

Thermochemical Equilibrium for Multiphysics Simulations of Nuclear Materials

**Development of the corrosion modelling
application Yellowjacket**

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PhD Candidacy Examination
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Outline

① Introduction

- Nuclear Energy
- Generation IV Reactors
- Multiphysics Simulations

② Goals of Research

- Impetus
- Outcomes

③ Thermodynamic Equilibrium

- Gibbs energy and chemical potential
- Conditions of Thermodynamic Equilibrium
- Gibbs Energy Minimisation

④ Computational Implementation

- Gibbs Energy Minimiser - Overview
- Gibbs Energy Minimiser
- Challenges and Thrust Areas

⑤ Progress and Timeline

- Current Progress
- Milestones

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Nuclear Energy Perspective

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- A doubling in annual capacity additions is needed to be on track with the IEA's Sustainable Development Scenario⁽²⁾.

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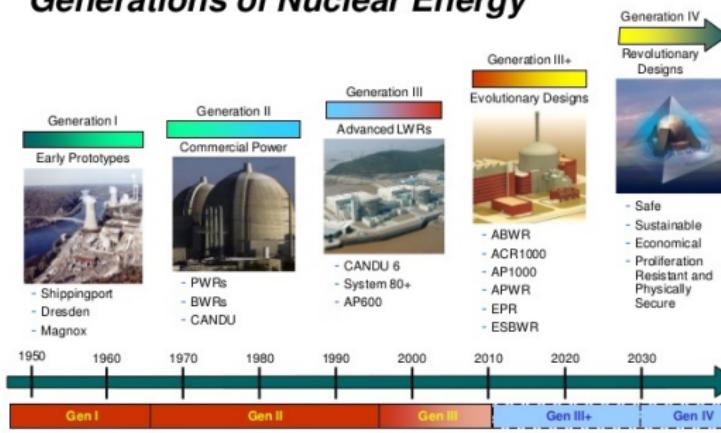
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- Most of the reactors currently in use are 2nd / 3rd generation Light Water Reactors or Pressurised Heavy Water Reactors.

Generations of Nuclear Energy



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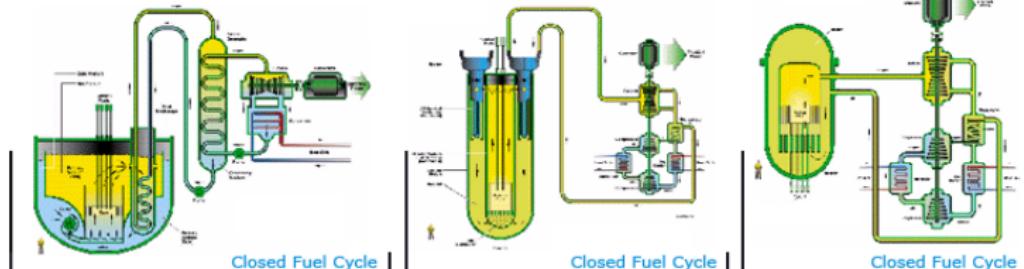
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 - **Proliferation resistance:** Increase the assurance that these systems are the least desirable route for diversion or theft of weapons-usable materials.

Generation IV Reactors

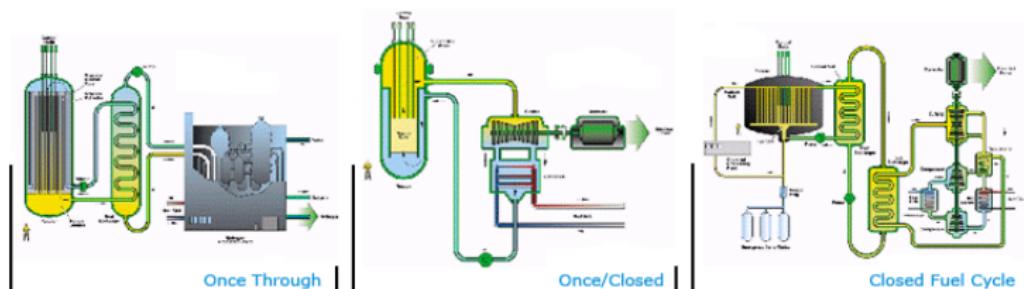
6 INNOVATIVE CONCEPTS WITH TECHNOLOGICAL BREAKTHROUGH



SODIUM FAST REACTOR

LEAD FAST REACTOR

GAS FAST REACTOR



VERY HIGH TEMPERATURE REACTOR

SUPERCRITICAL WATER REACTOR

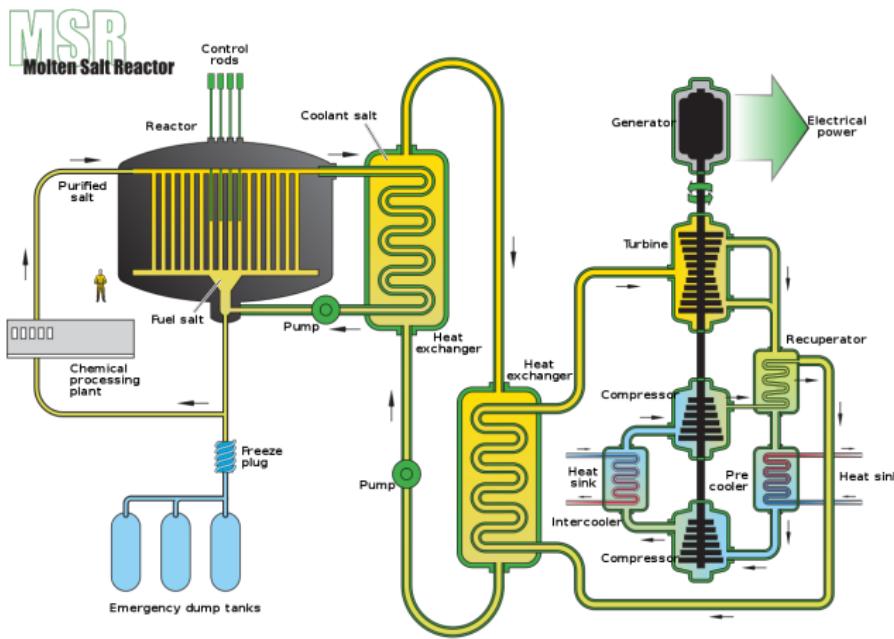
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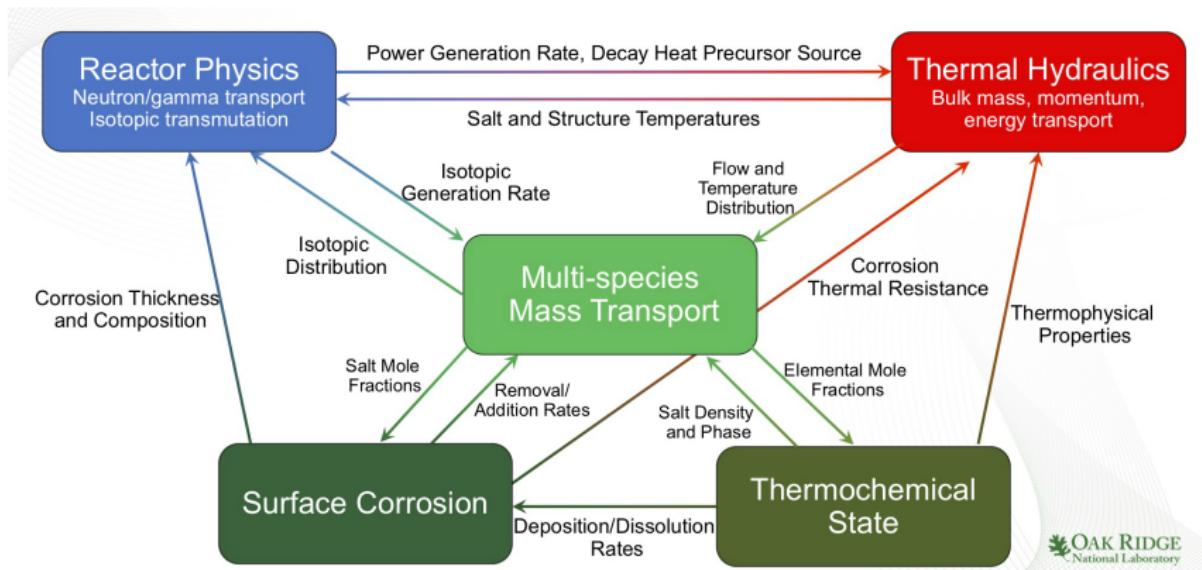


