

Thermochemical Equilibrium for Multiphysics Simulations of Nuclear Materials

**Development of the corrosion modelling
application Yellowjacket**

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PhD Candidacy Examination
December 9, 2019



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

⑤ Progress and Timeline

- Current Progress
- Timeline

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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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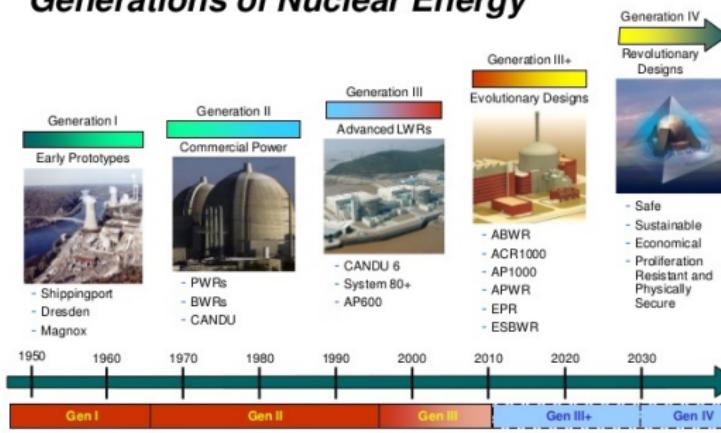
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Generations of Nuclear Energy



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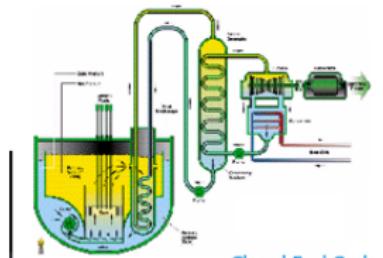
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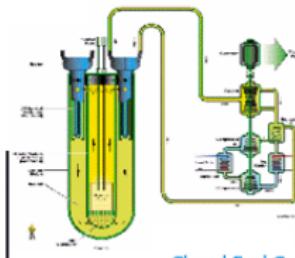
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 - **Proliferation resistance:** Increase the assurance that these systems are the least desirable route for diversion or theft of weapons-usable materials.

