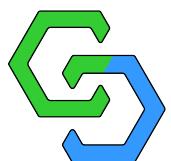


Introduction to ESPEI

Calphad database development and uncertainty quantification

Brandon Bocklund

June 25, 2023



Calphad modeling

Derivatives of Gibbs energy
enthalpy, entropy, heat capacity

Phase equilibrium data
phase boundaries



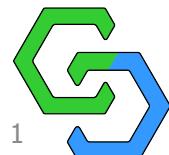
Gibbs Energy of Individual Phases

$$G^\phi(T, P, x_i) = G^{\text{srf}} + G^{\text{cnf}} + G^{\text{phys}} + G^{\text{xs}}$$

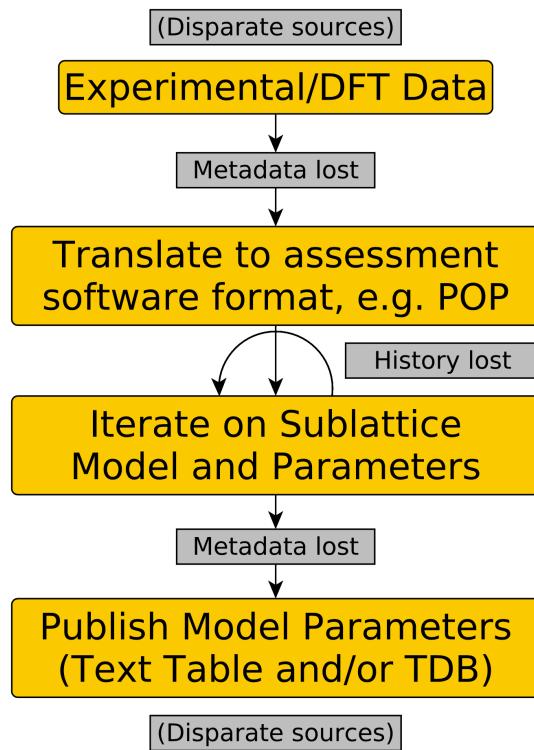
Equilibrium, phase diagrams,
driving forces, physical/chemical properties

Pure elements → Binary → Ternary → Multicomponent

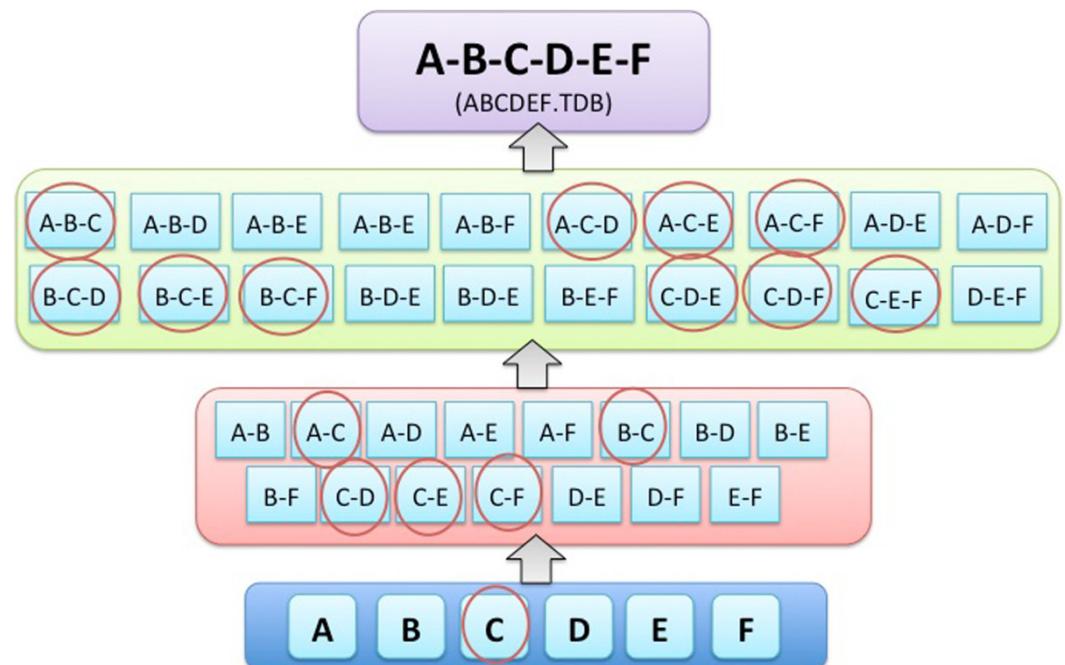
Kaufman & Bernstein: *Computer Calculation of Phase Diagrams* (1970)



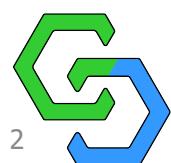
Calphad database development process



Otis, PhD Thesis (2016)

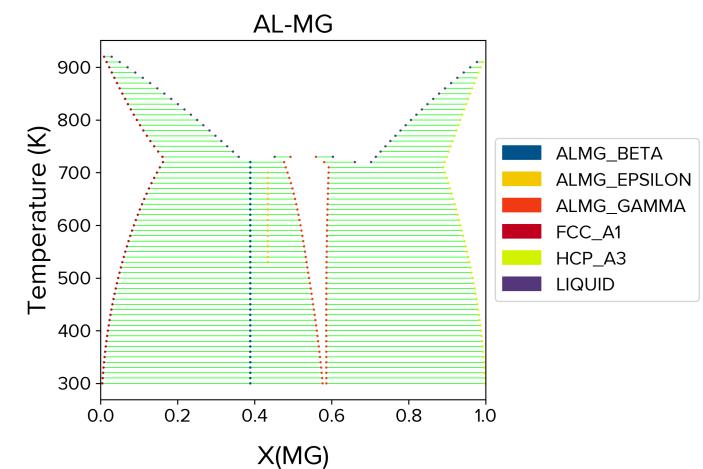
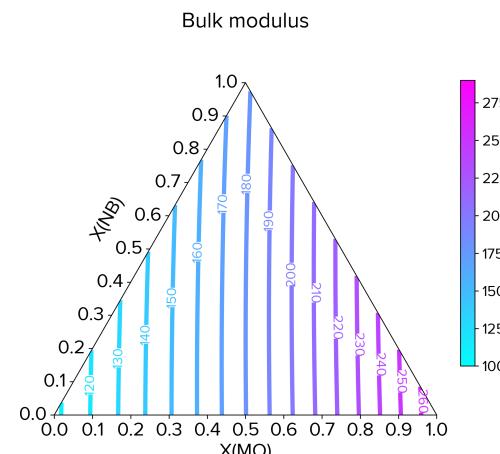
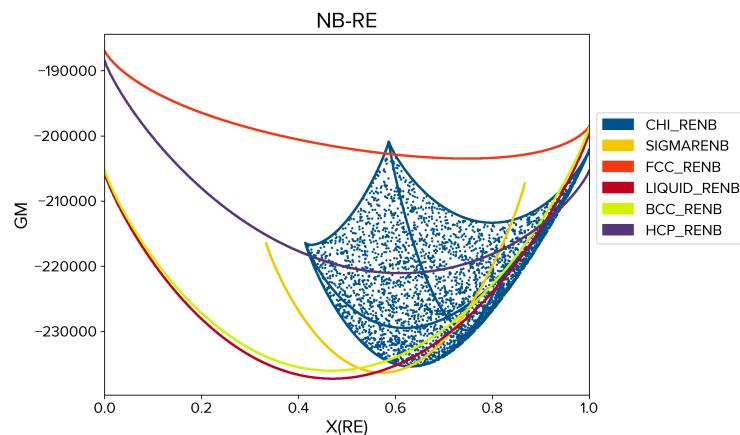


Campbell, IMMI (2014)



pycalphad: open-source Calphad library

- Initially released in April 2015
- Built on and integrated with the scientific Python stack
- Defines Calphad models symbolically using SymPy
- Fast numerical core written in Cython