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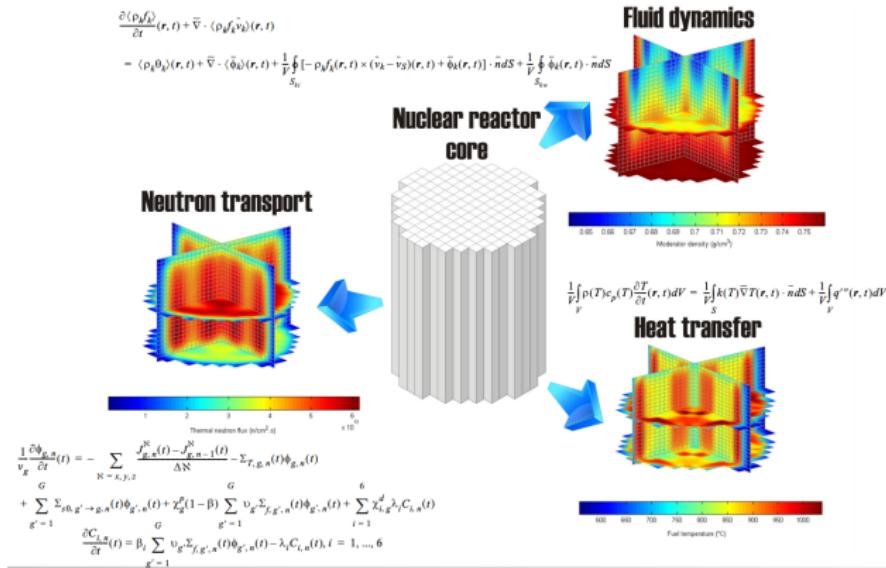


Simulation of Nuclear Reactors

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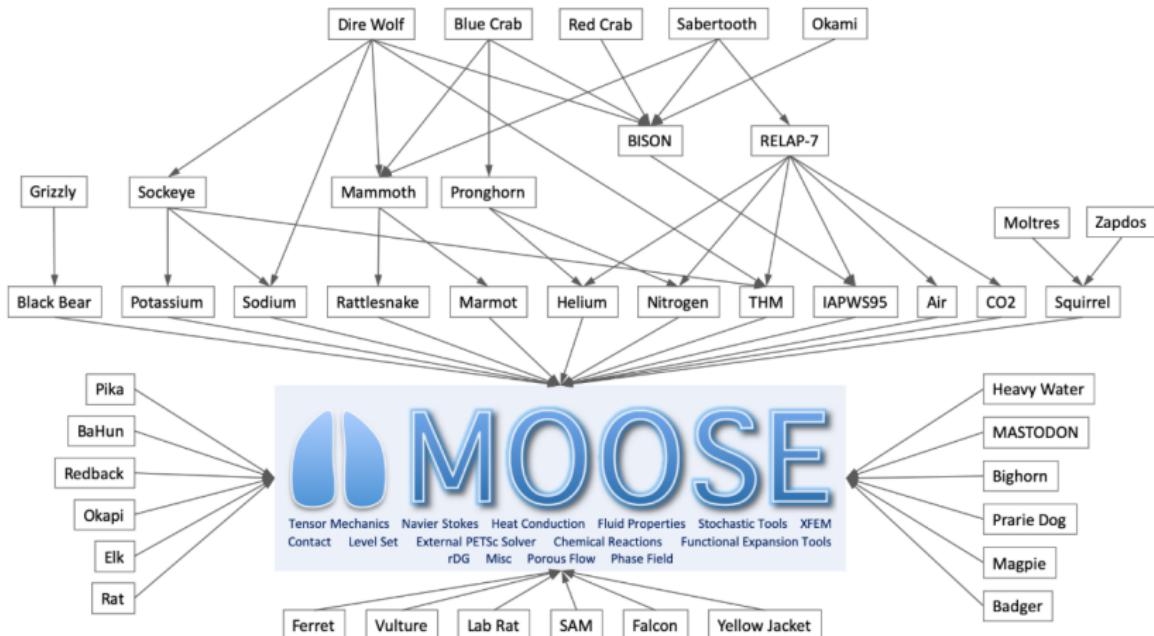
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- MOOSE includes a test suite and documentation system to allow for agile development while maintaining a NQA-1 process.

