GPU-Enhanced DFTB for Alloys

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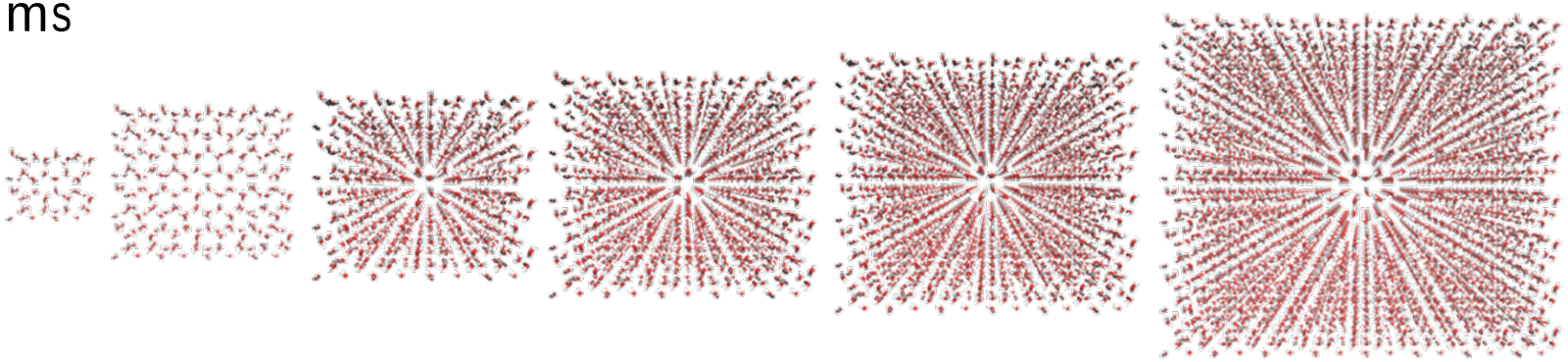
Project Description and Objectives

- **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

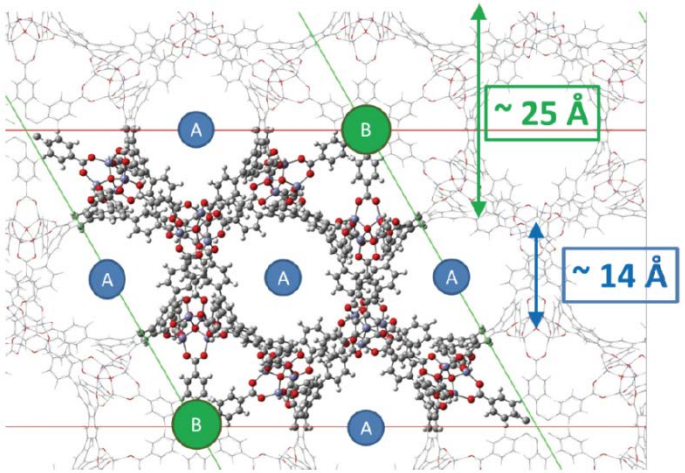


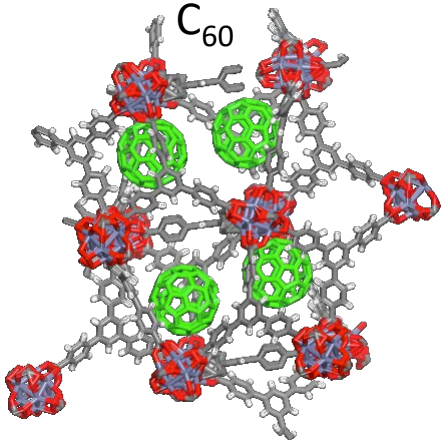
up to 15,000 atoms!

  - 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

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





K. Leong, M.E. Foster, B.M. Wong
J. Mater. Chem. A **2**, 3389 (2014)

> 1,000 atoms in unit cell
(geometry optimizations ~ minutes)

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

DFTB (a condensed summary)

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

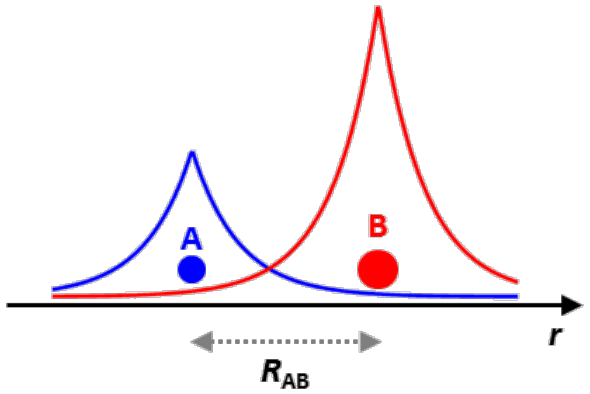
$$\hat{H}_{\mathrm{DFTB}} = \langle \phi_\mu | \hat{H}_o | \phi_\nu \rangle + \frac{1}{2} \hat{S}_{\mu\nu} \sum_X (\gamma_{AX} + \gamma_{BX}) \Delta q_X + E_{\mathrm{rep}}$$