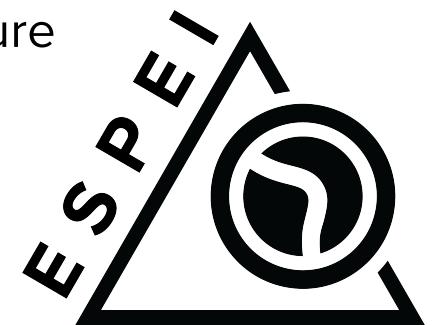


<https://pycalphad.org>

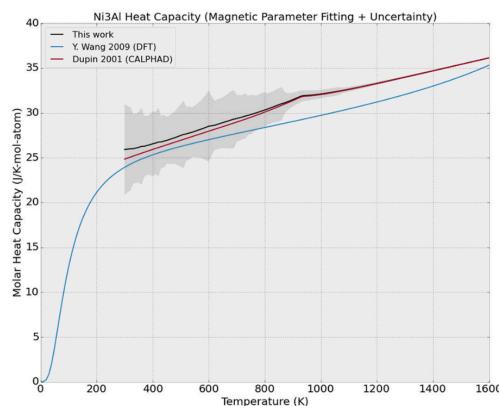
ESPEI: Database Development and UQ

Extensible Self-optimizing Phase Equilibria Infrastructure

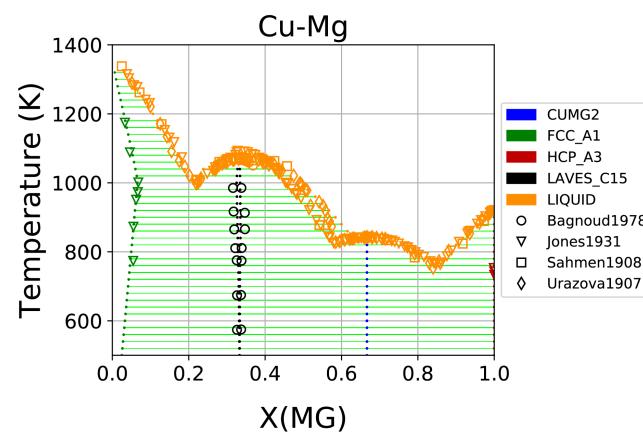
1. Parameterize Calphad models from single phase data
2. MCMC: Optimize and quantify uncertainty
3. Propagate uncertainty to properties



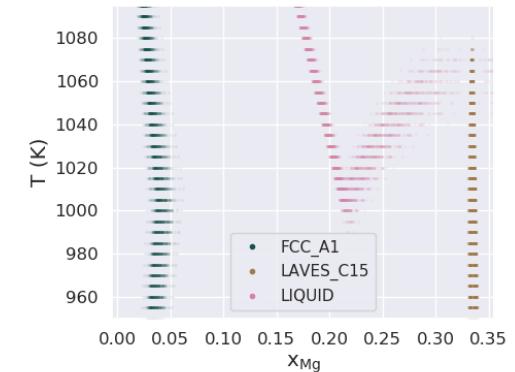
<https://espei.org>



Otis, Liu, JOM (2017)



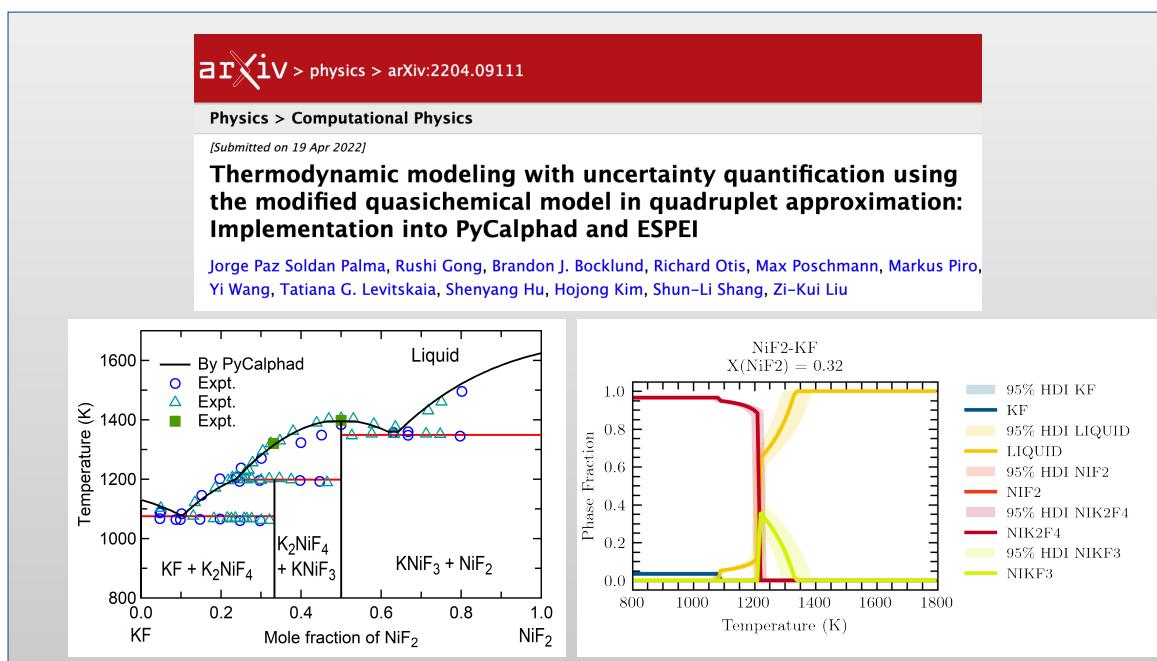
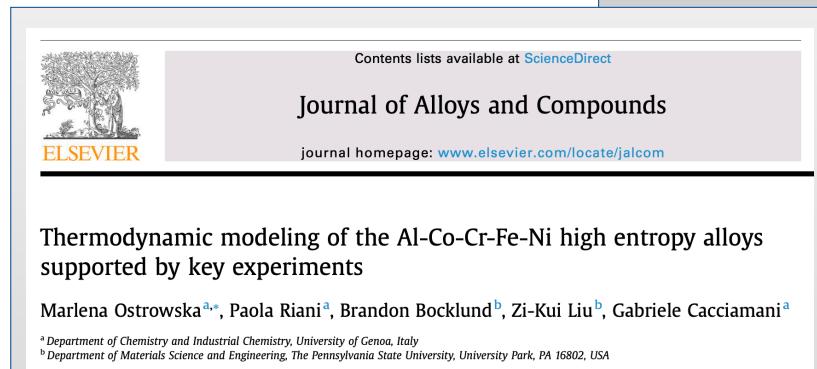
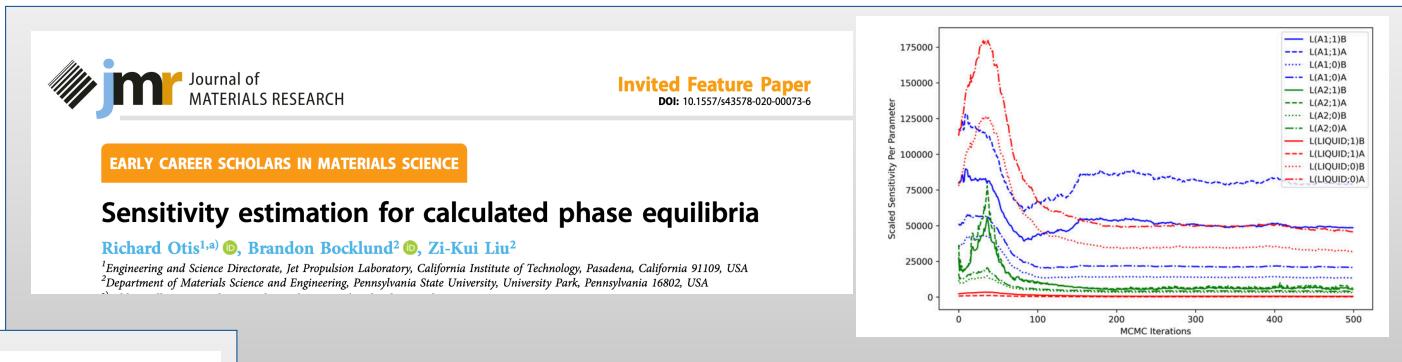
Bocklund, MRS Comm (2019)