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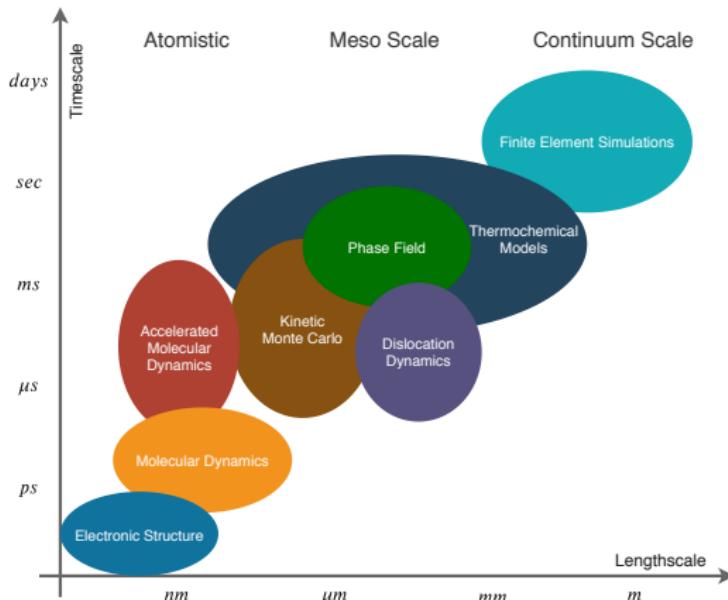


Nuclear Materials

- Nuclear materials are highly complex multiscale, multiphysics systems.

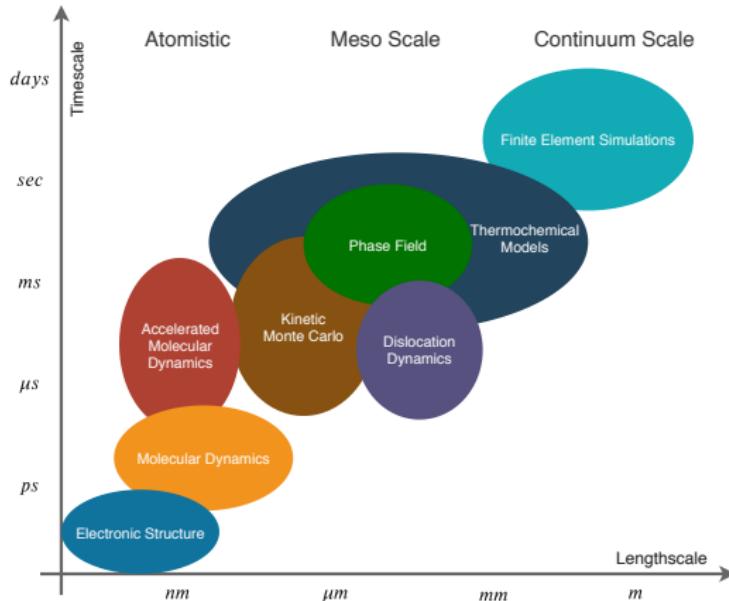
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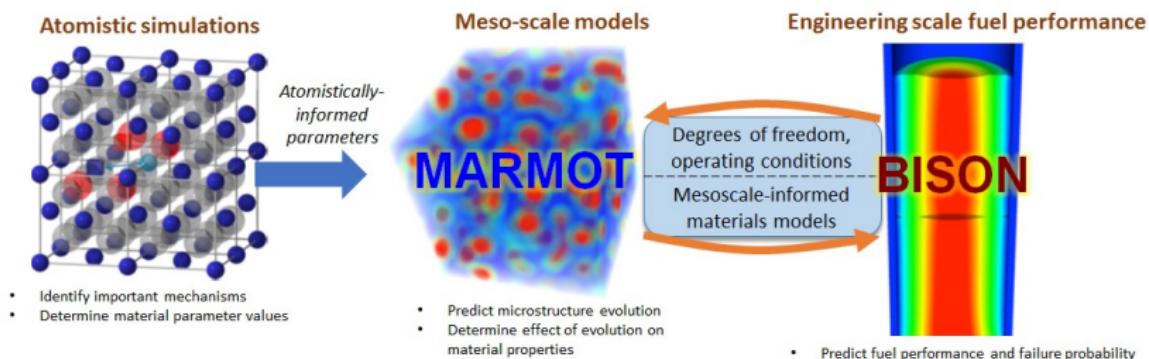
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- Design and development of nuclear materials can be supported by numerical simulations to make the process both time and cost efficient.

Nuclear Materials

- The materials simulation tools of MOOSE form the Fuels Product Line (FPL).
- The framework consists of MOOSE, fuel performance code Bison and mesoscale microstructural evolution tool Marmot.



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Currently, MOOSE lacks a corrosion modelling tool!

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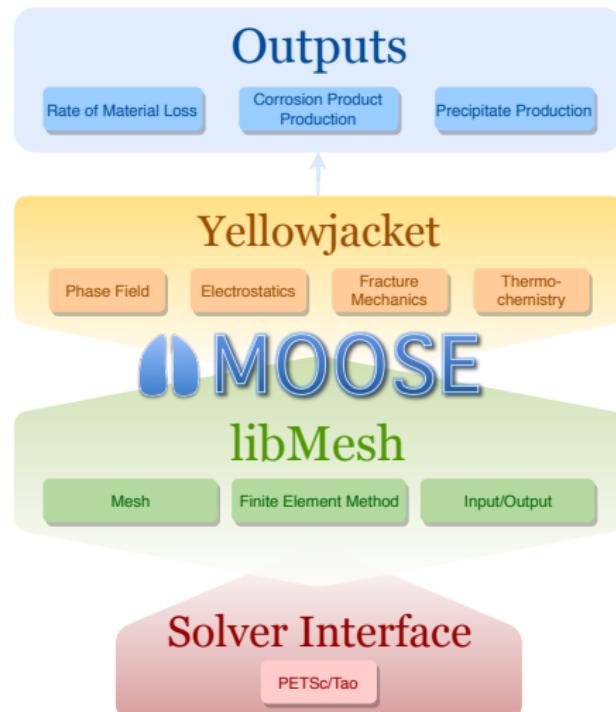
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- Collaboration between Ontario Tech University, University of Florida, Idaho National Laboratory and Los Alamos National Laboratory.
- Funded by the U.S. Department of Energy through Idaho National Laboratory and the development of thermochemistry solver is also supported by the Canada Research Chairs program.