0^{th} order Hamiltonian for core & valence electrons

overlap matrix

2^{nd} order terms depending on interatomic separation & charge fluctuations

- Computational savings: pre-parameterized "basis" functions



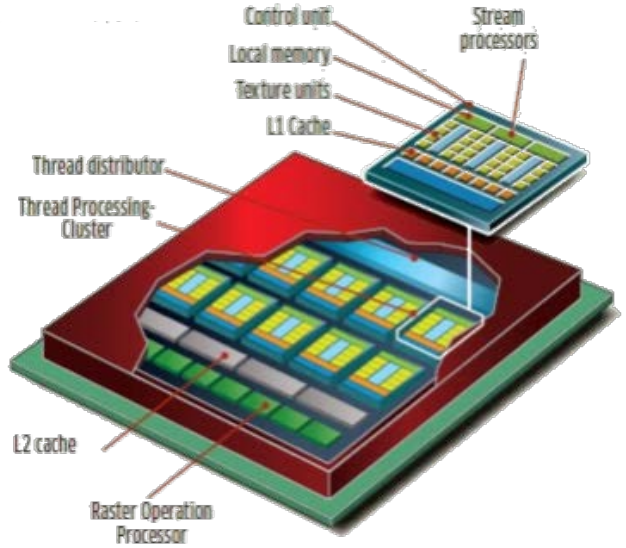
pre-tabulated as function of R_{AB}

→ simplifies integrals in SCF procedure

Specialized Computer Hardware

- Accelerated DFTB-based dynamics on alloy systems with massively-parallelized GPUs

NVIDIA
GPU processors

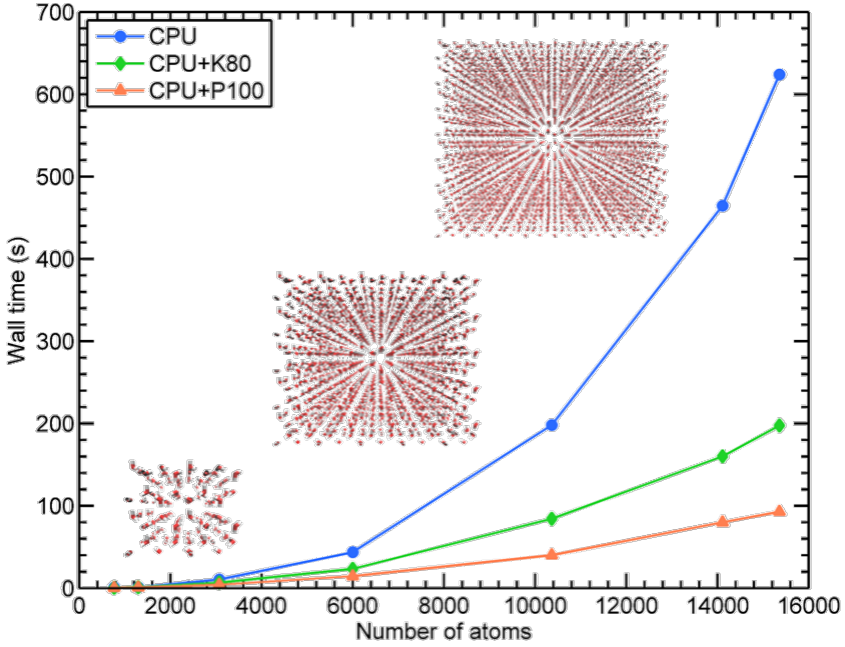


- Examined variety of algorithmic implementations & benchmarks of different hardware configurations
  - Recently accepted in *Journal of Chemical Theory & Computation* (IF: 5.4)