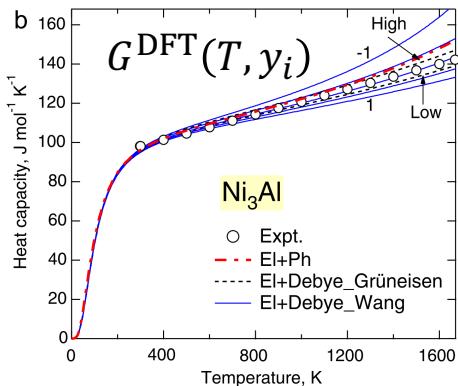
Paulson, Acta Mat. (2019)



Impact of ESPEI



Parameter selection in ESPEI

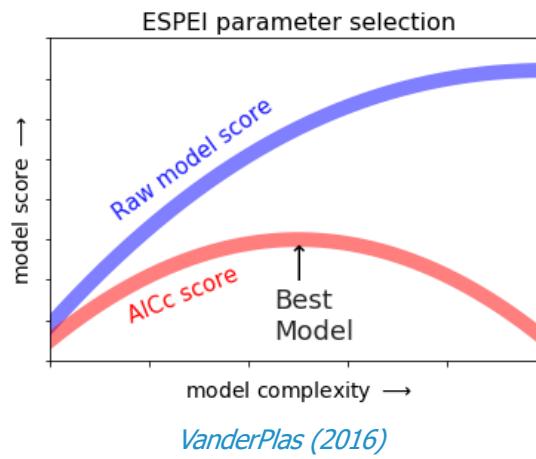


Shang, Comput. Mater. Sci. (2009)

Fit non-equilibrium
thermochemical data
to a functional form



Overfitting prevented with
corrected Akaike
information criterion



Temperature dependence: power expansion

$$G(T) = a + b T + c T \ln T + d T^2 + e T^{-1}$$

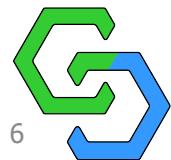
Composition dependence: Redlich-Kister polynomial

$$G^{\text{xs}}(T, y_i) = \sum_{i,j \neq i} y_i y_j (y_i - y_j)^v v_L$$

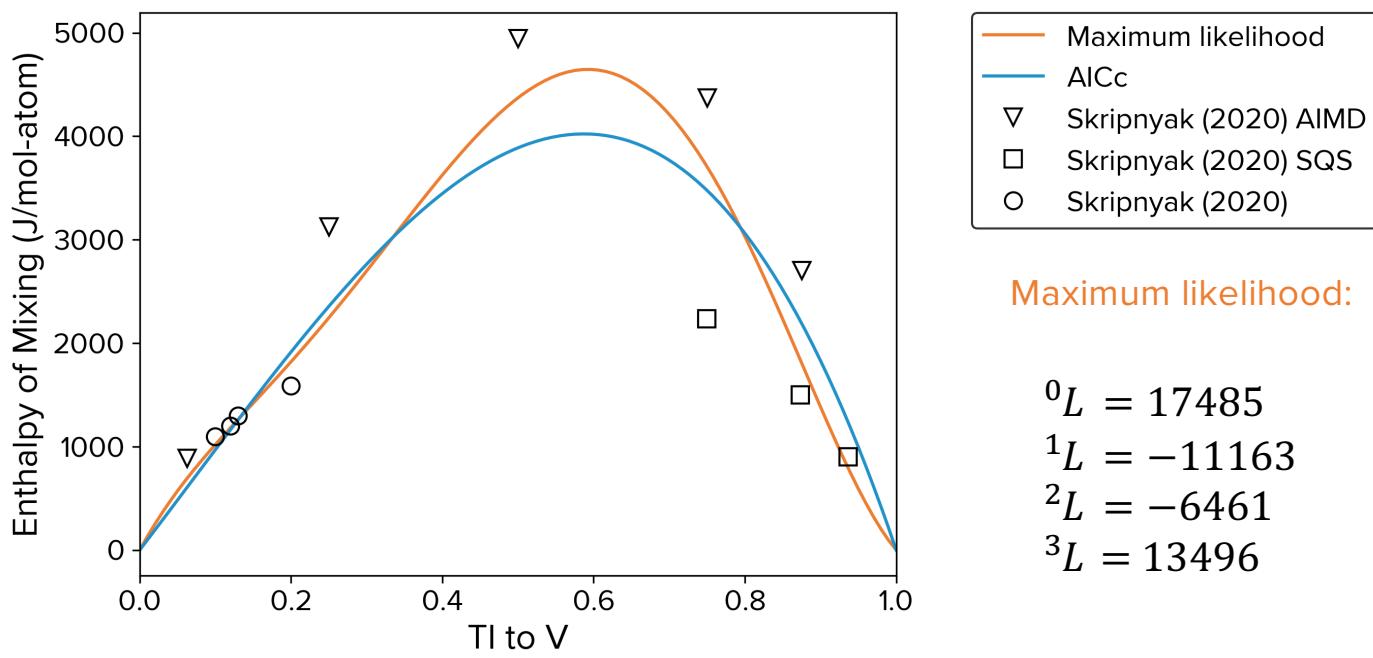
$$v_L(T) = a + b T + \dots$$

$$\text{AICc} = n \ln \frac{\text{RSS}}{n} + 2k + \frac{2k^2 + 2k}{n - k - 1}$$

RSS – Sum of square residuals
 k – # model parameters (model complexity)
 n – # data points



Parameter selection for bcc Ti-V



Maximum likelihood:

$$\begin{aligned} {}^0L &= 17485 \\ {}^1L &= -11163 \\ {}^2L &= -6461 \\ {}^3L &= 13496 \end{aligned}$$

$$\sum_{i,j \neq i} y_i y_j (y_i - y_j)^v v_L$$

AICc:

$$\begin{aligned} {}^0L &= 15552 \\ {}^1L &= -5977 \end{aligned}$$

Interactive Demo

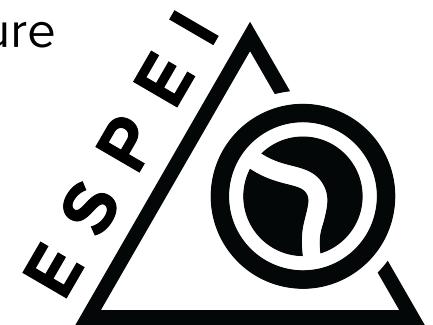
ESPEI Parameter Generation



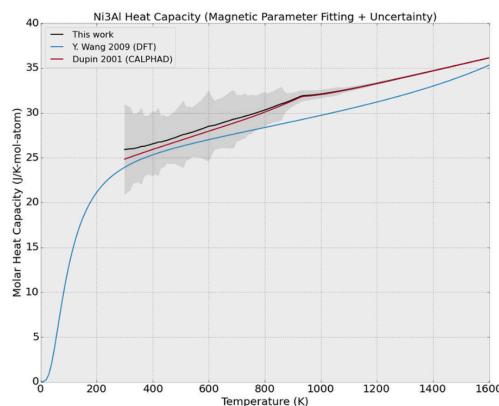
ESPEI: Database Development and UQ

Extensible Self-optimizing Phase Equilibria Infrastructure

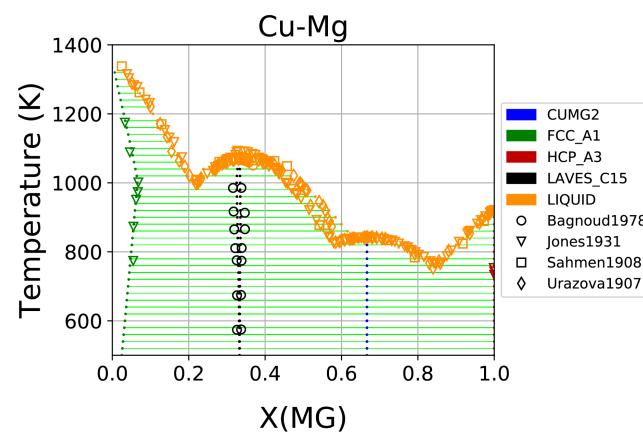
1. Parameterize Calphad models from single phase data
2. MCMC: Optimize and quantify uncertainty
3. Propagate uncertainty to properties



