derived MGPT potentials is their transferability to different structural environments at the same volume and temperature. A relevant and very sensitive test of this transferability is the calculation of the high-pressure melt curve, which requires the potentials to accurately describe both the high-temperature solid and the liquid simultaneously. This application is particularly timely because high-pressure melting in transition metals is currently highly controversial with static and dynamic high-pressure experiments yielding conflicting results. We believe that an accurate theoretical melt curve in the case of Mo can be obtained from two-phase co-existence MD simulations using a minimum cell size of

![Figure 11.](image-url)
256 atoms. We require, however, both a baseline QMD result and test MD/MGPT results. The former is quite challenging computationally and, in fact, has never been directly calculated for a high-Z metal like Mo. Our goal is to calculate 4-5 high-quality QMD melt points that are sufficient to define a smooth melt curve. To date we are about halfway to that goal. Preliminary two-phase MD/MGPT melt points have also been obtained from our derived potentials at 5000 and 10,000 K. In 2009, we plan to complete the QMD melt curve for Mo and fully test our derived potentials over a range of pressures and temperatures.

![Figure 12. Atomic structure of liquid Mo at \( T = 10,000 \) K and an atomic volume of 105.1 au, as obtained from direct QMD simulations, from MD/MGPT simulations with present converged 10,000 K potentials, and from MD/MGPT simulations with existing \( T = 0 \) potentials. On the left: pair correlation function, \( g(r) \); on the right: bond-angle distribution function, \( b(\theta) \). All results are for 54-atom simulations.](image)

5.1.4 Billion-atom MD/MGPT demonstration simulations with final optimized potentials.
These simulations will be performed once final optimized MGPT potentials for Mo are established.

5.2 First-principles materials property data bases for Ni and \( \text{Ni}_3\text{S}_4 \)
In addition to on-the-fly high-temperature QMD data, it is useful to have static \( T = 0 \) DFT databases of fundamental properties for interatomic-potential development on SCC relevant materials. This year such databases have been calculated for pure nonmagnetic Ni over an extended pressure range and for polymidymite \( \text{Ni}_3\text{S}_4 \) at ambient pressure. These calculations have been done with the same DFT plane-wave pseudopotential method used in the QMD simulations.

5.2.1 Nonmagnetic Ni properties at high pressure.
The pressure-dependent structural and mechanical properties of non-magnetic Ni have been calculated over a wide pressure range extending to above 100 GPa. The calculations use modern generalized gradient approximation (GGA) corrections to the exchange-correlation potential and energy within density-functional theory. To perform these calculations, we have constructed a plane-wave-based pseudopotential for Ni by solving for the all-electron Ni atom in the reference state \( 4s^{1.98}, 4p^{0.02}, \text{and } 3d^8 \). The energies of the core electrons were obtained by solving the scalar relativistic equations, while the valence electrons were treated nonrelativistically. The pseudopotential was modeled in the non-local norm-conserving Troullier-Martins form, with a total of 10 valence electrons generated using a plane-wave cutoff of 80 Ry. There is one projector for each component of angular momentum. The cutoff radii for the pseudized orbitals are 1.51, 1.51 and 1.32 Å for the \( 4s, 4p, \) and \( 3d \) valence orbitals, respectively. The \( d \)-component was chosen to be local. To improve the efficiency of our simulations, we transformed the pseudopotential into the Kleinman-Bylander form. The calculated zero-temperature structural and mechanical properties include the cold equation of state; fcc elastic moduli and zone-boundary phonons; fcc, bcc and hcp
structural energies; and the unrelaxed fcc vacancy formation energy. The observed ambient-pressure fcc phase is found to be thermodynamically stable throughout the pressure range studied. The calculated bulk and shear moduli and the $L$- and $X$-point zone-boundary phonons are displayed in figure 13. The elastic moduli and phonons are in reasonably good agreement with experiment [10] at ambient pressure and remain real and positive at high pressure, demonstrating that the fcc phase is mechanically stable in this regime. In the calculation of the vacancy formation energy for fcc Ni, we compared the total energy for a supercell with $N = 108$ atoms and no vacancy, [$E_{\text{tot}} (N, W_N)$], and the total energy for a supercell with $N-1$ atoms and one vacancy, placed at the center, [$E_{\text{tot}} (N-1, W_{N-1})$]. This procedure maximizes the cancellation of numerical errors in the calculation of $E_{\text{vac}}$, which is computed as $E_{\text{vac}}^i = E_{\text{tot}} (N-1, W_{N-1}) - (N-1)/N E_{\text{tot}} (N, W_N)$. Here $W_{N-1}$ and $W_N$ are the respective supercell volumes, such that $W_N (P) = NW_0 (P)$, where $W_0 (P)$ is the bulk equilibrium atomic volume at pressure, $P$. For comparison, we also calculated the fully relaxed vacancy formation energy for fcc Ni at zero pressure. This was found to be 1.92 eV, which is in reasonable agreement with the experimental value of 1.79 eV [11].