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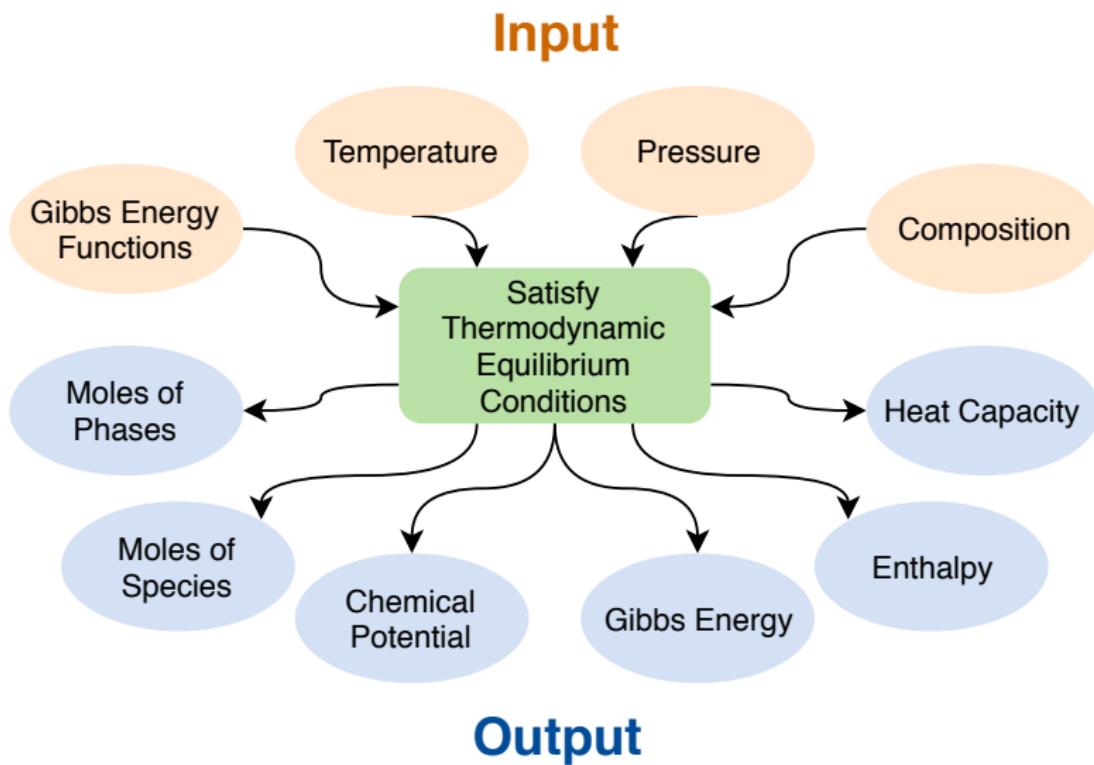
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- Direct coupling of thermodynamic equilibrium can augment multiphysics calculations by providing quantities such as the chemical potentials, Gibbs energies, etc.

Thermodynamics in Yellowjacket



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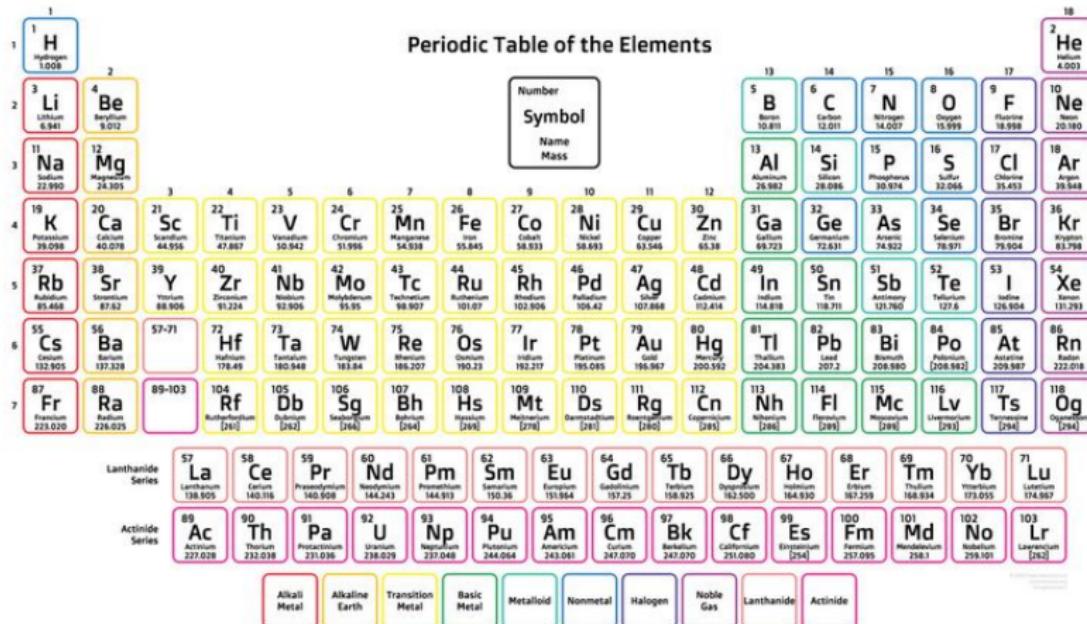
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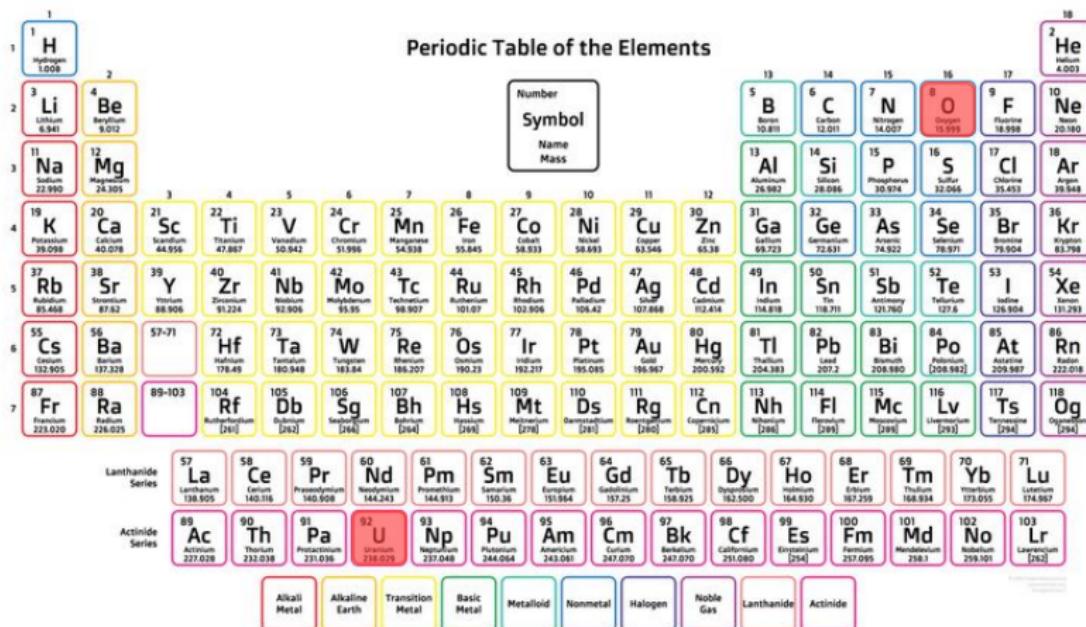
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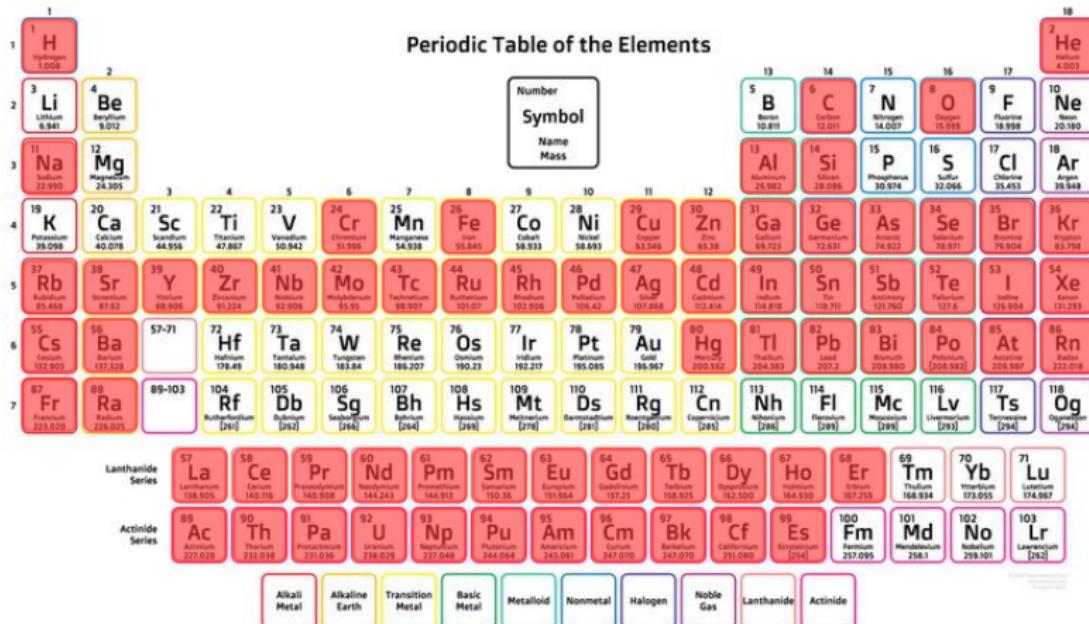
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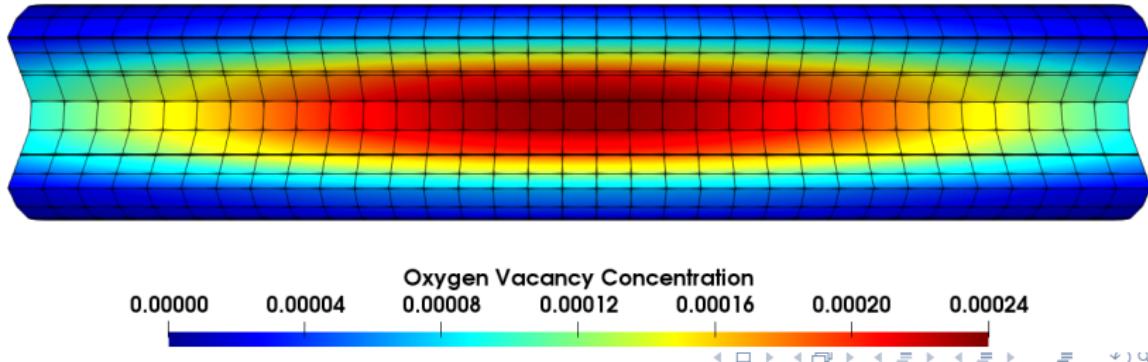
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- There is little freedom to make improvements or adapt them to specific needs.
- Thermochimica is an open-source code developed with the aim of direct coupling with multiphysics codes.
 - Written in Fortran 90.
 - Not developed within the MOOSE framework.
 - Needs significant work to meet the NQA-1 standards.