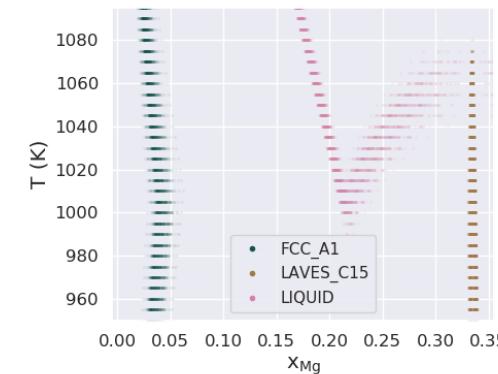
<https://espei.org>



Otis, Liu, JOM (2017)



Bocklund, MRS Comm (2019)



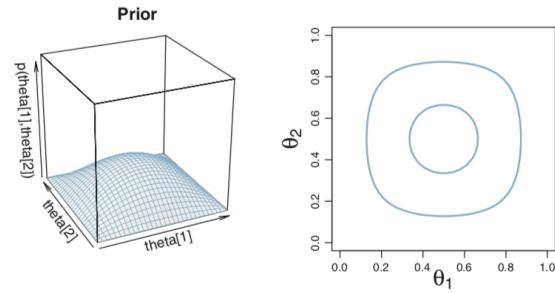
Paulson, Acta Mat. (2019)



MCMC: Bayesian parameter estimation

$$\text{Posterior} \quad \text{Likelihood} \quad \text{Prior}$$
$$\Pr(\boldsymbol{\theta}|\mathbf{D}) = \frac{\Pr(\mathbf{D}|\boldsymbol{\theta}) \Pr(\boldsymbol{\theta})}{\Pr(\mathbf{D})}$$

Data



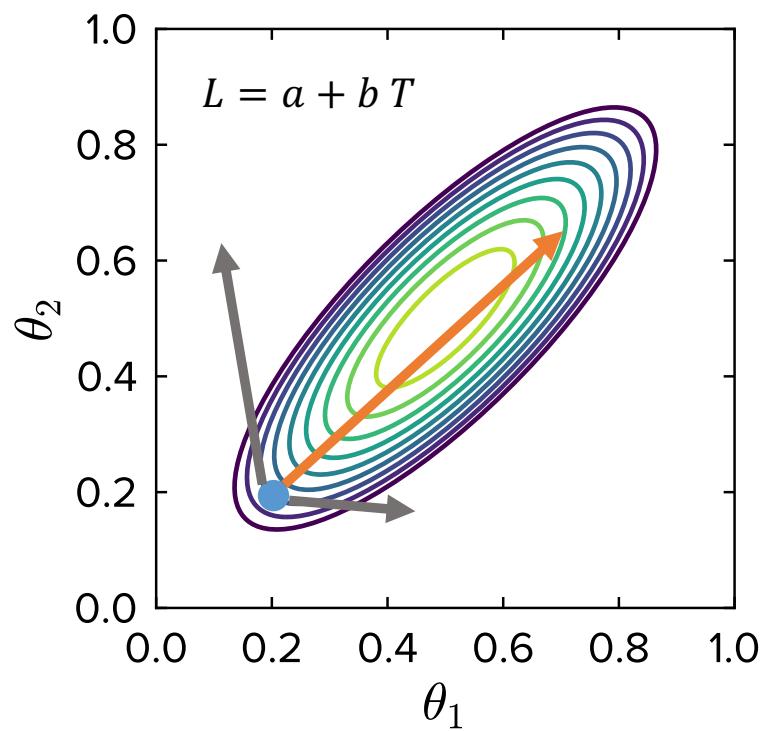
- **Markov chain**
 - Sequence of values that are independent from each other
- **Monte Carlo**
 - Random sampling

Core principle: the probability of a parameter value is proportional to the number of times the Markov chains visits that value

Kruschke, Academic Press (2015)

Ensemble MCMC: efficient exploration of correlated parameter space

Correlated Parameters

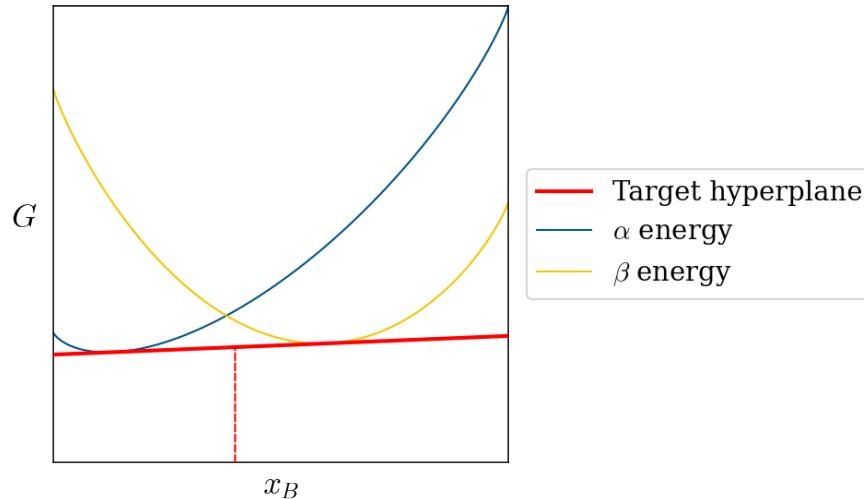


- Use many (an ensemble of) parameter chains simultaneously
 - Proposals are stretched by an affine transformation to a random chain in the ensemble
 - Key property: **affine invariance**
- In ESPEI: the ensemble is generated by multi-variate normal distribution from the initial parameters
 - Mean is at the parameter initial value
 - Standard deviation is a factor of the mean value
 - Wider initial ensemble → better coverage of parameter space, but may be far from the initial local minimum

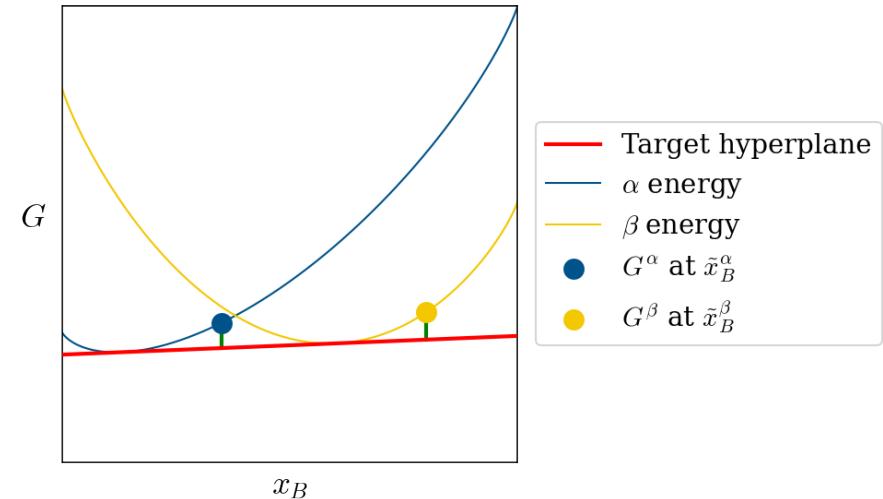
Calculation of phase equilibria error

Goal: Find the parameters that minimize the **driving forces** to the **target hyperplane** defined by the **experimental phase compositions**