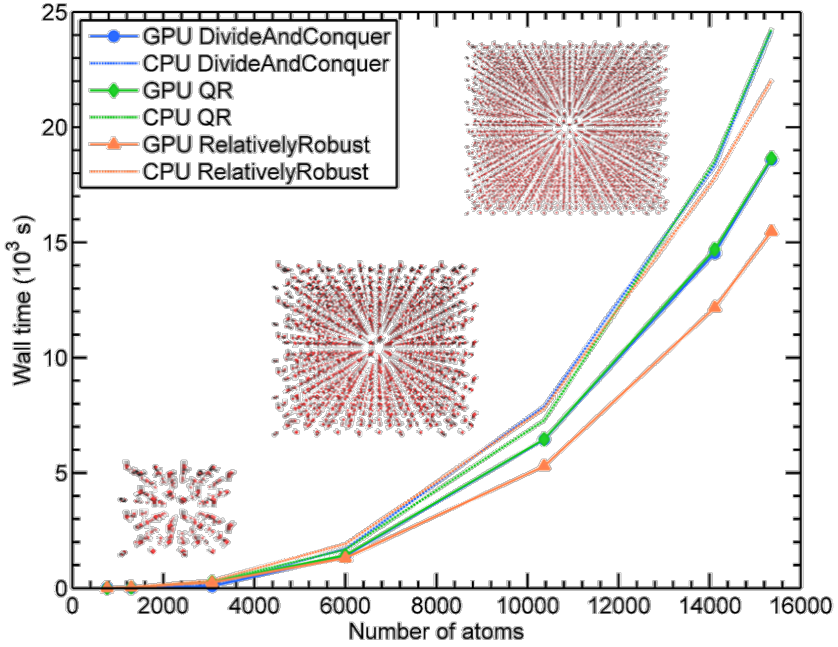
Results of Phase 1: GPU Acceleration

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

CPUs vs GPUs



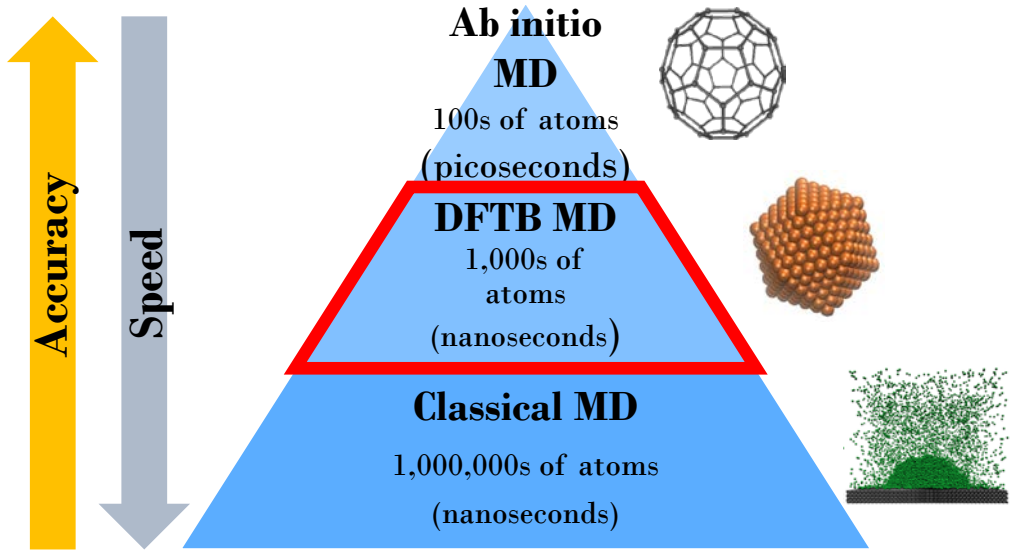
algorithm comparison



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

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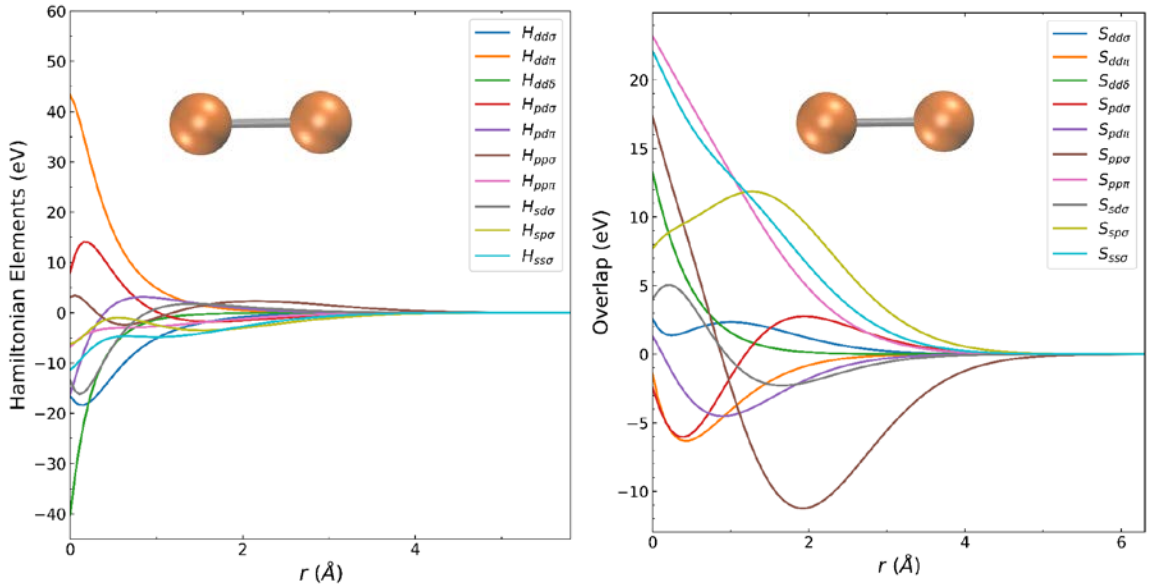
DFTB THEORY