Goals and Outcomes

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Outcomes

- ① Development of a new advanced Gibbs energy minimiser written in C++ within the framework of MOOSE platform.
- ② Full integration within the multiphysics framework MOOSE, with the intent of coupling to the phase field code Marmot.
- ③ Enhanced initialisation algorithms to improve the computational performance.
- ④ Investigation and implementation of robust global optimisation schemes to increase reliability and robustness.
- ⑤ Software Quality Assurance with rigorous verification and testing to comply with the NQA-1 guidelines required to be met for licensing.

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- Gibbs energy is the thermodynamic quantity that is minimised when a system reaches chemical equilibrium at constant temperature and pressure.

Chemical Potential

- Chemical potential of species i in phase λ is a measure of the change in Gibbs energy of the system by the introduction of species i .

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Gibbs Energy

- Integral Gibbs energy of a multicomponent, multiphase system can be expressed in terms of chemical potentials, $\mu_{i(\lambda)}$, of the species.

$$G_{sys} = RT \left(\sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} \tilde{\mu}_i + \sum_{\omega=1}^{\Omega} n_{\omega} \tilde{\mu}_{\omega} \right)$$

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- The Gibbs energy of the system can also be expressed in terms of the element potentials, Γ_j , and the number of moles, b_j , of the system components.

$$G_{\text{sys}} = \sum_{j=1}^C \Gamma_j b_j$$

Thermodynamic Equilibrium - Necessary Conditions

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Conservation of mass

$$b_j = \sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} \nu_{i,j} + \sum_{\omega=1}^{\Omega} n_{\omega} \nu$$

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Gibbs' Criteria

$$\mu_i = \sum_{j=1}^C \nu_{i,j} \Gamma_j$$

Thermodynamic Equilibrium - Sufficient Conditions

Gibbs plane

$$\pi_\lambda = \min_{\lambda} \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^C \nu_{i,j} \Gamma_j \right)$$

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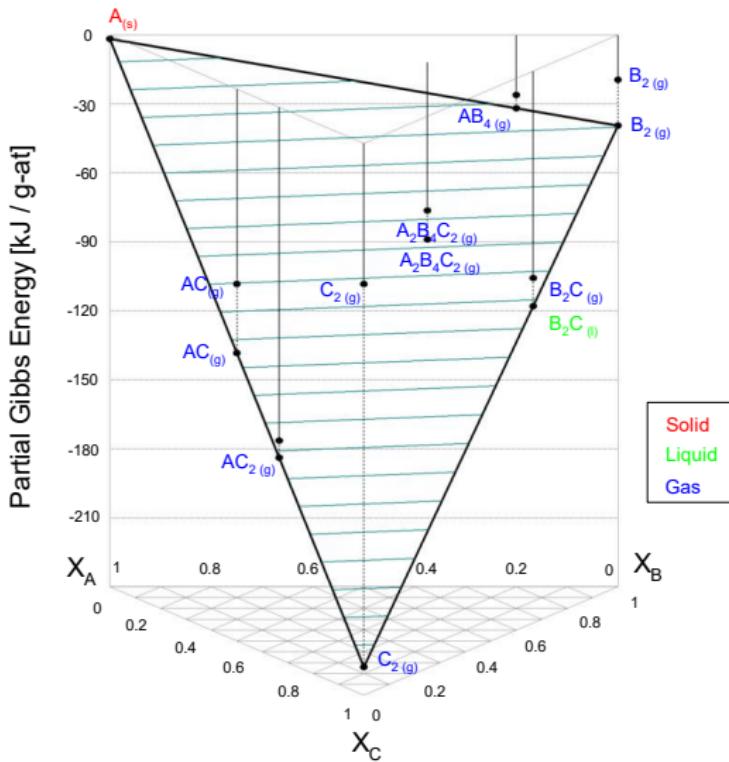
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Constraints