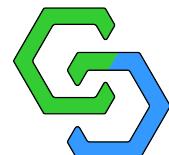
Target hyperplane: \tilde{x} known



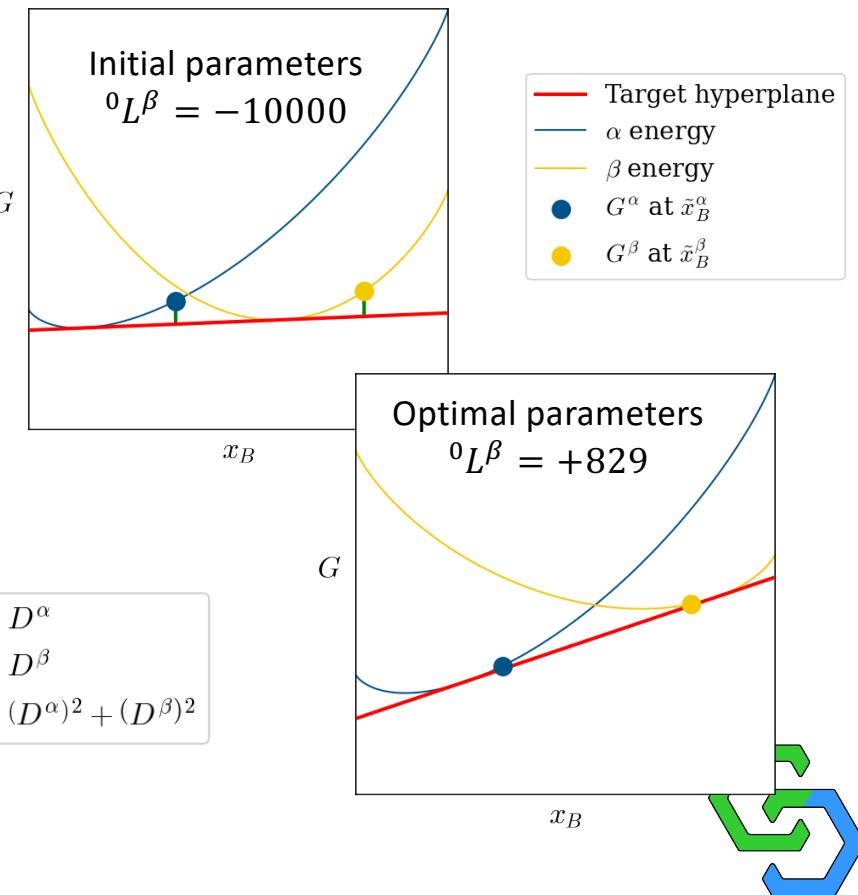
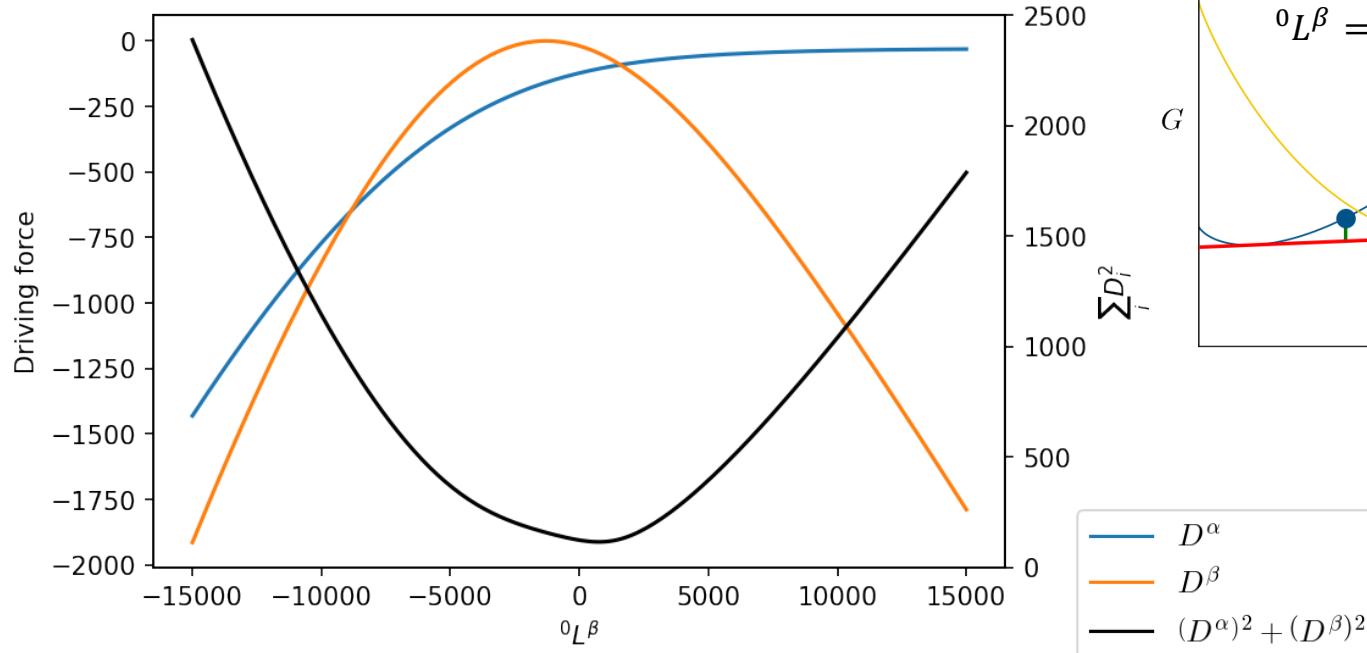
Driving forces: \tilde{x}^ϕ known