$$E_{\mathrm{DFTB}} = \sum_{i}^{occ} \langle \phi_i | H_0 | \phi_i \rangle + \frac{1}{2} \sum_{\alpha,\beta}^{N} \gamma_{\alpha\beta} \Delta q_\alpha \Delta q_\beta + E_{rep}$$

non-SCC H (**parametrized**)

Long-range electrostatic interactions

Short-range repulsion



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

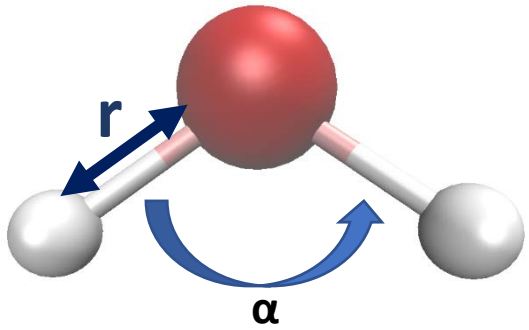
$$H_{\mu\nu}(\boldsymbol{r}) = \langle \phi_\mu(\boldsymbol{r}) | H_0 | \phi_\nu(\boldsymbol{r} - \boldsymbol{r_o}) \rangle, \; S_{\mu\nu}(\boldsymbol{r}) = \langle \phi_\mu(\boldsymbol{r}) | \phi_\nu(\boldsymbol{r} - \boldsymbol{r_o}) \rangle$$

$$H_0 = -\frac{1}{2}\nabla^2 + v_{eff}[\rho^a(\boldsymbol{r})] + v_{eff}[\rho^b(\boldsymbol{r} - \boldsymbol{r_o})]$$

Leveraging GPU-enabled DFTB

DFTB Parameterization - RESULTS

Compound	Multiplicity	Parameter*	DFT	DFTB	Δ(DFTB-DFT)	Δ(DFTB-DFT)%
FeH_2	3	r	1.54	1.503	-0.037	-2.40
		α	102.365	110.34	7.975	7.79
	5	r	1.66	1.58	-0.08	-4.82
		α	177.3	179.9	2.6	1.47
FeO	1	r	1.54	1.6	0.06	3.90
	3	r	1.58	1.68	0.1	6.33
	5	r	1.61	1.75	0.14	8.70
$Fe(CH3)_2$	1	r	1.92	1.89	-0.03	-1.56
		α	117.7	125.71	8.01	6.81
	3	r	1.94	2.13	0.19	9.79
	5	r	2.05	1.96	-0.09	-4.39