Generation IV Reactors

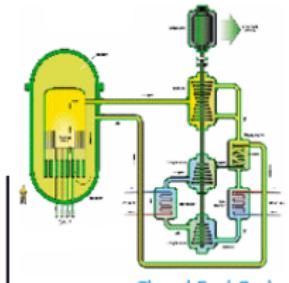
6 INNOVATIVE CONCEPTS WITH TECHNOLOGICAL BREAKTHROUGH



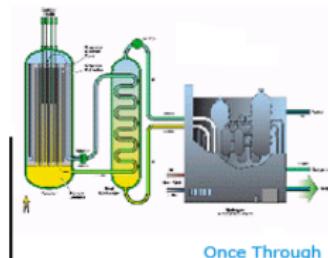
SODIUM FAST REACTOR



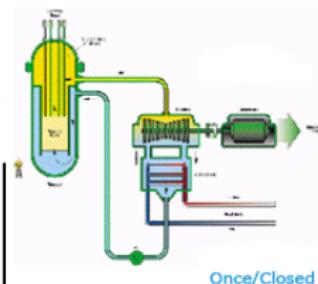
LEAD FAST REACTOR



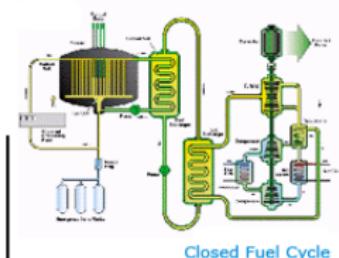
GAS FAST REACTOR



VERY HIGH TEMPERATURE REACTOR



SUPERCRITICAL WATER REACTOR



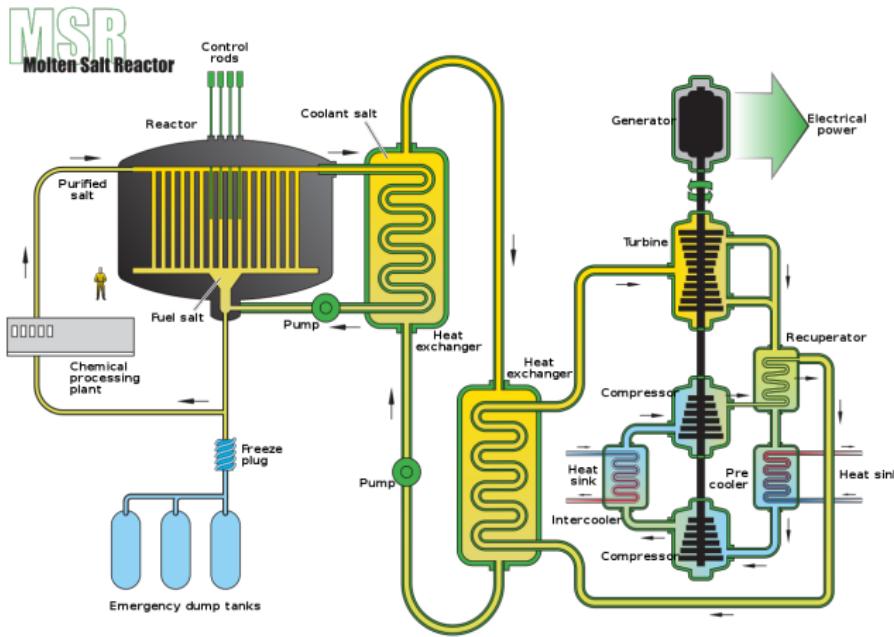
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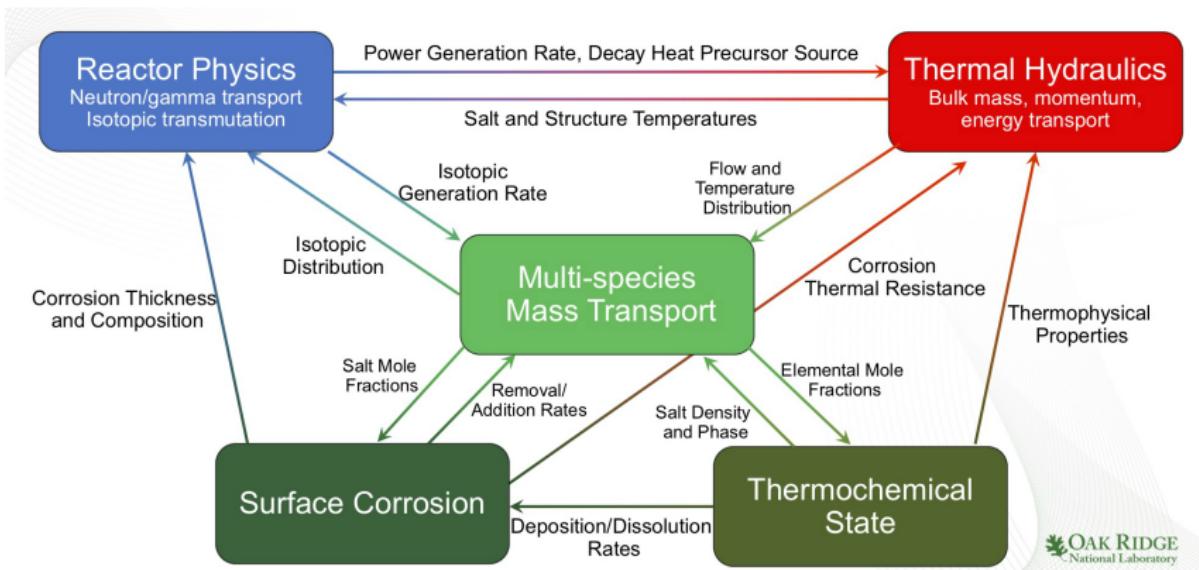


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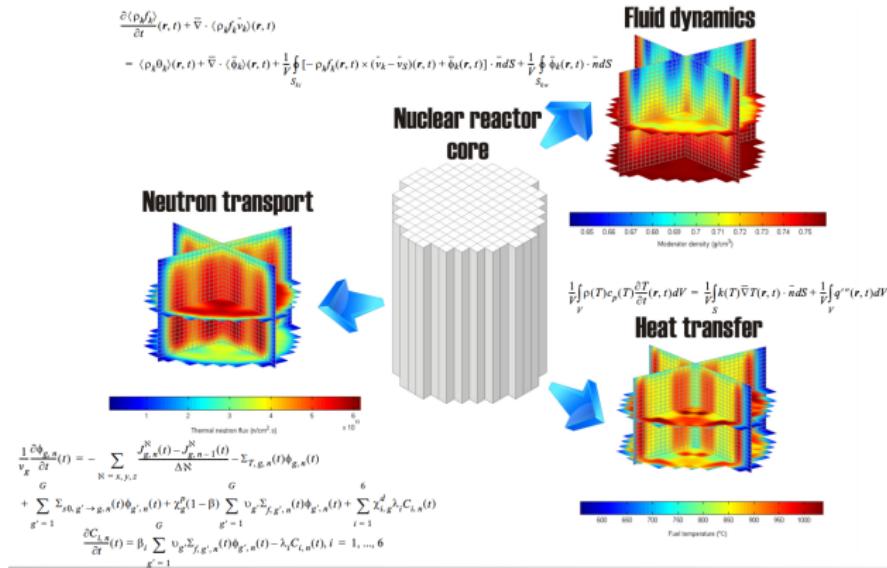


Simulation of Nuclear Reactors

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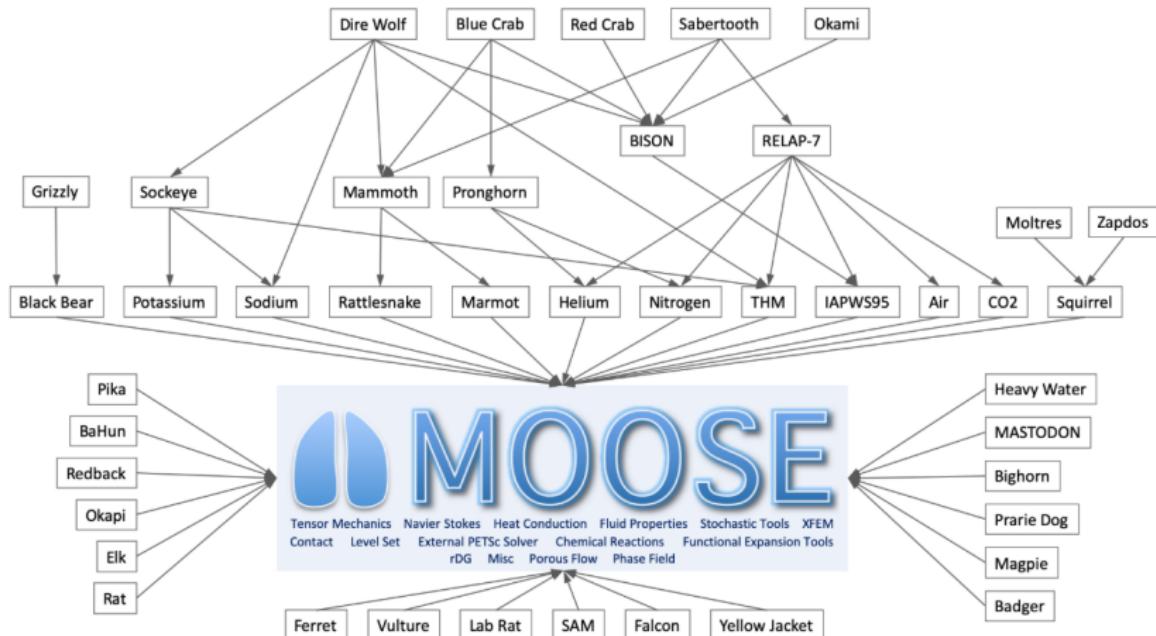
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- MOOSE includes a test suite and documentation system to allow for agile development while maintaining a NQA-1 process.