$$\sum_{i=1}^{N_\lambda} x_{i(\lambda)} = 1$$

$$x_{i(\lambda)} \geq 0$$

Thermodynamic Equilibrium - Sufficient Conditions



Solid
Liquid
Gas

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- Second order steepest descent method.
- Constrains Gibbs' phase rule while simultaneously minimising the mass balance and Gibbs' criteria residuals.

Gibbs Energy Minimisation

Optimise

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Outline

① Introduction

- Nuclear Energy
- Generation IV Reactors
- Multiphysics Simulations

② Goals of Research

- Impetus
- Outcomes

③ Thermodynamic Equilibrium

- Gibbs energy and chemical potential
- Conditions of Thermodynamic Equilibrium
- Gibbs Energy Minimisation

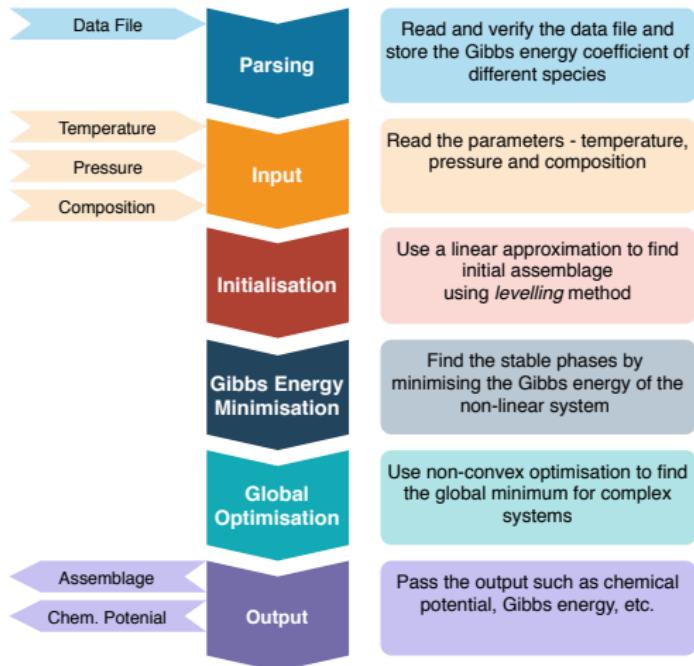
④ Computational Implementation

- Gibbs Energy Minimiser - Overview
- Gibbs Energy Minimiser
- Challenges and Thrust Areas

⑤ Progress and Timeline

- Current Progress
- Milestones

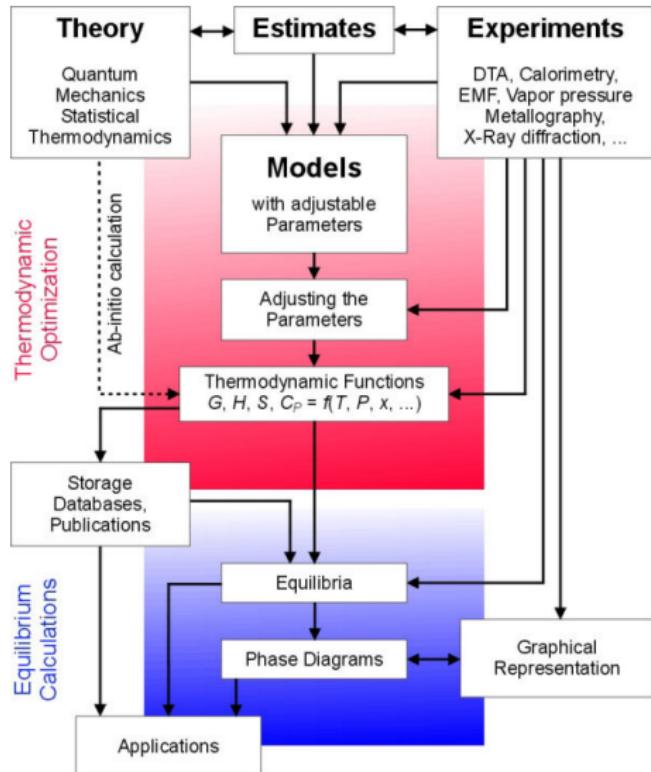
Computational Structure



Parsing and Input

- The data files are created using the well known Calphad method and can be available in different formats.

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- Yellowjacket uses ChemSage (*.dat) format datafiles, which can be generated by the commercial software FactSage.

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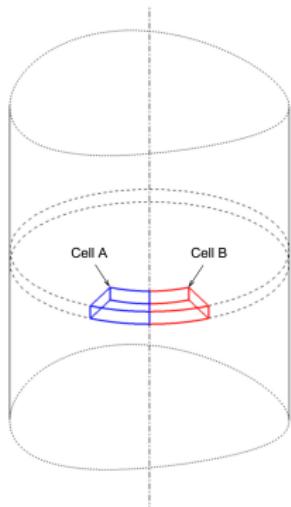
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- Levelling temporarily converts the non-linear optimisation problem into a linear optimisation problem by treating all species and phases as pure separate phases.

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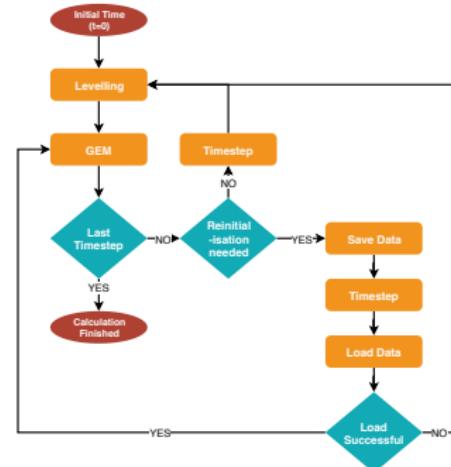
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- *Levelling* is an estimating process developed by Eriksson and Thompson (1989).
- Levelling temporarily converts the non-linear optimisation problem into a linear optimisation problem by treating all species and phases as pure separate phases.
- The number of iterations required to achieve convergence does not increase rapidly with the number of system components.