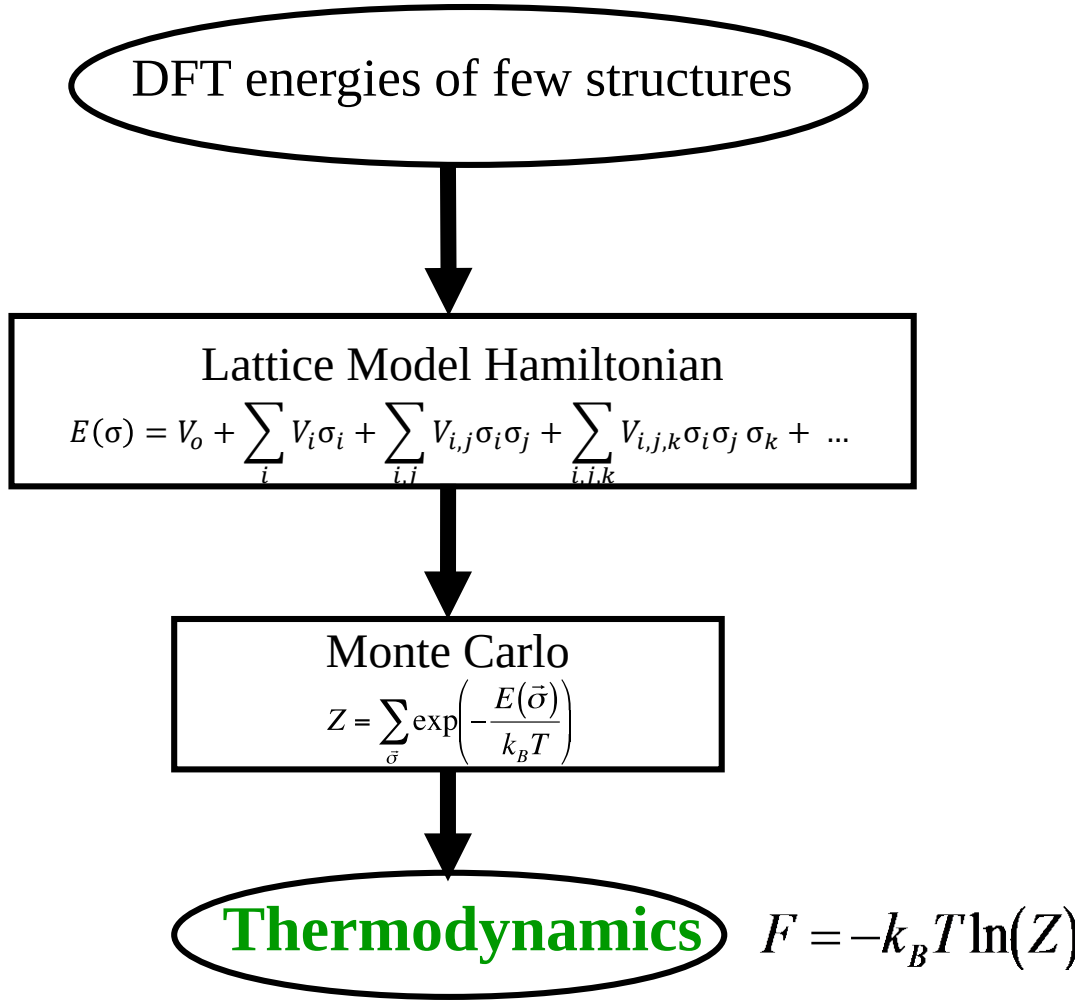


*r in Angstrom, α in degrees

Accelrys Software Inc., *Discovery Studio Modeling Environment, Release 8.0* , San Diego: Accelrys Software Inc., 2007.