MOOSE

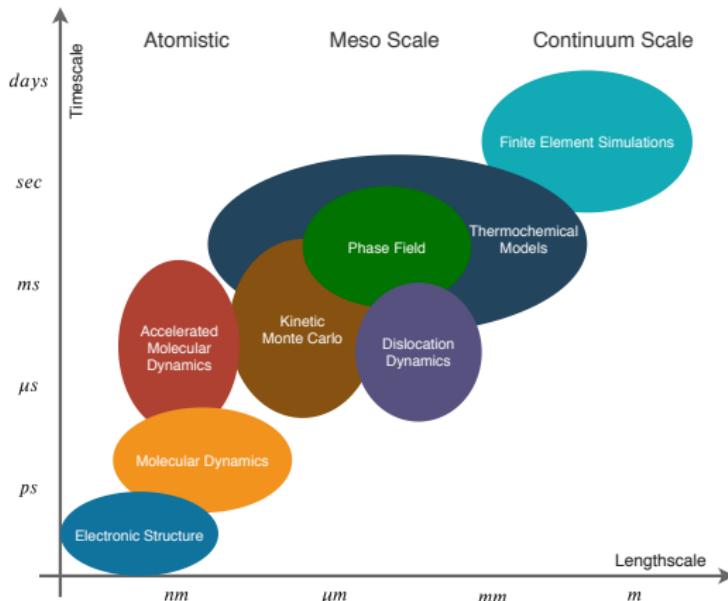


Nuclear Materials

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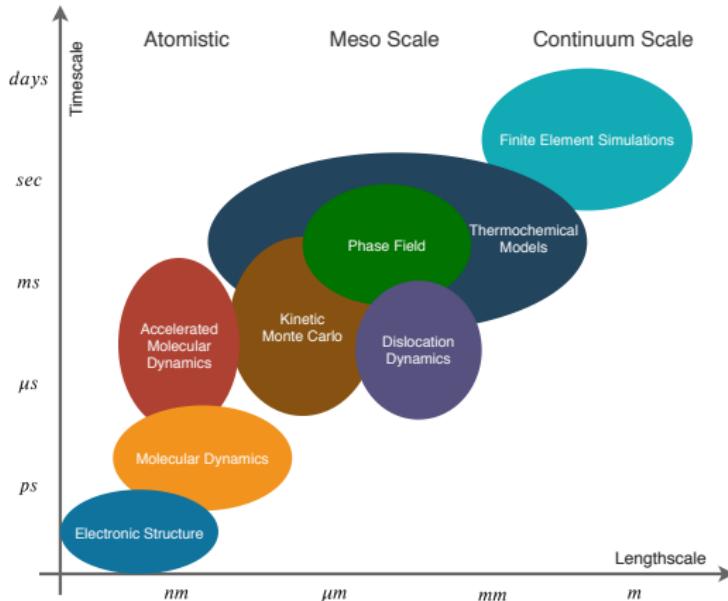
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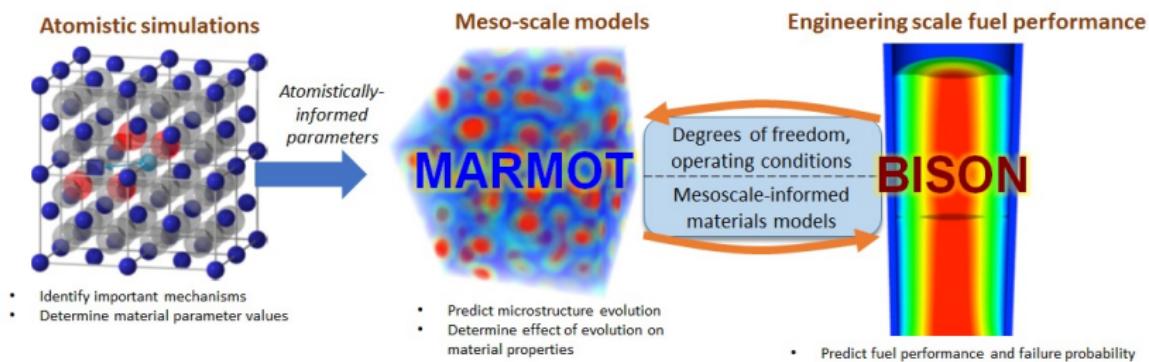
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- Design and development of nuclear materials can be supported by numerical simulations to make the process both time and cost efficient.

