GPU-Enhanced DFTB for Alloys

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Project Description and Objectives

• **Purpose:** incorporate GPUs into DFTB to accelerate calculations of multi-component alloys at high temperatures

• **Strategic alignment to Fossil Energy objectives:** GPU-enhanced DFTB enables fast predictions of complex, structural materials used in fossil energy power plants

• **Technology benchmarking**
  - **Classical molecular dynamics:** can handle large systems but cannot provide first-principles prediction of multi-component alloys
  - **Density functional theory (DFT):** can probe quantum-mechanical nature of alloys but cannot handle large sizes relevant to alloys
  - **Density functional tight binding (DFTB):** can probe large systems quantum-mechanically, but faster than DFT
Project Description and Objectives

• **Current Status of project**
  - Successfully incorporated GPUs into DFTB for extremely fast calculations of large systems
  - Project on-track to meet deliverables: goals/objectives have not changed
    - **Phase 1:** GPU parallelization done; **Phase 2:** DFTB parameterization in progress
  - **Industry/input or validation**
    - Recently presented at 2018 TechConnect World Innovation Conference & Expo to disseminate results for industrial partnerships
    - Gave invited talk at 2018 American Institute for Chemical Engineers (AIChE) Meeting: well-received by industry researchers at ExxonMobil

up to 15,000 atoms!
Why Use DFTB for Alloys?

• Density Functional Tight Binding (DFTB): course-grained, parameterized DFT with atomic-centered basis functions

• DFTB extremely fast for large systems

• Implemented GPU-enhanced DFTB in this project to accelerate dynamics calculations of alloys

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> 1,000 atoms in unit cell
(geometry optimizations ~ minutes)
DFTB (a condensed summary)

• **DFTB Hamiltonian** (more on this from Anshuman later)

\[
\hat{H}_{\text{DFTB}} = \langle \phi_\mu | \hat{H}_o | \phi_\nu \rangle + \frac{1}{2} \delta_{\mu\nu} \sum_X (\gamma_{AX} + \gamma_{BX}) \Delta q_X + E_{\text{rep}}
\]

- 0\textsuperscript{th} order Hamiltonian for core & valence electrons
- overlap matrix
- 2\textsuperscript{nd} order terms depending on interatomic separation & charge fluctuations

• **Computational savings: pre-parameterized “basis” functions**

  pre-tabulated as function of \( R_{AB} \)

  → simplifies integrals in SCF procedure
Accelerated DFTB-based dynamics on alloy systems with massively-parallelized GPUs

Examined variety of algorithmic implementations & benchmarks of different hardware configurations

Recently accepted in Journal of Chemical Theory & Computation (IF: 5.4)
Results of Phase 1: GPU Acceleration

- CPU/GPU benchmarks on large systems (~15,000 atoms!)
- Different algorithms exhibit varying performance
- Almost perfect application for large complex systems (i.e. alloys)
Leveraging GPU-enabled DFTB

Why DFTB?

- DFT good for small systems
- Classical molecular dynamics can handle large systems but are missing the QM part
- DFTB merges reliability of DFT with computational efficiency of tight binding
- Slater-Koster files used instead of DFT functionals

Challenges

- DFTB limited by set of parameters for elements in periodic table (Slater – Koster files)

Goal

- Create Slater – Koster files for missing element pairs
- Then leverage DFTB to calculate phase diagram of multi-component alloys
Leveraging GPU-enabled DFTB

**DFTB THEORY**

\[ E_{\text{DFTB}} = \sum_i^{\text{occ}} \langle \phi_i | H_0 | \phi_i \rangle + \frac{1}{2} \sum_{\alpha, \beta}^{N} \gamma_{\alpha \beta} \Delta q_{\alpha} \Delta q_{\beta} + E_{\text{rep}} \]