Initialisation

- Initialise using neighbour cells



- Initialise with last time step



Gibbs Energy Minimisation

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$$\mathbf{H} = \begin{bmatrix}
 r_{j=1,k=1} & \cdots & r_{j=1,k=C} & \phi_{j=1,\lambda=1} & \cdots & \phi_{j=1,\lambda=\Lambda} & \nu_{j=1,\omega=1} & \cdots & \nu_{j=1,\omega=\Omega} \\
 \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\
 r_{j=C,k=1} & \cdots & r_{j=C,k=C} & \phi_{j=C,\lambda=1} & \cdots & \phi_{j=C,\lambda=\Lambda} & \nu_{j=C,\omega=1} & \cdots & \nu_{j=C,\omega=\Omega} \\
 \phi_{\lambda=1,j=1} & \cdots & \phi_{\lambda=1,j=C} & 0 & \cdots & 0 & 0 & \cdots & 0 \\
 \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\
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Gibbs Energy Minimisation

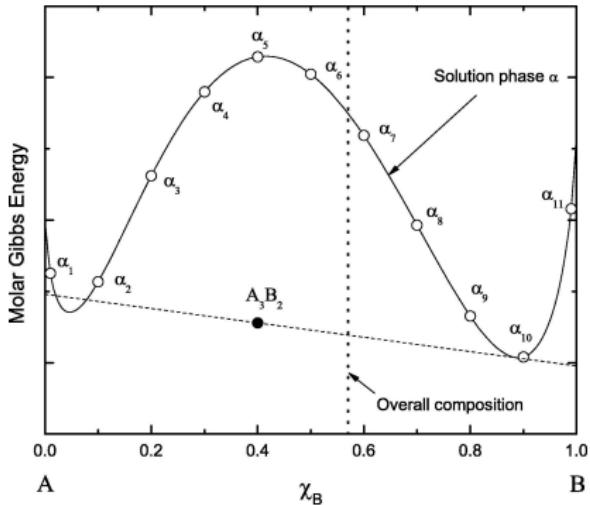
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$$\boldsymbol{\zeta} = \begin{bmatrix}
 b_{j=1} + \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_\lambda} \left(\frac{\mu_{i(\lambda)}^m}{RT} - 1 \right) n_{i(\lambda)}^m \nu_{i,j=1} \\
 \vdots \\
 b_{j=E} + \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_\lambda} \left(\frac{\mu_{i(\lambda)}^m}{RT} - 1 \right) n_{i(\lambda)}^m \nu_{i,j=E} \\
 \sum_{i=1}^{N_{\lambda=1}} \left(\frac{\mu_{i(\lambda=1)}^m}{RT} - 1 \right) n_{i(\lambda=1)}^m \\
 \vdots \\
 \sum_{i=1}^{N_{\lambda=\Lambda}} \left(\frac{\mu_{i(\lambda=\Lambda)}^m}{RT} - 1 \right) n_{i(\lambda=\Lambda)}^m \\
 \frac{\mu_{\omega=1}^m}{RT} \\
 \vdots \\
 \frac{\mu_{\omega=\Omega}^m}{RT}
 \end{bmatrix}$$

Global Optimisation

- The Gibbs energy function of non-ideal phases may be non-convex, yielding multiple local minima. This makes finding global minimum a challenge.



Output

- Outputs after the Gibbs energy minimisation and global optimisation include moles of phases, species mole fraction in each phase, chemical potentials, Gibbs energy, etc.
- The chemical potential of various species can be used to find the driving force for other reactions such as corrosion.
- These parameters can also be passed to other MOOSE based codes such as Marmot and Bison.

Challenges and Thrust Areas

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 - Armijo/Wolfe conditions must be efficiently implemented to make sure that Newton steps do not lead to divergence.

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 - Mathematically, global optimisation implies finding the Gibbs plane that satisfies the sufficient condition:

$$\pi_\lambda = \min_{\lambda} \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^C \nu_{i,j} \Gamma_j \right)$$

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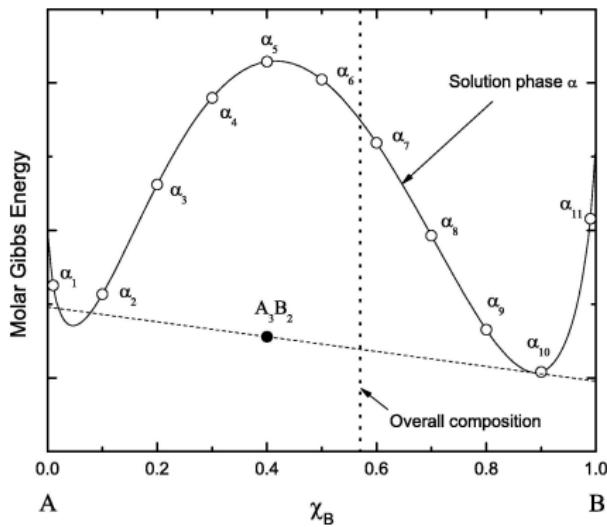
- No global optimisation technique guarantees the ability of finding a global extremum of a non-convex function.
 - Searching for a global minimum becomes increasingly more difficult as the size of the system increases.
 - The computational effort associated with performing this task can increase very rapidly in large systems.

Challenges and Thrust Areas

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- Originally, they relied on the grid construction method which is a brute force method.



Challenges and Thrust Areas

- Use the advanced algorithms available in literature to improve global optimisation for the thermochemistry solver.
- Through numerical experiments, perform a comprehensive review of both deterministic and stochastic methods of global optimisation applied to computational thermodynamics.
- implement the most suitable optimisation scheme.

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 - Use of CIVET for continuous testing and integration.

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 - Rigorous documentation of every function and their dependencies.