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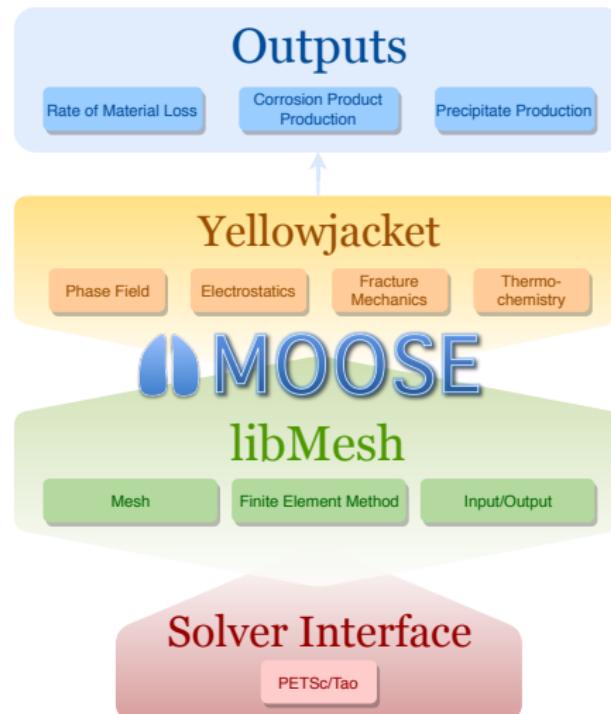
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- Collaboration between Ontario Tech University, University of Florida, Idaho National Laboratory and Los Alamos National Laboratory.
- Funded by the U.S. Department of Energy through Idaho National Laboratory and the development of thermochemistry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

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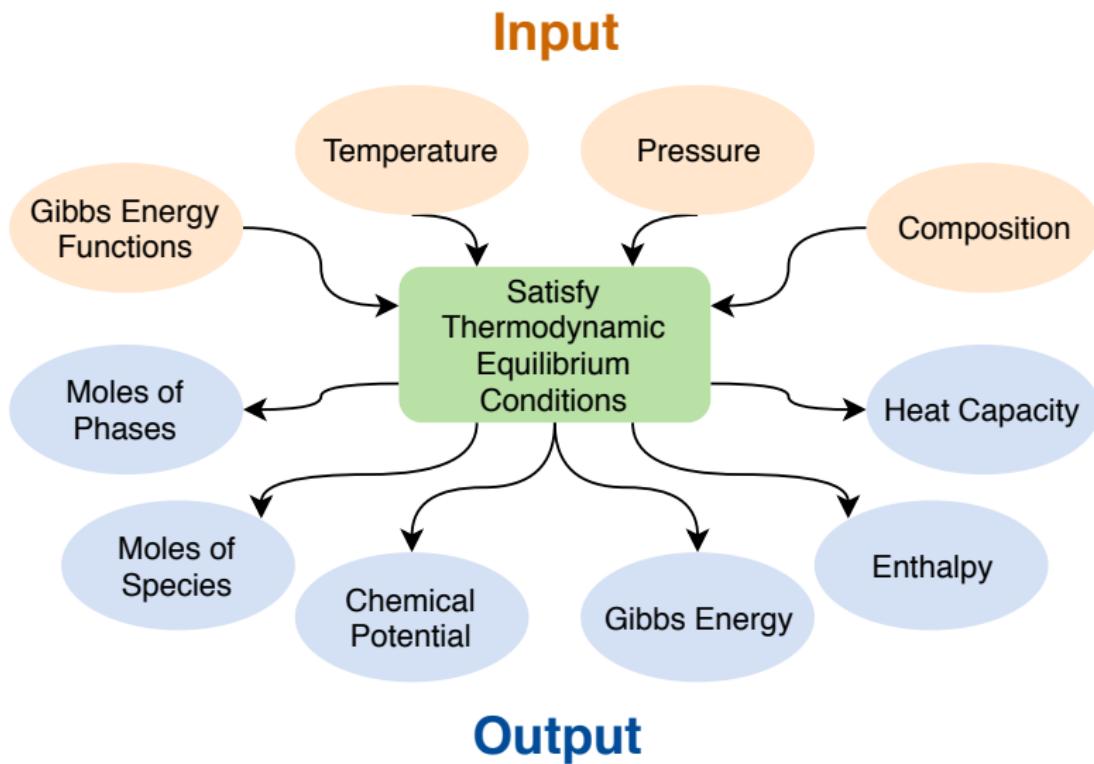
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- Direct coupling of thermodynamic equilibrium can augment multiphysics calculations by providing quantities such as the chemical potentials, Gibbs energies, etc.

