Multi-scale Simulation Including Chemical Reactivity in Materials Behavior Through Integrated Computational Hierarchies

MULTI-scale, MULTI-pass SIMULATIONS FROM MOLECULES TO MATERIALS

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F. Harris  R. Ochoa (College of N.J.)
S. Trickey  
M. Zerner (deceased 2000)
S. Sinnott
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University of Arizona

Massachusetts Institute of Technology

Washington State University
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Undergraduate Students: 14

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UA: 2  WSU: 1

http://www.qtp.ufl.edu/kdi
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FUNDP, Namur, Belgium: Collaborative Research; Personnel Exchanges

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Predictive simulation of chemo-mechanical processes in real materials

- Predictive theory: computationally feasible; 1st principles; reliable complement to experiment.

- Chemo-mechanical: chemistry ⇔ stress (reactivity, bond breaking, excited states, solvents, fracture, surfaces …)
Reactive solution + abrasive particles
Laser Mirror Photodetector Amplifier Controller Sample tip Cantilever

Atomic Force Microscopy

Si$_3$N$_4$ polycrystalline tip

Contact non-contact tapping

Tip used for applying stress AND probing results
White square was scanned 3 times at $F_N = 270$ nN. High $F_N$ scanning has no detectable effect in the absence of “corrosive” fluid.
SFM Image of a Typical Etch Pit on Cleavage Surface of Calcite

3 Å steps

“Fast Steps”

“Slow Steps”

5 nm

1.7 µm

“Fast Steps”

“Slow Steps”

obtuse

acute

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Predictive + Chemically Realistic = DEMANDING

- Multi-scale with
  
  Real Materials (many constituents, conformations, environments) and Real Chemistry
  
  Complex Phenomena

⇒

- Chemical Detail and Scale Parity Required
- Computational Resource Requirements
- Subtleties of Decomposition (regions, methods)
Challenge - Most simulations of a chemo-mechanical process (e.g. Fracture) involve a priori knowledge of the location and scale size of the quantum region.

Approach: multi-pass strategy. Use fast, realistic classical MD to identify likely quantum regions; then multi-scale with highly realistic, fast approximate QM

- Better QM approx. than tight-binding
- Potentials parameterized to embed QM optimally
- Algorithms to detect incipient QM region(s)
- Linkages between regions
- Validate with method/code suite ⇒ method linking
Some IMPLICATIONS

- Hierarchy of Regions ⇒ Re-examine Hierarchy of Methods
- Re-think/re-examine all Elements of Multi-scale Simulation

  Incompletely examined assumptions?
  Opportunities from other developments?
  Unnoticed threads in the literature?

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MAJOR TASKS

- Fast approx. QM well beyond Tight-binding
- Classical potentials to embed the QM
- Systematic location/characterization of regions & boundaries (not “by hand”)
- Cross-boundary information transfer characterized, codified
- Appropriate software (acquired, developed, integrated, front-ended, validated, …)
- Stay focused: physical-science-driven (scientific computation, not pretend computer science)
**User Interface -**

### Multi-Scale Multi-Pass Simulation from Molecules to Materials

Choose a route through the methods below.

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**Force Source: Approximate QM via Transfer Hamiltonian**

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State of the art in ab initio quantum chemistry is Coupled-Cluster theory:
\[
\exp(-T) H \exp(T) = \hat{H}_{cc}
\]
\[
\hat{H}_{cc} |0\uparrow = E_0 |0\uparrow
\]
\(E_0\) is the exact correlated energy.

Equations for the coefficients in \(T\), i.e. \(t_{ia}\), \(t_{ijab}\), etc., from
\[
\langle m \rangle |0\uparrow = 0
\]
with \(\langle m \rangle = \) single, double, triple, etc., excitations w/r to \(|0\uparrow\)

\[
\nabla (R) E(R) = \nabla \langle 0 |\hat{H}_{cc} |0\uparrow \rightarrow \text{exact forces on the nuclei.}
\]
“ab initio” - a Latin phrase meaning “expensive”

Our approach: train a simple Hamiltonian to reproduce behavior of $\hat{H}_{cc}$, hence transfer that behavior to low-cost QM