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



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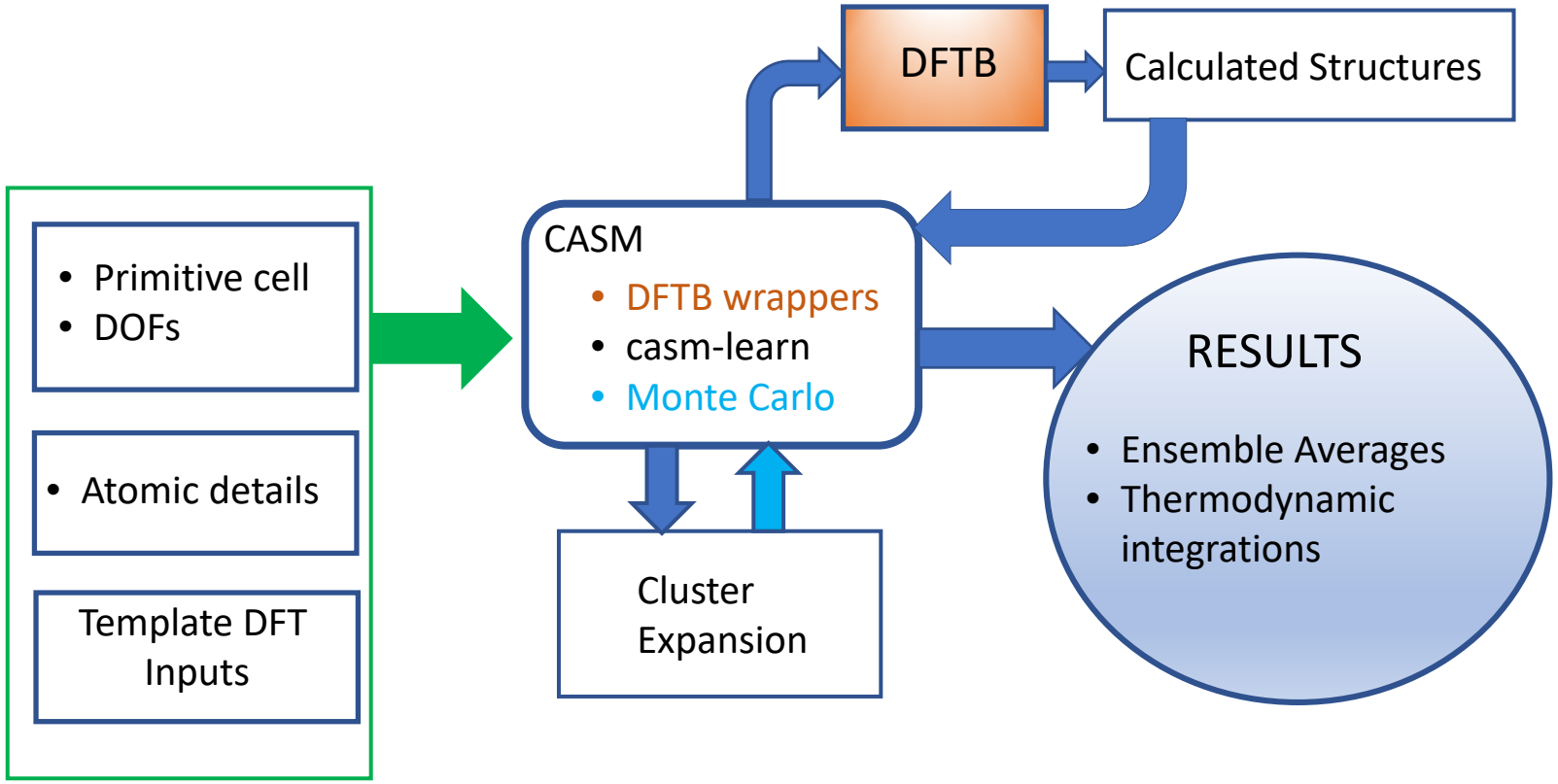
Phase Diagrams - CASM

CASM Workflow

- Carry out *ab-initio* calculations
- Fit cluster expansion (CE) Hamiltonians
- Perform MC simulations

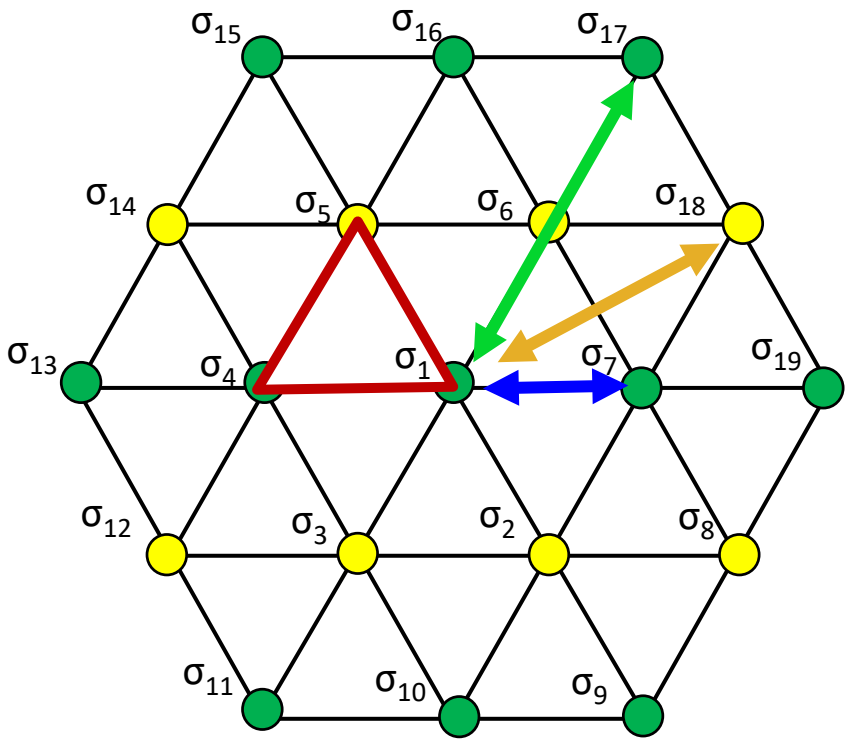


J. C. Thomas, A. Van der Ven, *Finite-temperature properties of strongly anharmonic and mechanically unstable crystal phases from first principles*, *Physical Review B*, **88**, 214111 (2013).