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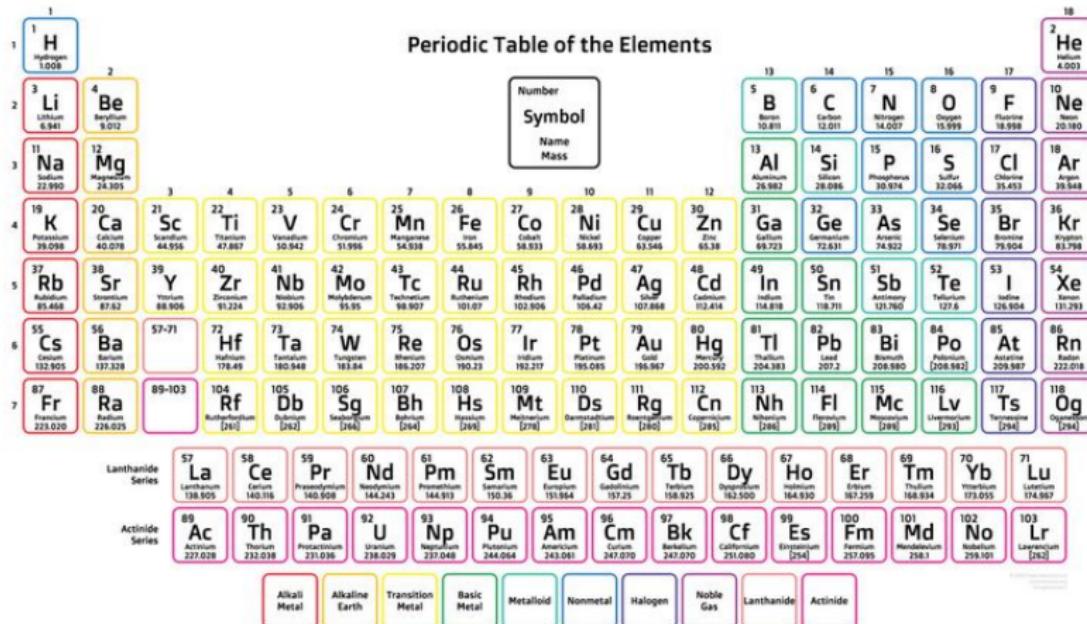
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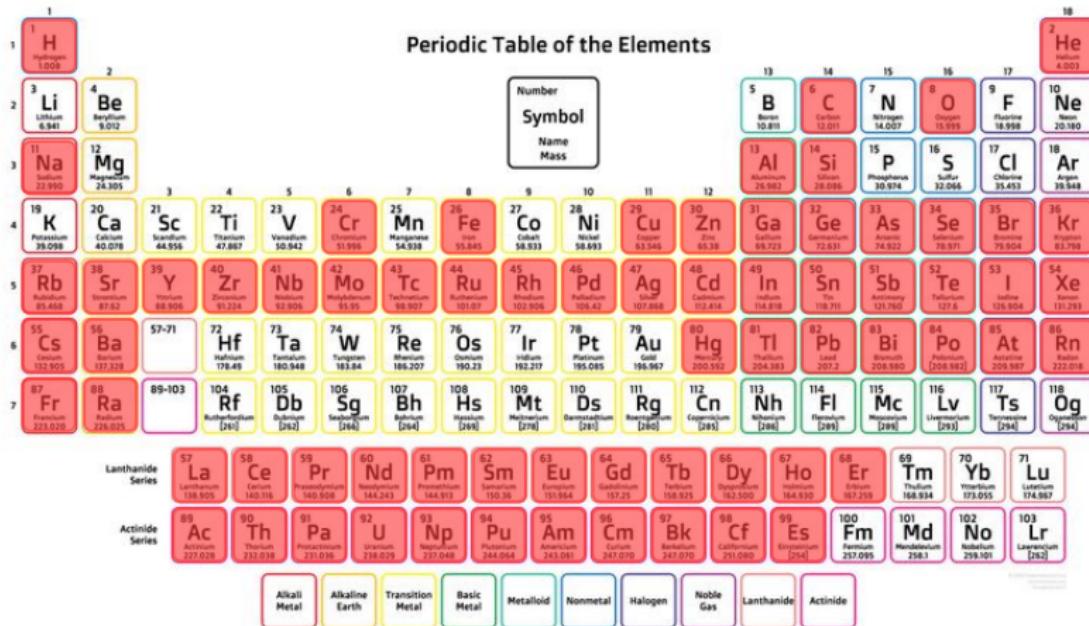
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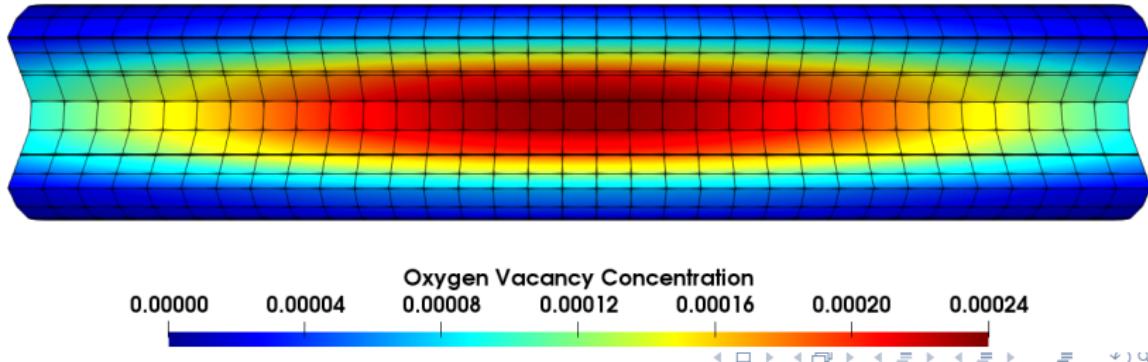
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- There is little freedom to make improvements or adapt them to specific needs.
- ThermoChimica is an open-source code developed with the aim of direct coupling with multiphysics codes.
 - Written in Fortran 90.
 - Not developed within the MOOSE framework.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

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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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- Non-ideal mixing phases

$$\mu_{i(\lambda)} = g_{i(\lambda)}^0 + \ln x_{i(\lambda)} + g_{i(\lambda)}^{ex}$$

Gibbs Energy

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

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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.

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

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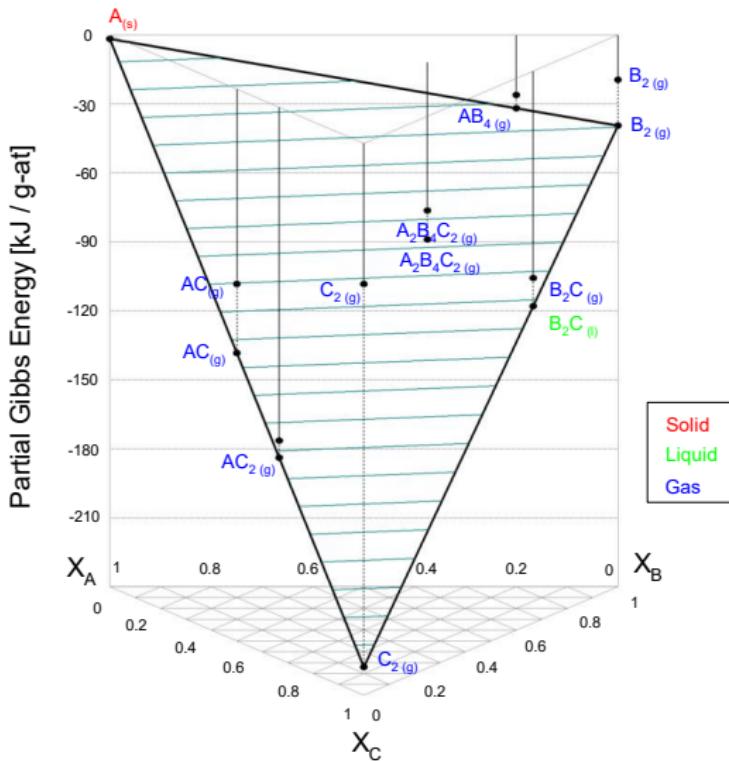
$$\mu_i = \sum_{j=1}^C \nu_{i,j} \Gamma_j$$