Analogous experiment: equilibrated alloy with EPMA-measured phase compositions

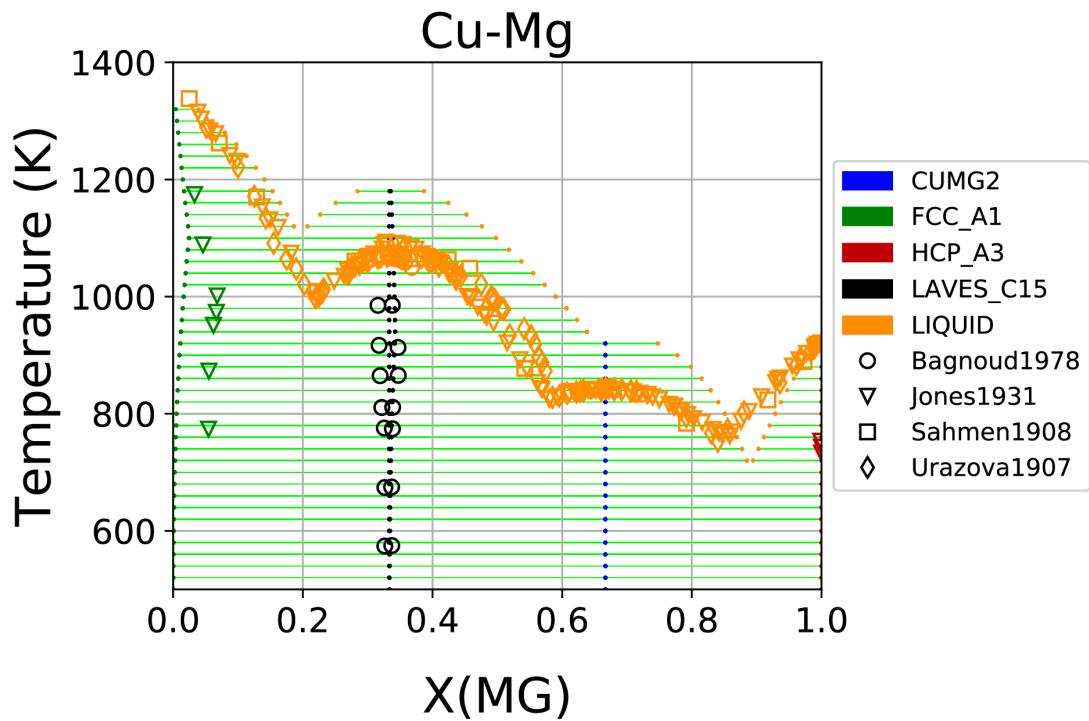


Parameters optimized by minimizing driving forces



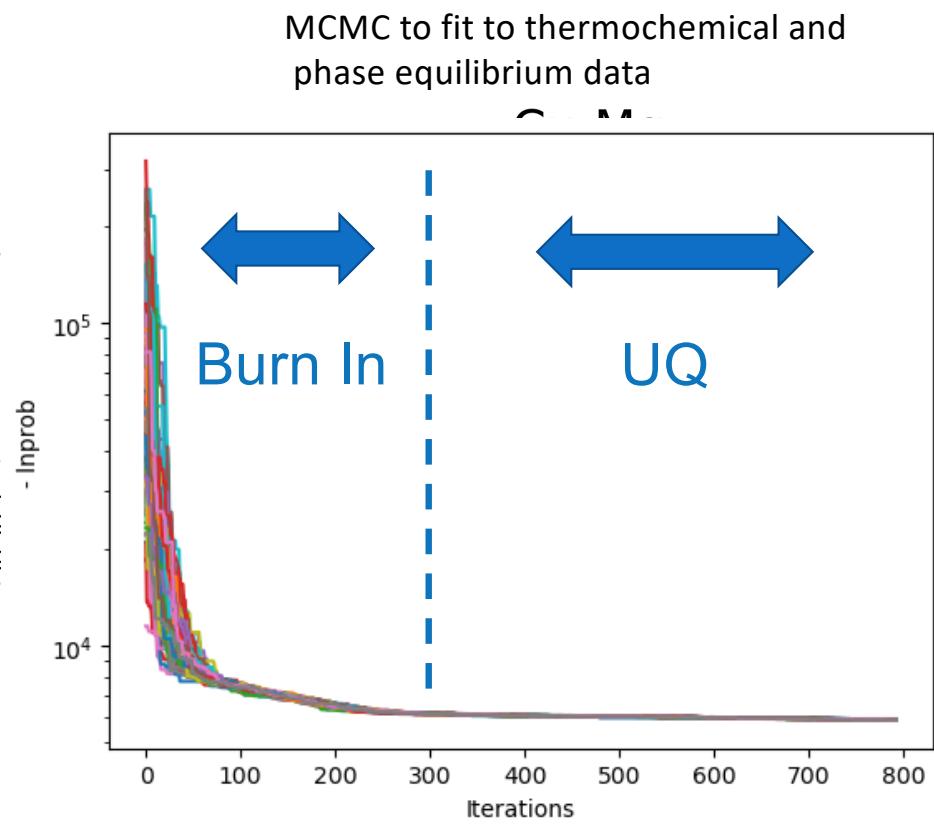
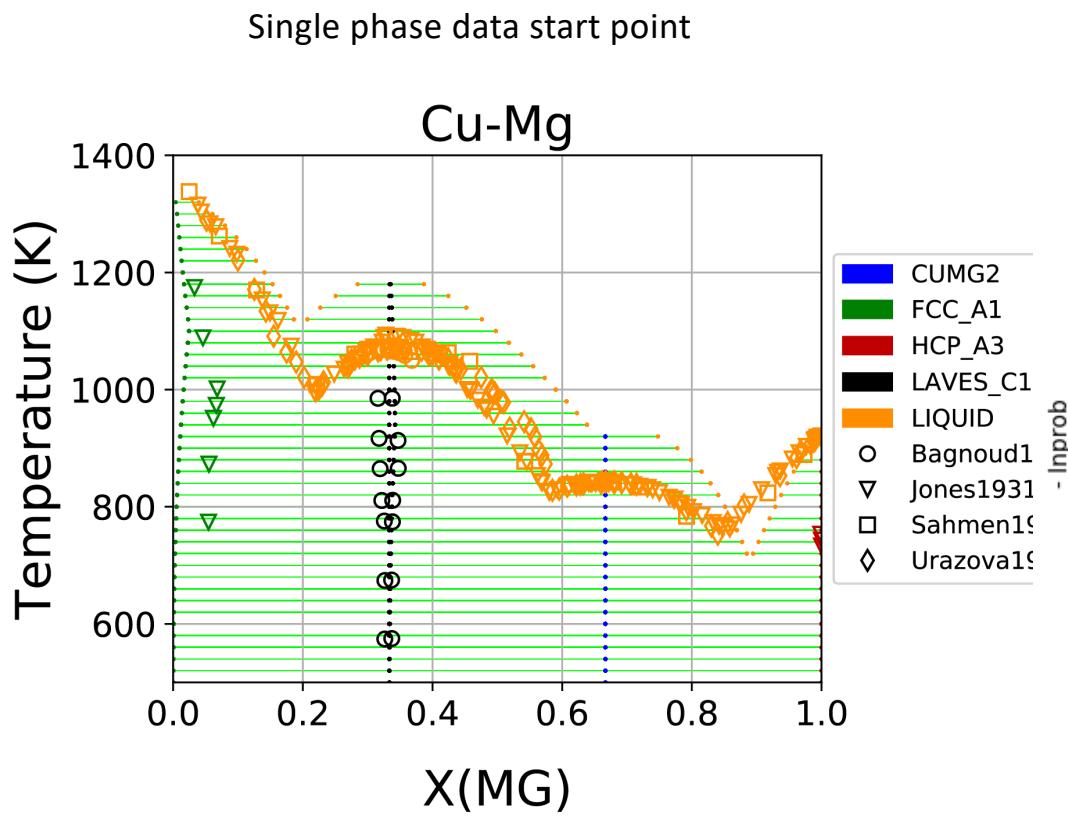
Applying parameter selection to Cu-Mg

Single phase data start point



Bocklund, MRS Comm (2019)

Updating selected parameters with MCMC



Bocklund, MRS Comm (2019)

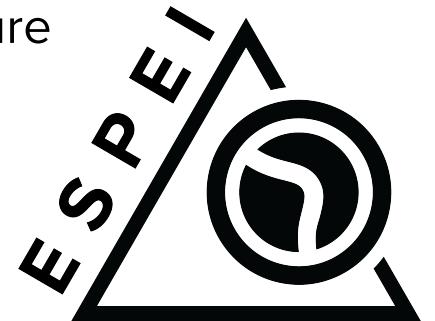
Interactive Demo

Optimization and Uncertainty Quantification

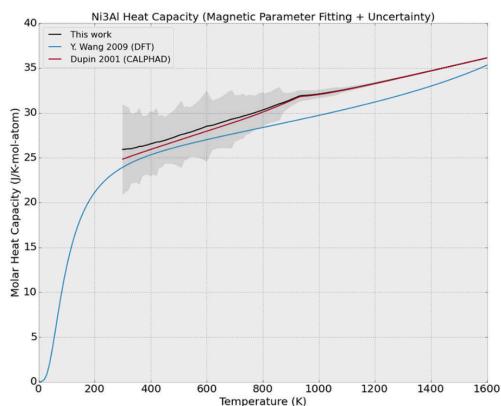
ESPEI: Database Development and UQ

Extensible Self-optimizing Phase Equilibria Infrastructure

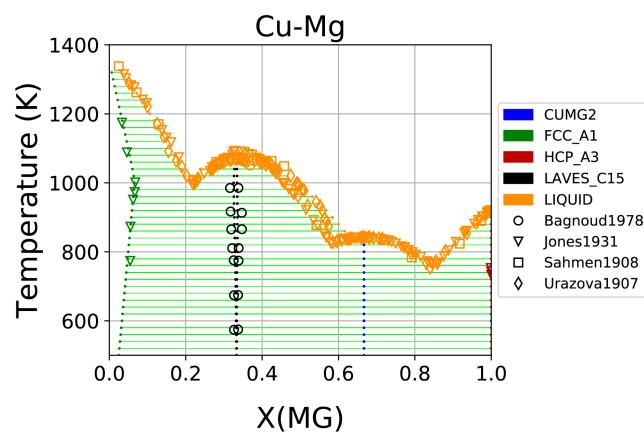
1. Parameterize Calphad models from single phase data
2. MCMC: Optimize and quantify uncertainty
3. Propagate uncertainty to properties



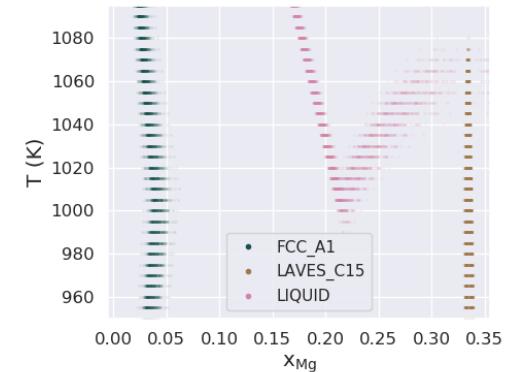
<https://espei.org>



Otis, Liu, JOM (2017)



Bocklund, MRS Comm (2019)



Paulson, Acta Mat. (2019)