**Figure 13.** Bulk and shear elastic moduli (left panel) and $L$- and $X$-point zone-boundary phonons (right panel) for nonmagnetic fcc Ni, as calculated from the present first-principles DFT electronic-structure calculations.

5.2.2 Materials properties of polymidymite Ni$_3$S$_4$

Polymidymite Ni$_3$S$_4$ is a sulfur-rich system and a good prototype system for the fundamental understanding of the electronic and structural properties associated with the SCC problem of sulfur concentrated at or near Ni grain boundaries. Polydymite Ni$_3$S$_4$ has two types of Ni atoms and one type of S atoms, Ni$^I$Ni$_2$$^II$S$_4$, in a cubic structure. The Ni$^I$ atom occupies $1/8$ of the tetrahedral site, the two Ni$^II$ atoms occupy half of the octahedral sites, which produces a trigonal distortion along the [111] direction, and the four S atoms are on an approximate close-packed fcc lattice (see figure 14). We have performed first-principles DFT electronic-structure calculations on the Ni$_3$S$_4$ solid at ambient pressure. The bulk properties of this system are important material parameters that will be used for interatomic-potential development on S-rich Ni-S systems. The calculated lattice constant for the ideal structure is 9.489 Å and three cubic elastic constants are $C_{11} = 201$ GPa, $C_{12} = 81$ GPa and $C_{44} = 115$ GPa. In addition, we have calculated the electronic properties of this system. In particular, the density of the states at the Fermi level $N(E_F) = 31.1$ states/eV-cell, with 56 atoms per cell. This leads to a band-structure electronic-heat-capacity
constant of $g = 6.542 \text{ mJ/mol-K}^2$, where 1 mol refers to 1 mol of Ni$_3$S$_4$.

5.3 Quantum-based interatomic potentials for Ni

Using the above DFT database for Ni, we have begun to develop $T = 0$ quantum-based MGPT potentials for this metal over the -20 to 100 GPa pressure range. In this regard, Ni requires certain different considerations than in the case of Mo, our prototype metal for the hybrid QMD-MD/MGPT simulations. In Mo the direct multi-ion $d$-state interactions are of primary importance and are retained through four-ion interactions, while $sp$-$d$ hybridization is of secondary importance and is retained only in the leading volume term of the total energy. This is the standard approach for MGPT [5-7]. In Ni, on the other hand, the $sp$-$d$ hybridization is of primary importance and the three- and four-ion interactions are of secondary importance. We have, therefore, now developed an advanced form of MGPT that restores the $sp$-$d$ hybridization from the full first-principles generalized pseudopotential theory in the two-ion pair potential, in a suitably screened form, and we have applied the new approach to Ni. In both the standard and advanced forms on MGPT, the potentials are volume dependent in the bulk, although the inclusion of the hybridization necessarily imparts a longer range to the two-ion potentials. Preliminary advanced MGPT potentials for Ni at three atomic volumes, including equilibrium, are displayed in figure 15. Optimization of these $T = 0$ potentials is currently in progress. The advanced MGPT methodology can be readily imported into the QMD-MD/MGPT algorithm to develop corresponding temperature-dependent potentials for Ni and Ni-based materials, and this is now planned as part of the SCC project.