- **\( E_{\text{rep}} \)** lumps together many-body effects (e.g., exchange-correlation)
- **\( H_0 \)** and overlap *matrix elements parametrized beforehand* from DFT calculations

\[ H_{\mu \nu} (r) = \langle \phi_\mu (r) | H_0 | \phi_\nu (r - r_o) \rangle, \quad S_{\mu \nu} (r) = \langle \phi_\mu (r) | \phi_\nu (r - r_o) \rangle \]

\[ H_0 = -\frac{1}{2} \nabla^2 + v_{\text{eff}} [ \rho^a (r) ] + v_{\text{eff}} [ \rho^b (r - r_o) ] \]
# DFTB Parameterization - RESULTS

<table>
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<th>Compound</th>
<th>Multiplicity</th>
<th>Parameter*</th>
<th>DFT</th>
<th>DFTB</th>
<th>Δ(DFTB-DFT)</th>
<th>Δ(DFTB-DFT)%</th>
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<td>FeH₂</td>
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</tr>
</tbody>
</table>

*r in Angstrom, α in degrees

Leveraging GPU-enabled DFTB

Phase Diagrams

- High temperature phases upon heating are relevant in fossil fuel technologies
- Use Cluster Approach to Statistical Mechanics (CASM) to obtain phase diagram
- Construction of phase diagram requires comparison of free energies of different phases as function of temperature & composition
- Compact way to approximate energy of any configuration

\[
E(\sigma) = V_0 + \sum_i V_i \sigma_i + \sum_{i,j} V_{ij} \sigma_i \sigma_j + \sum_{i,j,k} V_{ijk} \sigma_i \sigma_j \sigma_k + \ldots
\]

Monte Carlo

\[
Z = \sum_{\sigma} \exp\left(-\frac{E(\bar{\sigma})}{k_B T}\right)
\]

Thermodynamics

\[
F = -k_B T \ln(Z)
\]
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Phase Diagrams - CASM

CASM Workflow

• Carry out *ab-initio* calculations

• Fit cluster expansion (CE) Hamiltonians

• Perform MC simulations

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CALCULATION OF PHASE DIAGRAM

- Calculate DFT Energy ($E$)
- Use calculated $E$ to find ECIs
- Monte-Carlo (MC) to find phase boundaries

\[ E = V_1 \sigma_1 + V_{1,7} \sigma_1 \sigma_7 + V_{1,18} \sigma_1 \sigma_{18} + V_{1,17} \sigma_1 \sigma_{17} + V_{1,4,5} \sigma_1 \sigma_4 \sigma_5 + \ldots \]

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Phase Diagrams - RESULTS

\[ E(\sigma) = V_0 + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \ldots \]

Each red circle belongs to specific configuration of HCP-based ZrO_x

Leveraging GPU-enabled DFTB

Phase Diagrams - RESULTS

- Calculate DFT Energy (E)
- Use calculated E to find ECIs
- Monte-Carlo (MC) to find phase boundaries
Preparing Project for Next Steps

Market Benefits/Assessment

- **Current market gap:** existing simulation tools (i.e. MD/DFT) not capable of predicting dynamics of large alloy systems
- **Benefits:** project goals directly translate to understanding (1) structural deformation in complex alloys & (2) reactive processes in these complex systems

Technology-to-Market Path

- **Technology transfer is high:** many technologies depend on structural materials, including furnaces and structural composites in buildings
- **New research:** first demonstration of accelerating DFTB with GPUs for large systems
- ExxonMobil expressed some interest at AIChE; still open to other academic/industry collaborations (send e-mail to: bryan.wong@ucr.edu)
Concluding Remarks

• Applicability to Fossil Energy and alignment to strategic goals
  • GPU-enhanced DFTB enables fast predictions of complex, structural materials used in fossil energy power plants
  • Better than MD & orders of magnitude faster than DFT

• Next step: incorporate GPU-DFTB into CASM for predicting phase diagrams of alloy systems

• First demonstration of accelerating DFTB-based dynamics with GPUs for large systems
  • Recently accepted in Journal of Chemical Theory & Computation (IF: 5.4)
  • Featured by editors on next month’s cover!