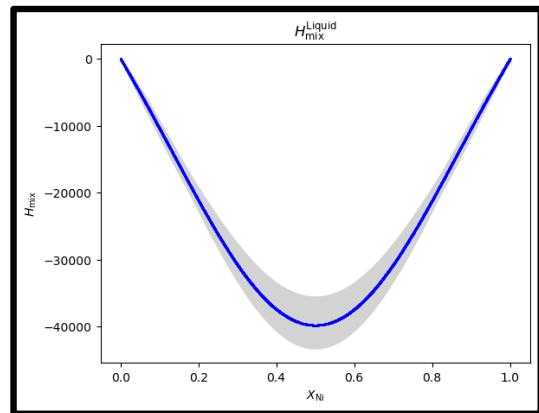


Propagate uncertainty to thermodynamic properties

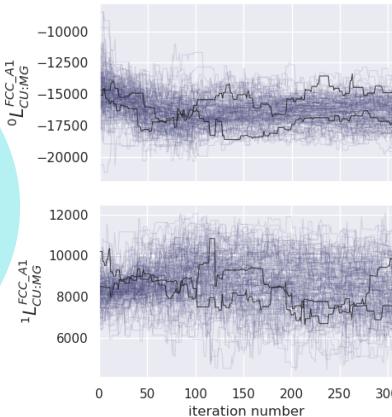
CALPHAD models

```
...
PARAMETER G(FCC_A1,CU;0)    1 GFCCCU#; 10000 N !
PARAMETER G(FCC_A1,MG;0)    1 GFCCMG#; 10000 N !
PARAMETER L(FCC_A1,CU,MG;0) 1 VV0002#; 10000 N !
PARAMETER L(FCC_A1,CU,MG;1) 1 VV0001#; 10000 N !
...
```

Superimposed CALPHAD predictions: Cu-Mg



Parameter distribution
samples from MCMC



arXiv:1901.10510

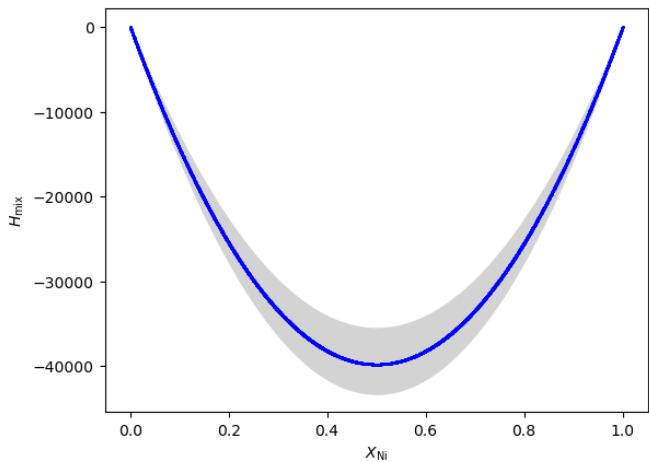
Paulson, Acta Mat. (2019)