Figure 14. Crystal structure and electronic charge density of polymidymite Ni$_3$S$_4$. There are two types of Ni atoms in this system: the NiI atom occupies 1/8 of the tetrahedral site and the two NiII atoms occupy half of the octahedral sites. There are a total of 56 atoms in the supercell, including 24 Ni atoms and 32 S atoms.

Figure 15. Preliminary calculated MGPT two-ion pair potential, $v_2(r;\Omega)$, for Ni at three atomic volumes, where $\Omega = 73.82 \text{ a.u.}$ is the observed equilibrium volume in the fcc material. The long-range oscillations in the potentials result primarily from $sp$-$d$ hybridization.

Figure 16. Schematic representation of nanoindentation of Al thin film.
6. Quasi-continuum modeling from electrons to finite elements

6.1 Development of QCDFT method
Lu at California State University Northridge has developed a concurrent multiscale method that makes it possible to simulate multi-million to billions atoms effectively based on the density functional theory (DFT). The method, termed QCDFT, is formulated within the framework of quasicontinuum method, and with DFT as its sole energetic input; that is, there is no empiricism in the formulation. The only underlying energy functional in QCDFT is either Kohn-Sham DFT or orbital-free DFT. The unimportant degrees of freedom are systematically coarse-grained out by finite-element interpolation scheme. The development of QCDFT represents a major progress in quantum simulation of materials properties and opens door for many applications that are beyond the reach of existing quantum simulation methods. The code has been parallelized with MPI. The QCDFT method has been applied to nanoindentation of an Al thin film. The results suggest that QCDFT is an excellent method for quantum simulation of materials properties at length-scales that are relevant to experiments [12]. Figure 16 shows a schematic representation of the sample and the indenter. Figure 17 presents an overview of the entire system and domain partition in the nanoindentation simulation.

![Diagram](image)

**Figure 17.** Domain partition in QCDFT with nanoindentation. DFT atoms are blue and buffer atoms are green. The energy of the finite-elements and the interaction energy between the buffer atoms and DFT atoms are calculated by DFT as well.
6.2 Validation of EAM potentials using sparse grid and first-principles calculations

We have demonstrated that the sparse grid method can be used to greatly reduce the necessary first-principles DFT calculations in order to validate the accuracy of empirical potentials. We have examined three different EAM potentials of Al by computing energy and stress as a function of uniform hydrostatic deformations. The EAM results deviate significantly from the corresponding DFT values for large compressions, while the results agree reasonably well to the DFT values for expansions. The failure of the EAM potential is attributed to the uniform electron density approximation adopted in the EAM theory. In compressed configurations, the local electron density gradient increases considerably, and the uniform electron density approximation is no longer valid, hence EAM fails. We have identified a critical value of the electron density gradient beyond which EAM energetics deviate significantly from the DFT values. We have tested this critical value for the case of the generalized stacking fault energy surface calculations and found that for the run-on stacking fault where the maximum local density gradient exceeds the critical value, EAM indeed fails in giving the correct energy (see figure 18). For all other stacking faults where the critical value is not exceeded, EAM gives reasonable results. We have proposed a solution to improve the transferability of EAM potentials by considering the gradient of electron density in the analytical expression of EAM energy—the embedding function should depend not only on electron density but also on its gradient.