Transfer the *dynamics* generated by $\hat{H}_{cc}$ - Parameterize $\hat{H}_T$ such that

$$\nabla(R)E(R) = \nabla(R) \langle 0_T | \hat{H}_T | 0_T \rangle$$

$$= \nabla(R) \langle 0 | \hat{H}_{cc} | 0 \rangle$$

Use NDDO form for $\hat{H}_T$ (simplified HF)
PYROSILICIC ACID
Comparison of forces for pyrosilicic acid dissociating into neutral fragments.
Coupled-cluster forces can be encoded reliably

TH is a far simpler operator than CC ⇒ rapid determination of forces for ~500-1000 atoms

Unlike TB, TH is determined fully self-consistently

Unlike DFT, applicable to ~100 atoms/processor, TH mimics CC results, which are superior in bond-breaking and transition state regions of molecules

TH approach is applicable to any and all systems once a suitable reference set of CC cluster results is available.
CC results obtainable only for relatively small clusters ~ 10-15 atoms.

CC must be on representative clusters for each system.

Objective: CC parameters essentially independent of the cluster.
Multi-Scale Multi-Pass Simulation from Molecules to Materials

Choose a route through the methods below.

### FORCE GENERATION
- Quantum Mechanics
  - Transfer Hamiltonian
  - DFT
- Adaptive Potentials
  - Streitz-Mintmire
- Classical Mechanics
  - BKS/TTAM
  - Brenner

### MOLECULAR DYNAMICS
- Cheng BO MD
- Harris MD
- Yip MD
- DL_POLY
- Snott MD

### CONTINUUM MODELS
- None
- SCRF
- FE 2D
- COSMO

### KINETIC MONTE-CARLO (Jackson)
- No
- Yes

Embedding Potential: QM-adapted, as-published, etc.
Typical previous work: fit
\[ V_{ij} = Q_i \frac{Q_j}{R_{ij}} + \alpha_{ij} \exp(-\beta_{ij} R_{ij}) - \gamma_{ij}/R_{ij}^6 \]
to energetics from a small molecule plus experimental structure and properties of crystal (e.g. H$_4$SiO$_4$ & α-quartz)

Our approach: Fit the potential to the QM that will be embedded (different parameters for DFT vs. $\hat{H}_T$ embedding). Emphasize dynamics over energetics.

Fitted parameters are very different from published.
Unexpected results along the way

- Calculated Si-O-Si angle in $\text{H}_6\text{Si}_2\text{O}_7$ is $180^\circ$ (multiple methods); potential-fitting literature says bent
- Equilibrium O-Si-O angle in $\text{H}_4\text{SiO}_4$ not tetrahedral; two popular potentials are fit to tetrahedral clusters
- $\alpha$-quartz does not have a double minimum w/r cell volume in DFT and Gaussian basis (brittle, not ductile)
CLASSICAL POTENTIAL FITTING: $H_4SiO_4$
CLASSICAL POTENTIAL FITTING: α Quartz

SiO$_2$ Nanorod Tensile Fracture - Pair Potential From alpha-Quartz DFT

- Published BKS
- BKS-HL
- BKS-PBE
- Published TTAM
- TTAM-HL
- TTAM-PBE

Stress [GPa]

Strain

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Other Ongoing Work: Adaptive potentials (Rappé-Goddard, Streitz-Mintmire, et al.)

- better, because they allow for charge transfer and bond breaking,
- but computationally “pricey”

⇒ Parameterize reactivity indices (electronegativity, softness) to embed QM
⇒ Develop faster algorithms
**User Interface -**

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- No
- Yes

**Links between regions/regimes**

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Classical Mechanics

Quantum Mechanics

Continuum Mechanics

Pseudoatoms
• Attach $H$ atoms to broken covalent bonds to satisfy the valence structure.
• These link $H$ atoms do not interact with CM atoms, but terminate QM correctly. Make interface “transparent”.
QM --- QM : DFT
CM --- CM : BKS potential
QM --- CM : BKS potential

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LINK ATOMS - OPTIMIZED GEOMETRIES

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The force acting on Si (1) as a function of Si (1) – O (b) bond length
The force acting on O (b) as a function of O (b) – Si (2) bond length
The force acting on Si (2) as a function of O (b) – Si (2) bond length
Challenge – Molecular Dynamics frequently does not permit long enough time scales to observe phenomena of interest. Inclusion of realistic QM worsens the problem.