Phase Diagrams - CASM

CALCULATION OF PHASE DIAGRAM

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

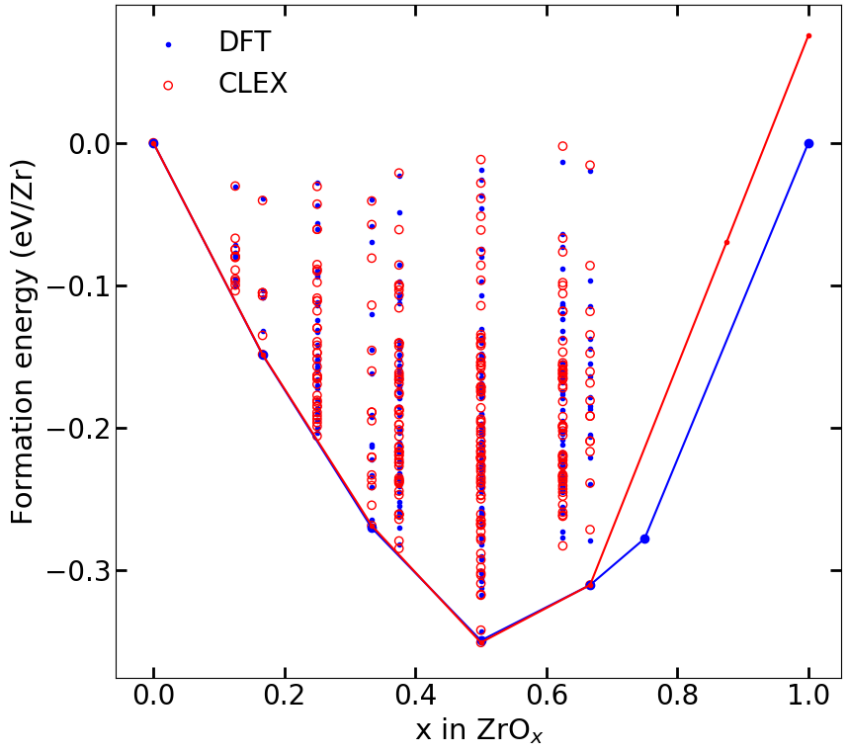


$$E = V_1\sigma_1 + V_{1,7}\sigma_1\sigma_7 + V_{1,18}\sigma_1\sigma_{18} + V_{1,17}\sigma_1\sigma_{17} + V_{1,4,5}\sigma_1\sigma_4\sigma_5 + \ldots$$

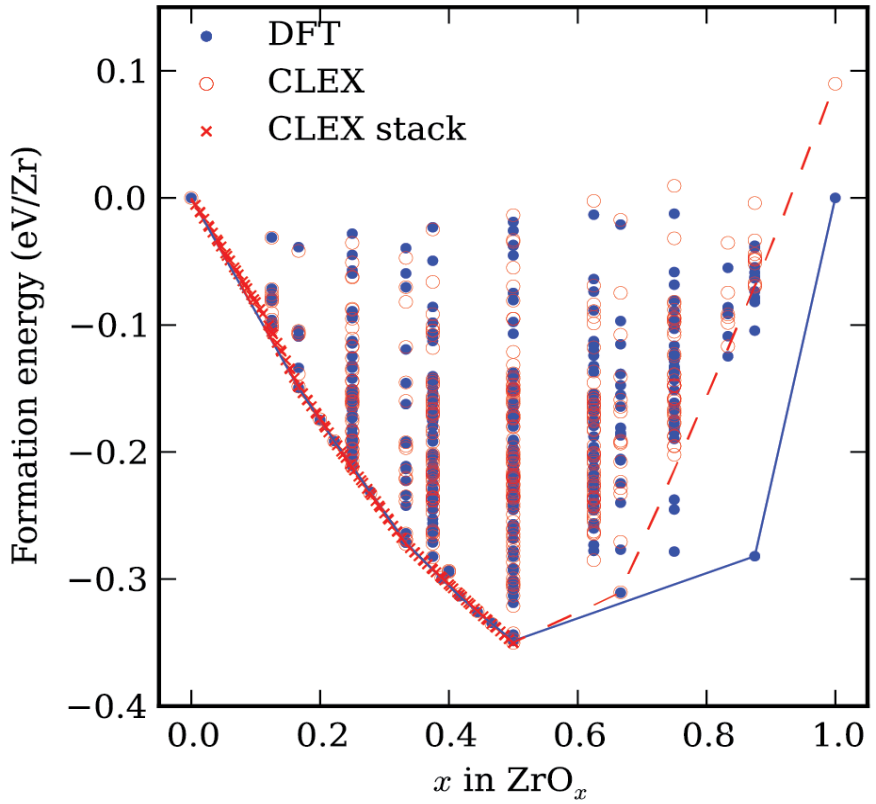
J. C. Thomas, A. Van der Ven, *Finite-temperature properties of strongly anharmonic and mechanically unstable crystal phases from first principles*, *Physical Review B*, **88**, 214111 (2013).