Thermodynamic Equilibrium - Sufficient Conditions

Gibbs plane

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

Thermodynamic Equilibrium - Sufficient Conditions



Gibbs Energy Minimisation

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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

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

Constraint

$$F = C - \Phi + 2 + \Xi$$

Optimise

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

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

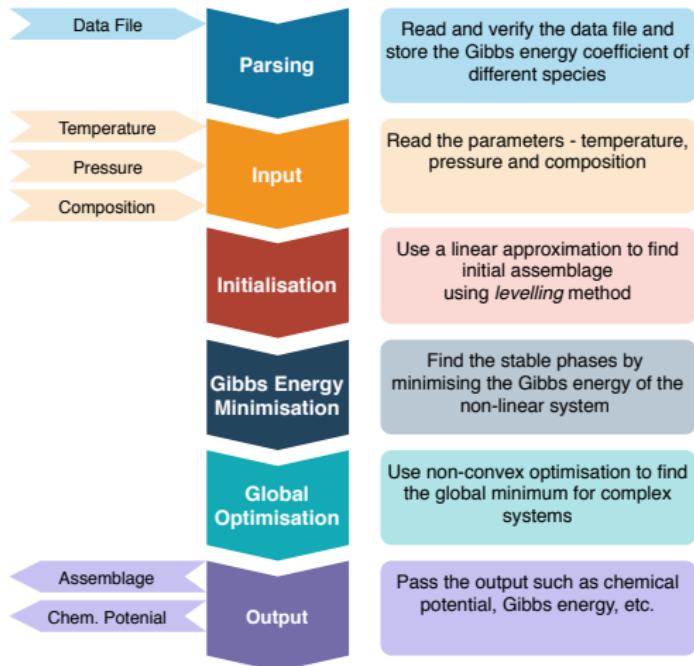
④ Computational Implementation

- Gibbs Energy Minimiser - Overview
- Gibbs Energy Minimiser

⑤ Progress and Timeline

- Current Progress
- Timeline

Computational Structure



Parsing

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

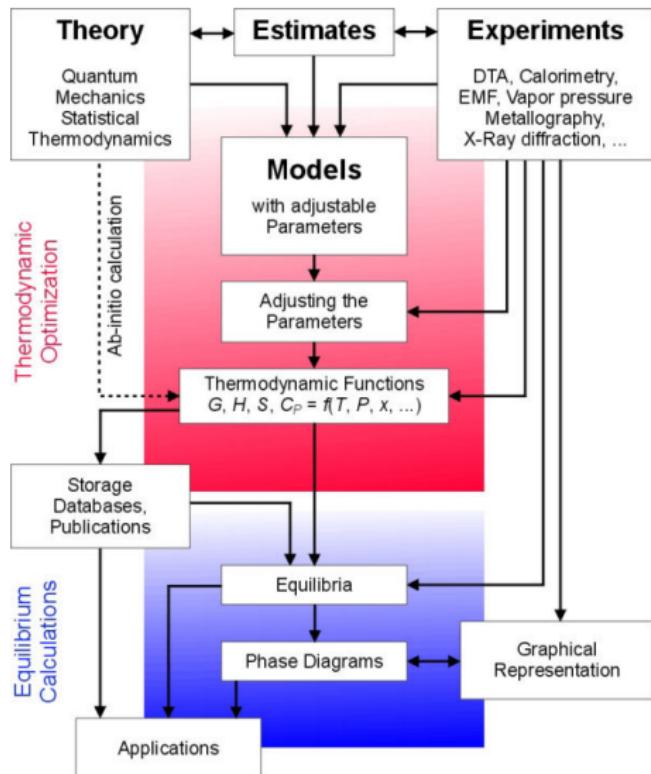
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- Most commonly used formats are ThermoCalc (*.tdb) and ChemSage (*.dat).
- Yellowjacket uses ChemSage (*.dat) format datafiles, which can be generated by the commercial software FactSage.

Parsing



Input

- Temperature, pressure and composition are required at each time step and for each mesh element.
- At each time step MOOSE can provide these inputs to Yellowjacket.