![Figure 18. The valence charge density and its gradient for a run-on stacking fault of Al. The length and direction of the arrows represent the magnitude and direction of the charge density gradient. Two layers of Al atoms stack right on top of each other in the [111] direction (in the middle of the figure) constitute a run-on stacking fault.](image1)

![Figure 19. Difference between Ercolessi-Adams embedded atom method (EAM) potential and first-principles (VASP) calculations for the energy (dE = E_{EAM} - E_{VASP}) versus change of solid angle of the deformed cell and the change of cell volume in the left panel. The difference of stress tensor dS = ||S_{EAM} - S_{VASP}|| is shown in the right panel. The results are represented in a sparse grid with only 8433 points to represent 1,291,467,969 points in a uniform grid with the same precision. The sparse grid is being incorporated in the QCDFT method to perform DFT calculations for local region.](image2)
7. *Accelerated molecular dynamics for stress corrosion cracking*

As discussed above, accurate simulation of stress-corrosion cracking depends on building a hierarchical multiscale framework. At the largest scale, the externally applied stress is imposed on the system, requiring a continuum-level (e.g., finite-element or quasi-continuum) treatment. This information is passed to successively finer, more accurately described levels. Ultimately, at the finest level, a small number of the most crucial atoms at the crack tip (region A, order 100 atoms) are modeled with a full electronic structure calculation (e.g., DFT). To reach appropriate time scales, accelerated molecular dynamics (AMD) simulations are employed on a small region (region B, ~1000 atoms) that includes this DFT region A as a subset. The atoms in region B other than the DFT atoms are described with a highly accurate semiempirical potential. After the entire system has been brought into thermal equilibrium using MD coupled to FEM, a shell of atoms outside region B is held fixed at their time-averaged positions to provide proper boundary conditions for region B while an AMD simulation is performed within that region. This AMD simulation proceeds until a thermally activated transition takes this subsystem to a new state. For example, one bond at the crack tip may break, allowing the crack to extend by a few angstroms. At this point, communication with the rest of the system is required, to allow the strain field of the overall system to re-equilibrate with the modified region B. The newly relaxed shell of atoms around region B is then fixed in place again and new AMD is performed until the next reactive event. This procedure is repeated to advance the infrequent-event dynamics of the entire system.

In technologically relevant systems, the crack tip may be in contact with a liquid phase, and this liquid may play a critical role in promoting (or perhaps even inhibiting) the fracture. In the procedure above, if standard MD is employed to evolve the active region, the liquid poses no particular problem, but in the context of accelerated molecular dynamics, the liquid is problematic because the barriers separating one potential energy basin from another are extremely low. While AMD methods are powerful for compressing the time scale of transitions from long time scales (e.g., microseconds or milliseconds) down to the picosecond time scale, direct application of any of the AMD methods in this solid-liquid case will not give any computational boost because basin-to-basin transitions in the liquid are already occurring on the picosecond time scale.

As a step toward solving this problem, we are developing a variation on one of the AMD methods, parallel-replica dynamics [2], to treat the dynamical evolution of a solid surface that is in contact with a liquid phase. The key is to define the concept of a super-state, so that the separation of time scales between intra-super-state and inter-super-states dynamics is restored. We then apply parallel-replica dynamics at the super-state level. A simple strategy to reach this goal is to define super-states simply based on the configuration of the slow degrees of freedom (DOF) in the system, i.e., every state in which the slow DOF are in the same configuration belongs to the same super-state, notwithstanding the state of the fast DOF. If the typical time scale over which the fast DOF evolve is sufficiently faster than that of the slow DOF, the validity of the super-state parallel replica approach should be assured and it should give a computational boost.

![Figure 20. Silver adatom on Ag(100) surface in contact with Lennard-Jones liquid at T = 600K.](image)
For typical solid/liquid interfaces—for example, a metal in contact with a liquid like water at room temperature—this segregation of DOF into fast and slow subsets should be easy to define: coordinates of the liquid atoms form the fast subset while coordinates of the solid atoms form the slow subset, since transitions in such a liquid will occur thousands of time faster than rearrangements of the solid atoms.