Leveraging GPU-enabled DFTB

Phase Diagrams – RESULTS



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

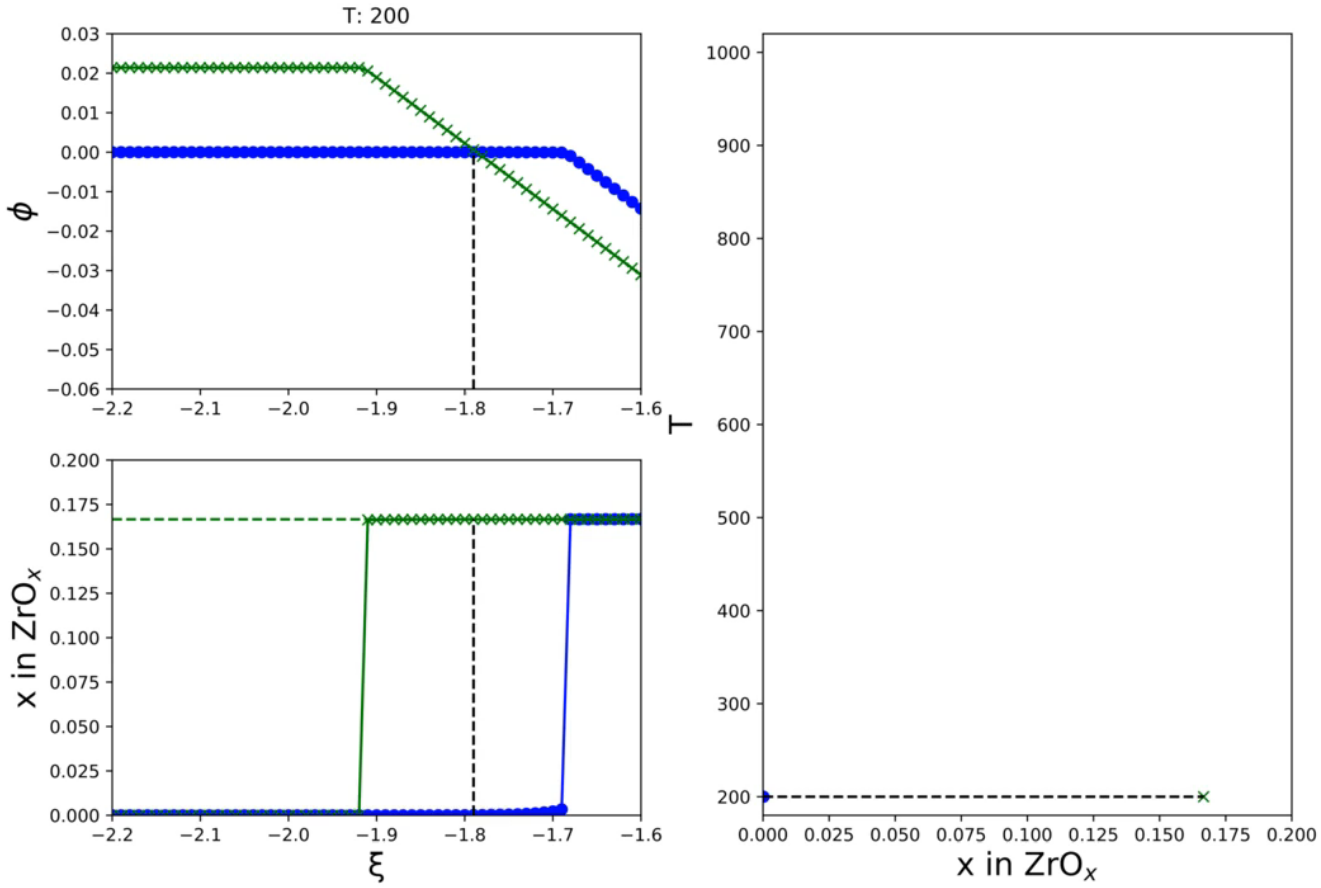


Each red circle belongs to specific configuration of HCP-based ZrO_x

B. Puchala, A. Van der Ven, Thermodynamics of the Zr-O system from first-principles calculations, Physical Review B, 88, 094108 (2013).

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!**