Initialisation

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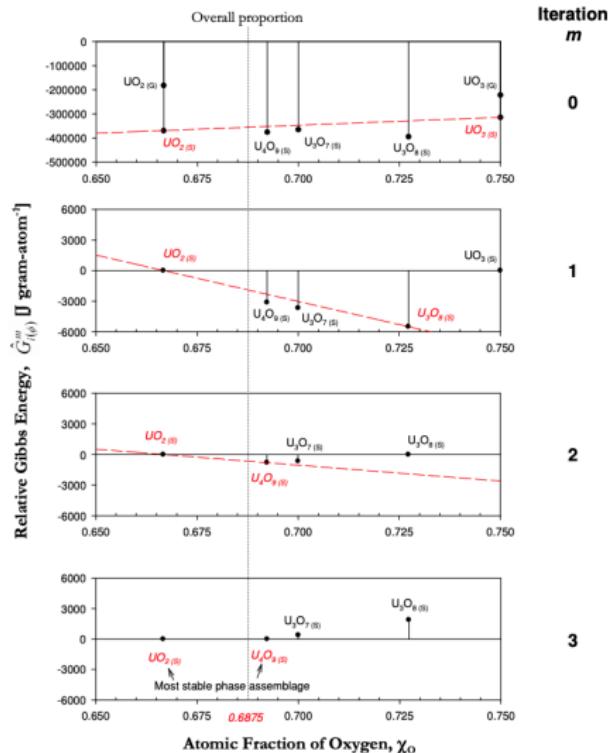
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Initialisation

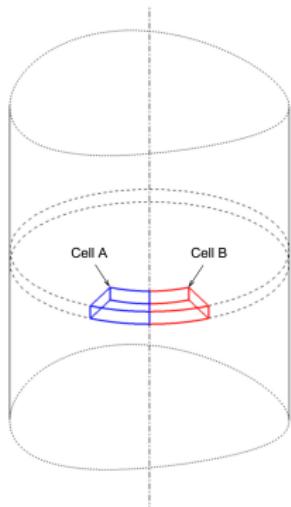
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- *Levelling* is an estimating process developed by Eriksson and Thompson (1989).
- Levelling converts the non-linear optimisation problem into a linear optimisation problem by treating all species and phases as pure separate phases.
- The number of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

Initialisation

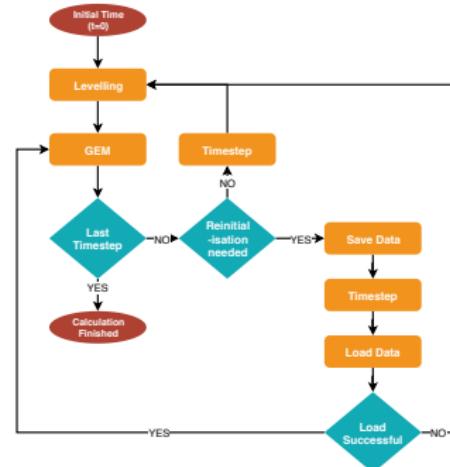


Initialisation

- Initialise using neighbour cells



- Initialise with last time step



Gibbs Energy Minimisation

- Hessian Solver

$$H \cdot \pi = \zeta$$

Gibbs Energy Minimisation

- Hessian Solver

$$\mathbf{H} \cdot \boldsymbol{\pi} = \boldsymbol{\zeta}$$

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

Gibbs Energy Minimisation

- Hessian Solver

$$H \cdot \pi = \zeta$$

$$\pi = \begin{bmatrix} \pi_{j=1}^{m+1} \\ \vdots \\ \pi_{j=E}^{m+1} \\ \pi_{\lambda=1}^{m+1} \\ \vdots \\ \pi_{\lambda=\Lambda}^{m+1} \\ \pi_{\omega=1}^{m+1} \\ \vdots \\ \pi_{\omega=\Omega}^{m+1} \end{bmatrix}$$

Gibbs Energy Minimisation

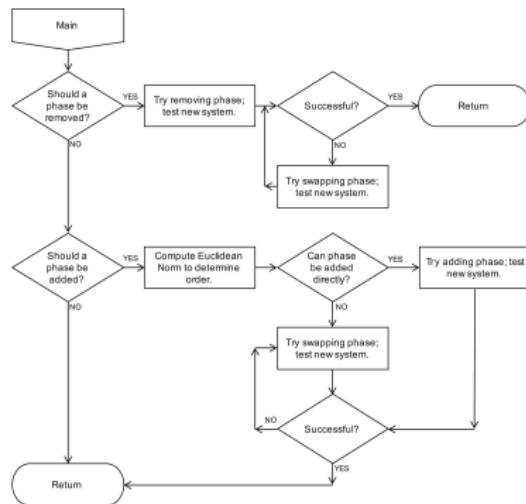
- Hessian Solver

$$\mathbf{H} \cdot \boldsymbol{\pi} = \boldsymbol{\zeta}$$

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

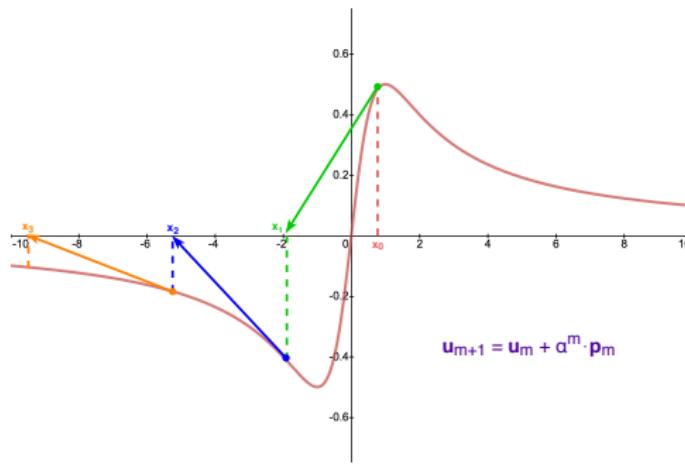
Gibbs Energy Minimisation

- Phase assemblage algorithm



Gibbs Energy Minimisation

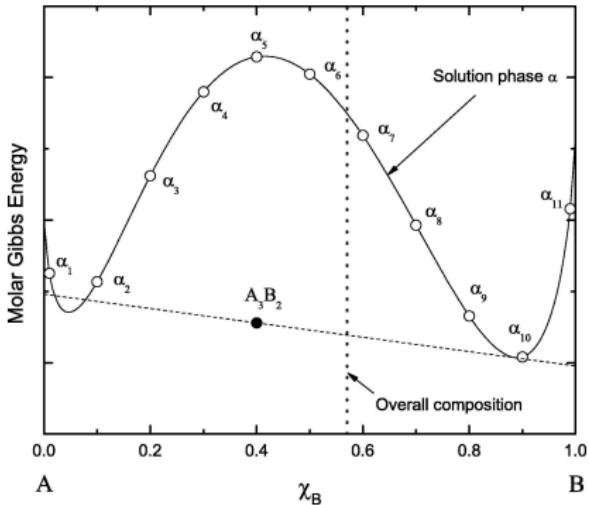
- Line Search algorithms



- Use of Wolfe/Armijo conditions can help avoid divergence.