To test this approach, we have carried out super-state parallel replica simulations of the diffusion of an adatom on a silver (100) surface (modeled using an embedded atom method potential) in contact with a film of a prototypical fluid (modeled using a Lennard-Jones potential), as shown in figure 20. The distribution of 500 adatom hopping times at 600K is shown in figure 21 for a direct simulation using conventional molecular dynamics and for a super-state parallel replica simulation. The results clearly show that transition statistics are equivalent for the two approaches, implying that our super-state definition restores the time scale separation essential for the validity of the AMD methods. In this case the parallel replica simulation was quite efficient, with a parallel efficiency of around 0.8 on 8 processors, despite the presence of very fast transitions in the liquid. We expect that at lower temperatures, much greater boosts will be possible.

Note that the agreement between MD and AMD is not due to a negligible effect of the liquid on the adatom dynamics. Indeed, as shown in figure 22, the transition rate of the adatom on the wet surface is around 1.6 times slower than on the dry surface at 600K, increasing to a factor 3.5 at 500K. The rate corrections due to the liquid are thus significant and have a nontrivial temperature dependence.

While these results are encouraging, challenges remain. For example, correctly treating the dynamics of dissolved solid atoms is problematic since their diffusion rate in the liquid will be effectively decelerated. Also, we must recognize when a solid atom is still part of the solid and when to declare it liquidlike, to prevent dramatic loss of boost. Similarly, it may be necessary to begin treating liquid atoms as solid if they react with the solid atoms, or if they form persistent ordered structures. We are developing methods to determine these characteristics on the fly.

References

[1] Chen Y, Lu Z, Nomura K, Wang W, Kalia R K, Nakano A and Vashishta P 2007 Interaction of voids and nanoductility in silica glass Phys. Rev. Lett. 99:155506
[2] Célarié F, Prades S, Bonamy D, Ferrero L, Bouchaud E, Guillot C and Marlière C 2003 Glass breaks like metals, but at the nanometer scale Phys. Rev. Lett. 90:075504-1
[3] Nomura K, Chen Y-C, Kalia R K, Nakano A and Vashishta P 2008 Defect Migration and Recombination in Nanoindentation of Silica Glass”, Phys. Rev. Lett. (submitted)
[4] Hood R Q, Yang L H and Moriarty J A 2008 Quantum molecular dynamics of uranium at high pressure and temperature Phys. Rev. B (in press)
[5] Moriarty J A, Belak J F, Rudd R E, Söderlind P, Streitz F H and Yang L H 2002 Quantum-based atomistic simulation of materials properties in transition metals J. Phys.: Condens. Matter 14:2825
[6] Moriarty J A, Benedict L X, Glosli J N, Hood R Q, Orlikowski D A, Patel M V, Söderlind P, Streitz F H, Tang M and Yang L H 2006 Robust quantum-based interatomic potentials for multiscale modeling in transition metals J. Mater. Research 21:563
[7] Moriarty J A, Glosli J N, Hood R Q, Klepeis J E, Orlikowski D A, Söderlind P and Yang L H 2008 “Quantum-Based Atomistic Simulation of Metals at Extreme Conditions,” in TMS 2008 Annual Meeting Supplemental Proc. Vol. I: Materials Processing and Properties (TMS, Warrendale, PA) 313
[8] Moriarty J A, Yang L H, Hood R Q, Vashishta P, Kaxiras E and Voter A F 2008 Toward petascale atomistic simulations with quantum-level accuracy 3rd Institutional Computing Grand Challenge Proposal (LLNL)
[9] Yang L H 2000 in Industrial Strength Parallel Computing ed. A Koniges (Morgan Kaufmann Publishers: San Francisco) 297
[10] Birgeneau R J, Cordes J, Dolling G and Woods A D B 1964 Normal modes of vibration in nickel Phys. Rev. 136:A1359
[11] Schultz H and Ehrhart P 1991 in Atomic Defects in Metals ed. H Ullmaier, Landolt-Börnstein, New Series, Group III (Springer, Berlin)
[12] Zhang X and Lu G 2007 Quantum mechanics/molecular mechanics methodology for metals based on orbital-free density functional theory Phys. Rev. B 76:245111