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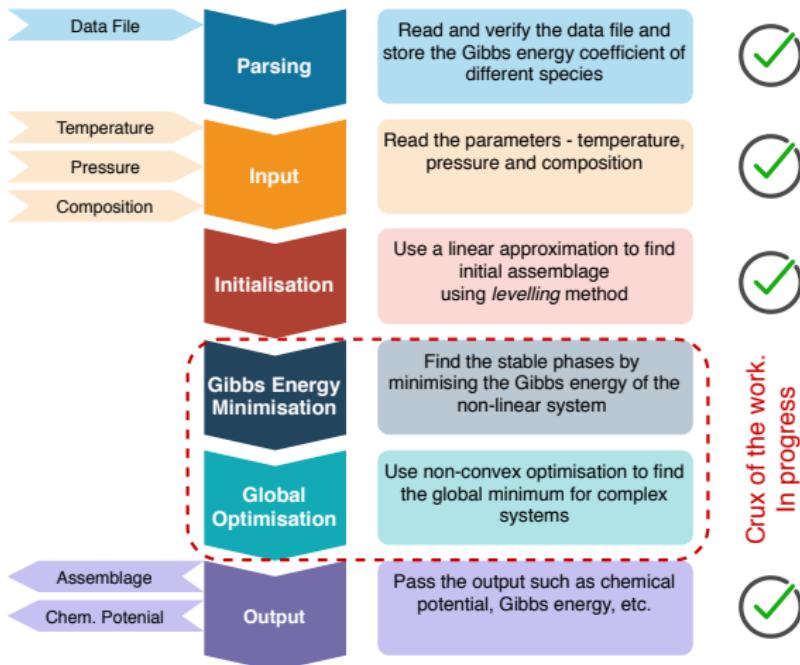
Progress - Coursework

Coursework			
Item	Timeline	Status	
MCSC-6010G: Mathematical Modelling	Sep. - Dec. 2018	Complete	
MCSC-6030G: High Performance Computing	Sep. - Dec. 2018	Complete	
NUCL-6005G: Computational Thermodynamics [PhD level elective]	Sep. - Dec. 2018	Complete	
MCSC-6020G: Numerical Analysis	Sep. - Dec. 2019	Complete	

Progress - Publications

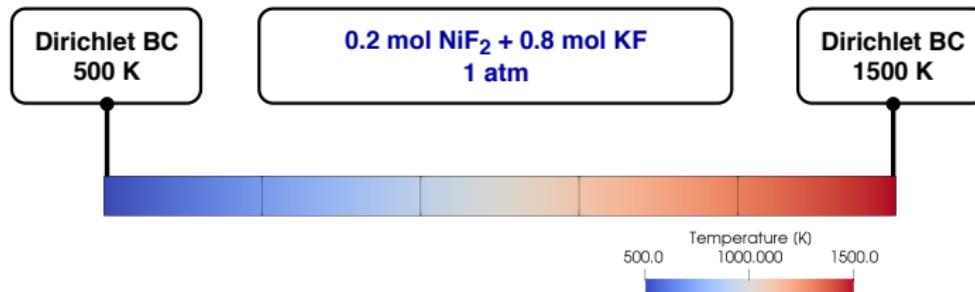
- ① M. Piro, M. Poschmann and **P. Bajpai**, *On the interpretation of chemical potentials computed from equilibrium thermodynamic codes: Applications to molten salts*, Journal of Nuclear Materials, 526 (2019) 151756.
- ② **P. Bajpai**, M. Poschmann, M. Piro, *Derivations of useful partial molar excess Gibbs energy of mixing expressions of common thermodynamic models*, To be submitted to CALPHAD Computer Coupling of Phase Diagrams and Thermochemistry. [In preparation]
- ③ **P. Bajpai**, M. Poschmann, D. Andrš, C. Bhave, M. Tonks and M. Piro, *Development of a new thermochemistry solver for multiphysics simulations of nuclear materials*, TMS 2020 Supplemental Proceedings, TMS 2020 - 149th Annual Meeting & Exhibition, San Diego, February 23-27, 2020. [Accepted]
- ④ **P. Bajpai**, M. Poschmann, D. Andrš and M. Piro, *Progress in developing a new thermochemistry code for corrosion modelling and multiphysics simulation of nuclear fuels*, 39th Annual Conference of the Canadian Nuclear Society and 43rd Annual CNS/CNA Student Conference, Ottawa, June 23-26, 2019.

Progress - Research

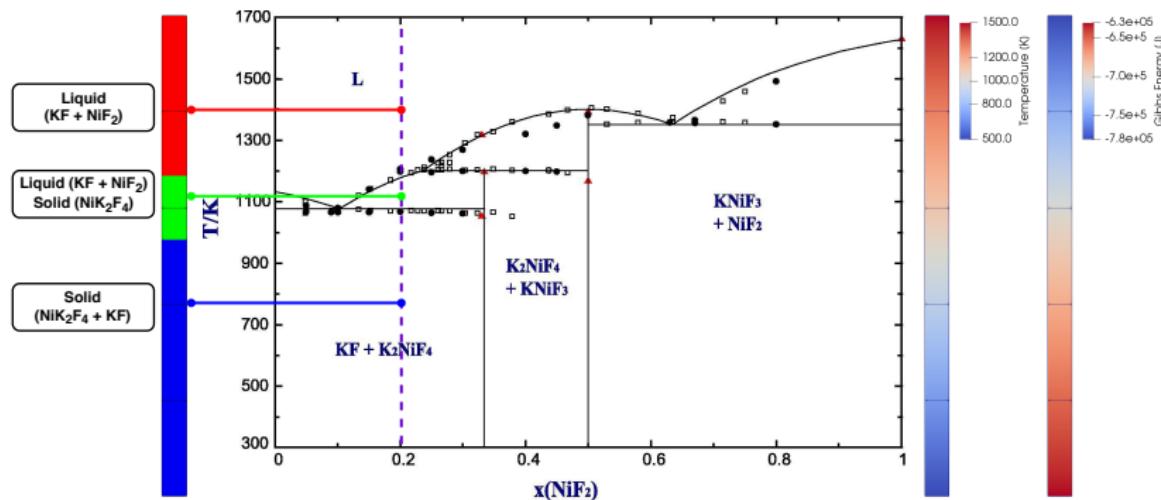


Demonstration Problem

- Initial focus on Ni alloys interacting with molten $\text{LiF}_2 - \text{KF}$ salts.



Demonstration Problem



Milestones - Research

Research		
Item	Timeline	Status
Literature review of computational thermodynamics and GEM	Sep. - Dec. 2018	Complete
Implement data file parsing code	Feb. - Mar. 2019	Complete
Implement linear solver (levelling)	Apr. - Jun. 2019	Complete
Implement communication between Yellowjacket and MOOSE	Jul. - Aug. 2019	Complete
Implement non-linear solver for GEM (homogeneous)	Sep. - Feb. 2020	In progress
Implement non-linear solver for GEM (heterogeneous)	Mar. - May 2020	Planned
Demonstration of non-linear solver capabilities	May - Jun. 2020	Planned
Begin integration of thermodynamic solver with Marmot	Jul. - Aug. 2020	Planned
Comparative study of global optimisation strategies	Sep. - Dec. 2020	Planned
Implementation of global optimisation algorithm	Jan. - Mar. 2021	Planned
Demonstration of global optimisation capabilities	Apr. - May 2021	Planned
Complete integration into MOOSE	Jun. - Aug. 2021	Planned
Verification and testing	Sep. - Dec. 2021	Planned

Thanks for your attention!

Questions?