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.



Global Optimisation

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

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

- 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.

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.

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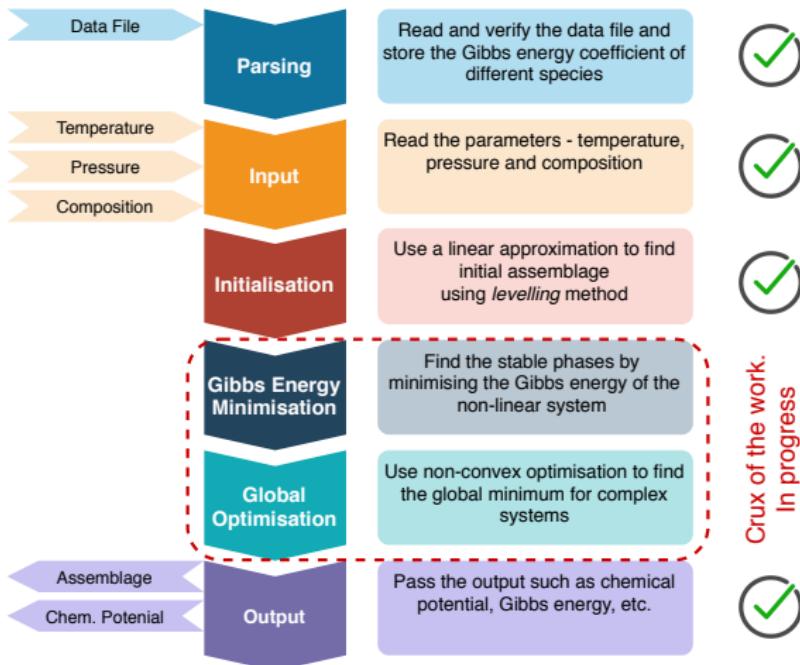
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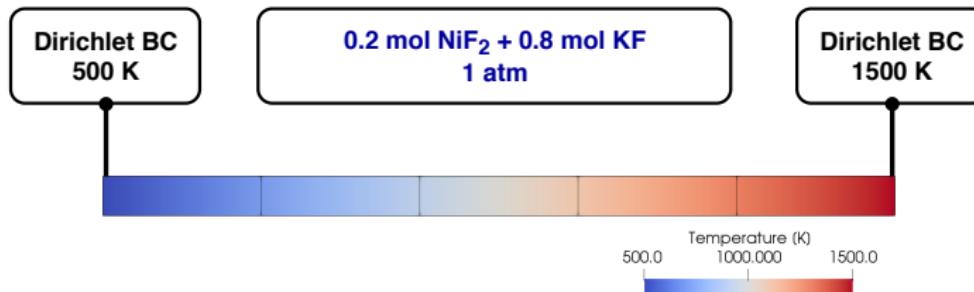
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Current Progress

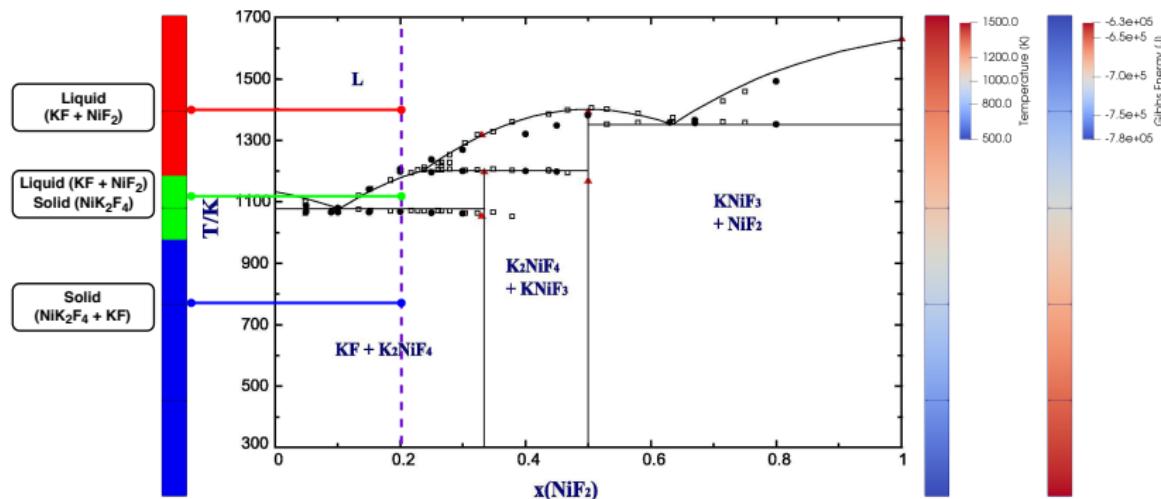


Demonstration Problem

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



Demonstration Problem



Timeline - 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	

Timeline - 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. - Dec. 2019	In progress
Implement non-linear solver for GEM (heterogeneous)	Jan. - Mar. 2020	Planned
Demonstration of non-linear solver capabilities	Mar. - May 2020	Planned
Begin integration of thermodynamic solver with Marmot	Jun. - 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?