- Approach 1: Hybrid MD
- Approach 2: Kinetic Monte Carlo
- Approach 3: Finite Difference Time Domain
Objective – Keep the classical Molecular Dynamics on a QM leash.

Our Approach – Do good QM forces (in QM region) only every N steps. Calculate and store differences. Run classical MD in that region for next (N-1) steps with forces corrected by those differences. Repeat.

Benefit: one → several orders of magnitude speedup over the time for QM at every step.
KINETIC MONTE CARLO -

- *KMC* probabilistically implements events on a small scale to show a large scale morphology.

- **Objective** – Move aggressively but reliably to important parts of phase space.

- **Our Approach** – *Extract probabilities from MD simulations (particularly ensemble MD).*

- **Benefit:** multiple orders of magnitude speedup relative to classical MD.

- **Requirements:**
  - Setting up a lattice
  - Bookkeeping, bookkeeping, bookkeeping
$V_\_ = V_0 e^{-n(\phi - E(n,r))}$

- Screw dislocation
  
  $E(n,r) = \begin{cases} \frac{E_n}{r} & 1 < n < Z \\ 0 & 1 \geq n \geq Z \end{cases}$

- Unstressed bond strength - $\phi$
- Geometric energy - $E_n$
φ controls cross-section and roughness

(a) φ = 1    $E_n = 0.5$

(b) φ = 5    $E_n = 0.5$

(c) φ = 7    $E_n = 0.5$

(d) φ = 9    $E_n = 0.6$
Kinetic Monte Carlo – Etch Pit Stress Effects

- $E_n$ controls aspect ratio of the pit
- (a) $E_n = 0.2$
- (b) $E_n = 0.3$
- (c) $E_n = 0.5$
- (d) $E_n = 0.7$
  \[\phi = 7.0\]
Finite Difference Time Domain method: expand time scale between MD and FE
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Linked Laboratory Tool Suite

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CHALLENGES and APPROACHES -

- Challenge – Multi-scale software rigidly linked or used unlinked with much “interface massaging”. Greatly limits the flexibility of application, and makes it difficult to obtain essential comparisons that establish predictive accuracy.

- Our Approach: Linked Laboratory. Flexible, user-level linking of mostly autonomous modules into one framework that allows choice among
  - classical, DFT, and transfer Hamiltonian forces
  - several MD programs tailored to various classes of application
  - continuum methods (FE, Self-consistent Reaction Field)
SOFTWARE APPROACH

➢ Research-problem-driven: Focuses on enabling the researcher to link the needed tools

➢ Open-source as much as possible

➢ Uses the concepts but not the high-investment stringency of highly structured, object-oriented methodology

➢ Therefore does not require large, high-priority investment in software engineering

➢ Tech-transfer - Should lay the groundwork for highly-structured commercial packages (not our role).

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Multi-Scale Multi-Pass Simulation from Molecules to Materials

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CONCLUSION -

- Re-examination ⇒ creation and development of needed scientific components and supporting software

- Additional linkages under construction (e.g. hybrid MD, adaptive potentials, KMC)

- Further work needed (e.g. good models for calculated inputs to KMC, adaptation/incorporation of progress in parallelization, systematic identification of QM region, methodology for selecting reference suite of molecules, faster adaptive potentials ….)

- Initial stages of some proof-of-approach simulations on realistic chemo-mechanical problems underway ….

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SILICA & WATER (HYDROLYTIC WEAKENING) -

- X waters interacting with Y SiO$_2$s
- Study proton transfer and bonding rearrangement
- Direct Born-Oppenheimer MD for molecular study
- MD embedded (link atom) BO-MD for silica surface

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SILICA & WATER (HYDROLYTIC WEAKENING)
SiO$_2$(H$_2$O)$_5$ -

Hydration energy = 2.13 eV
SILICA & WATER (HYDROLYTIC WEAKENING)

SiO$_2$(H$_2$O)$_6$ -

Hydration energy = 0.44 eV

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NANOROD FRACTURE– TTAM vs. Transfer Hamiltonian