18

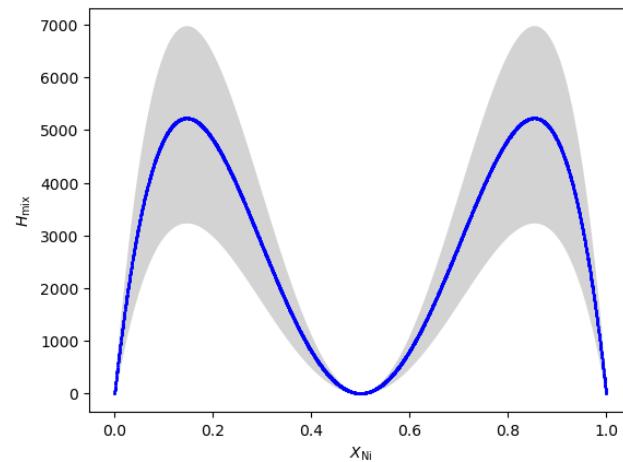


Uncertainty quantification in liquid interaction parameters

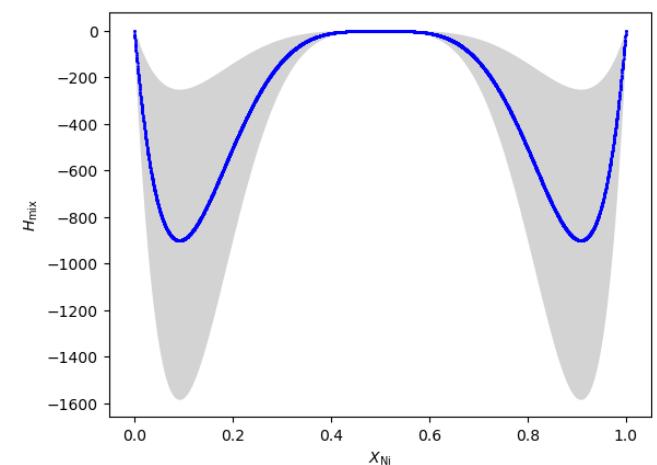
0_L^{liquid}



1_L^{liquid}

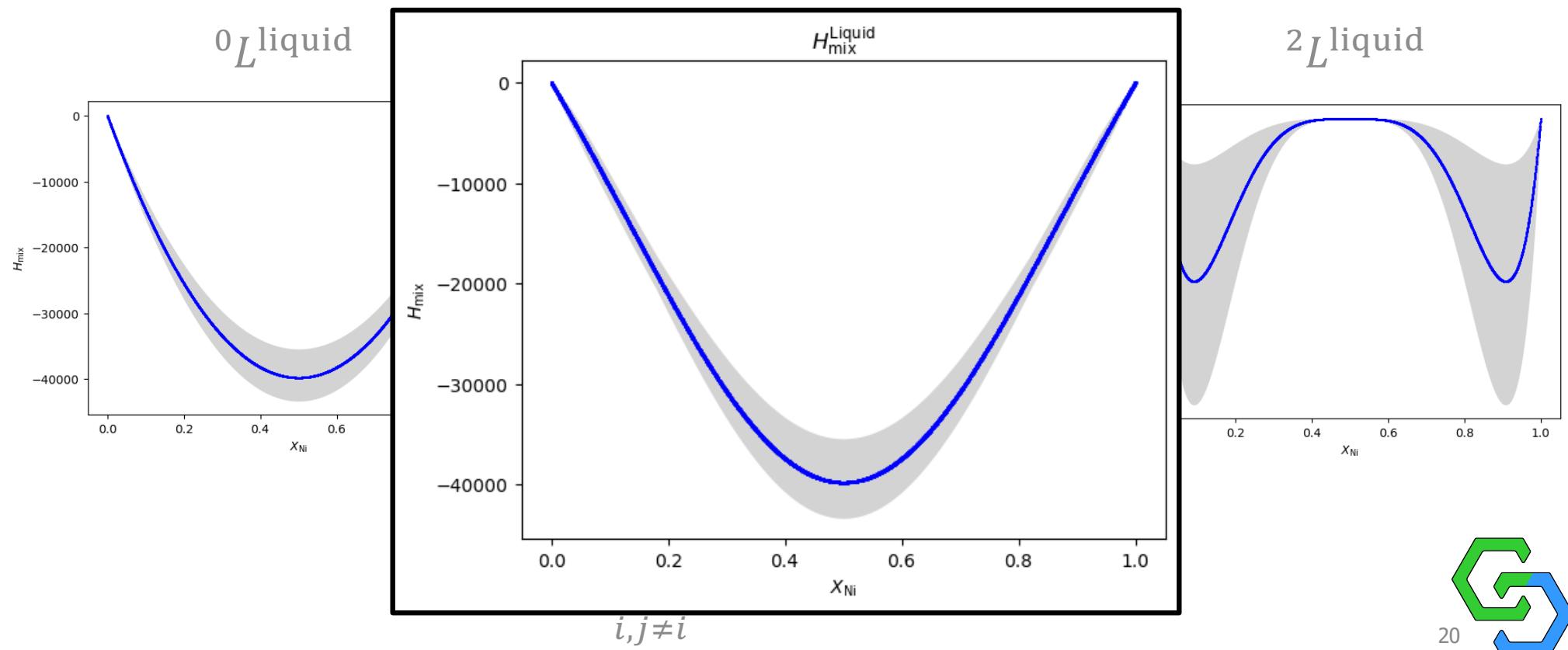


2_L^{liquid}

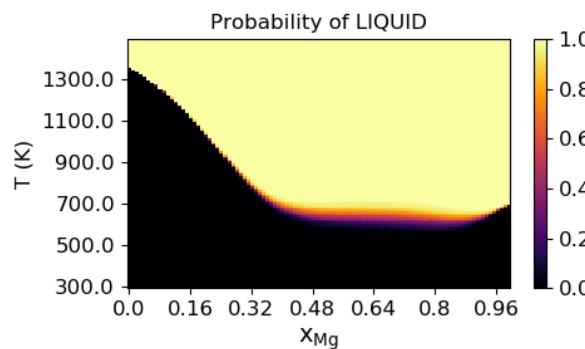
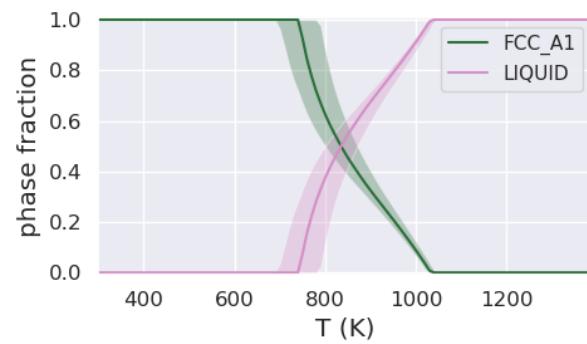
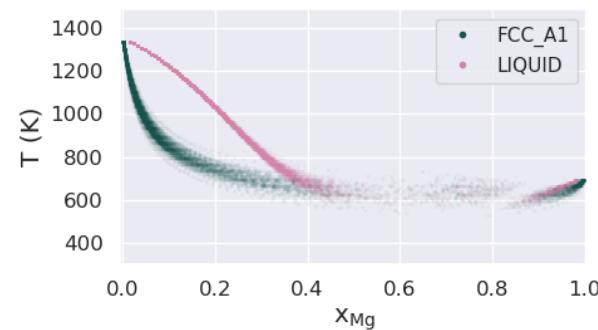
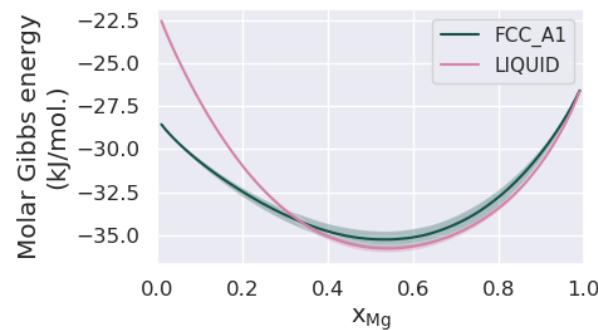


$$\sum_{i,j \neq i} x_i x_j (x_i - x_j)^\nu \nu L$$

Uncertainty quantification in liquid interaction parameters

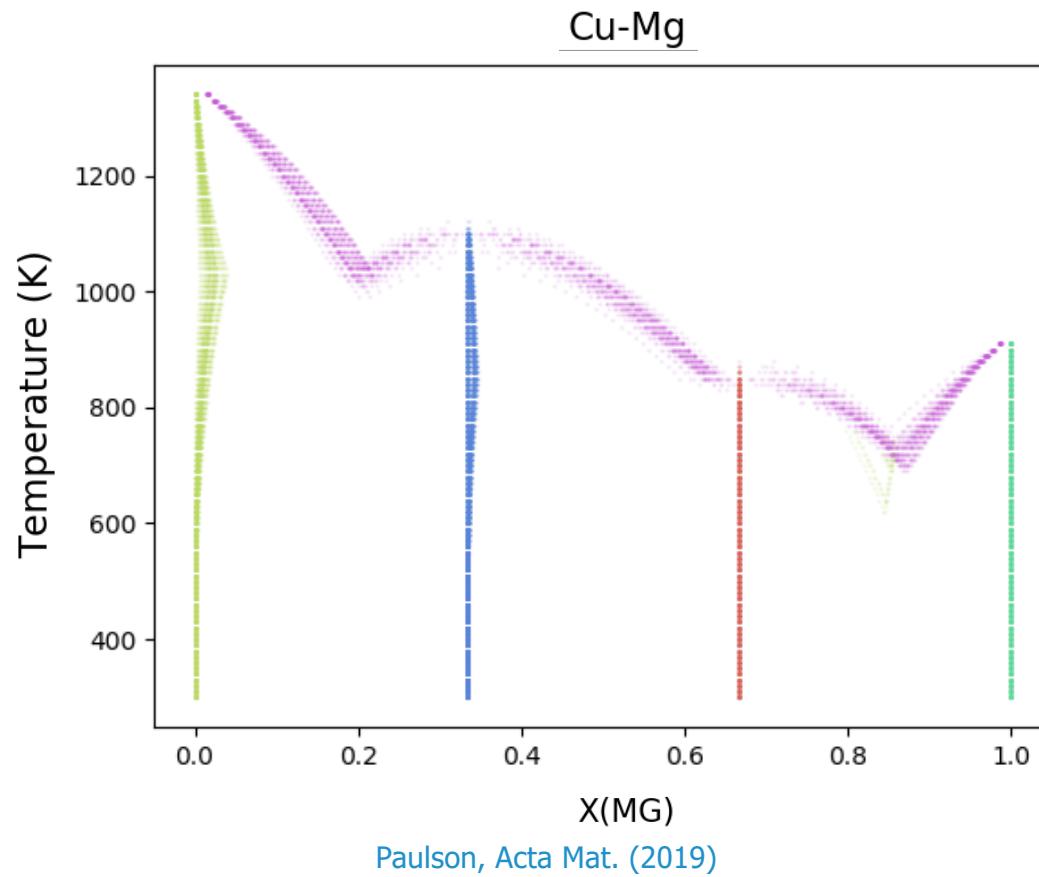


Propagation of uncertainty to calculated properties and phase diagrams

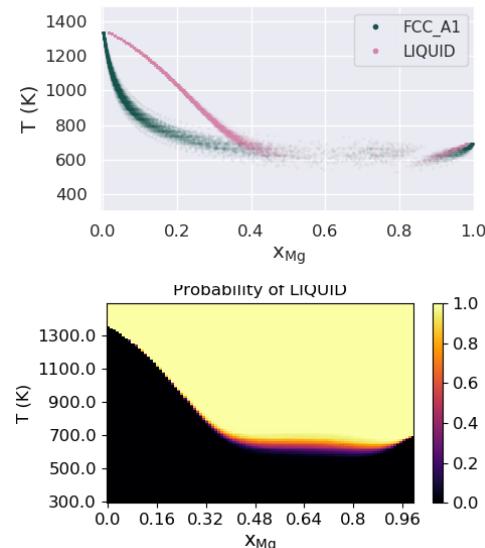
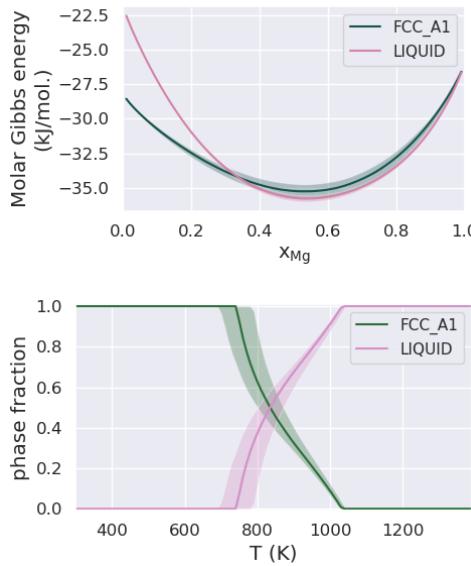


Paulson, Acta Mat. (2019)

Propagation of uncertainty to calculated properties and phase diagrams



PDUQ: Phase Diagram Uncertainty Quantification package



Noah Paulson

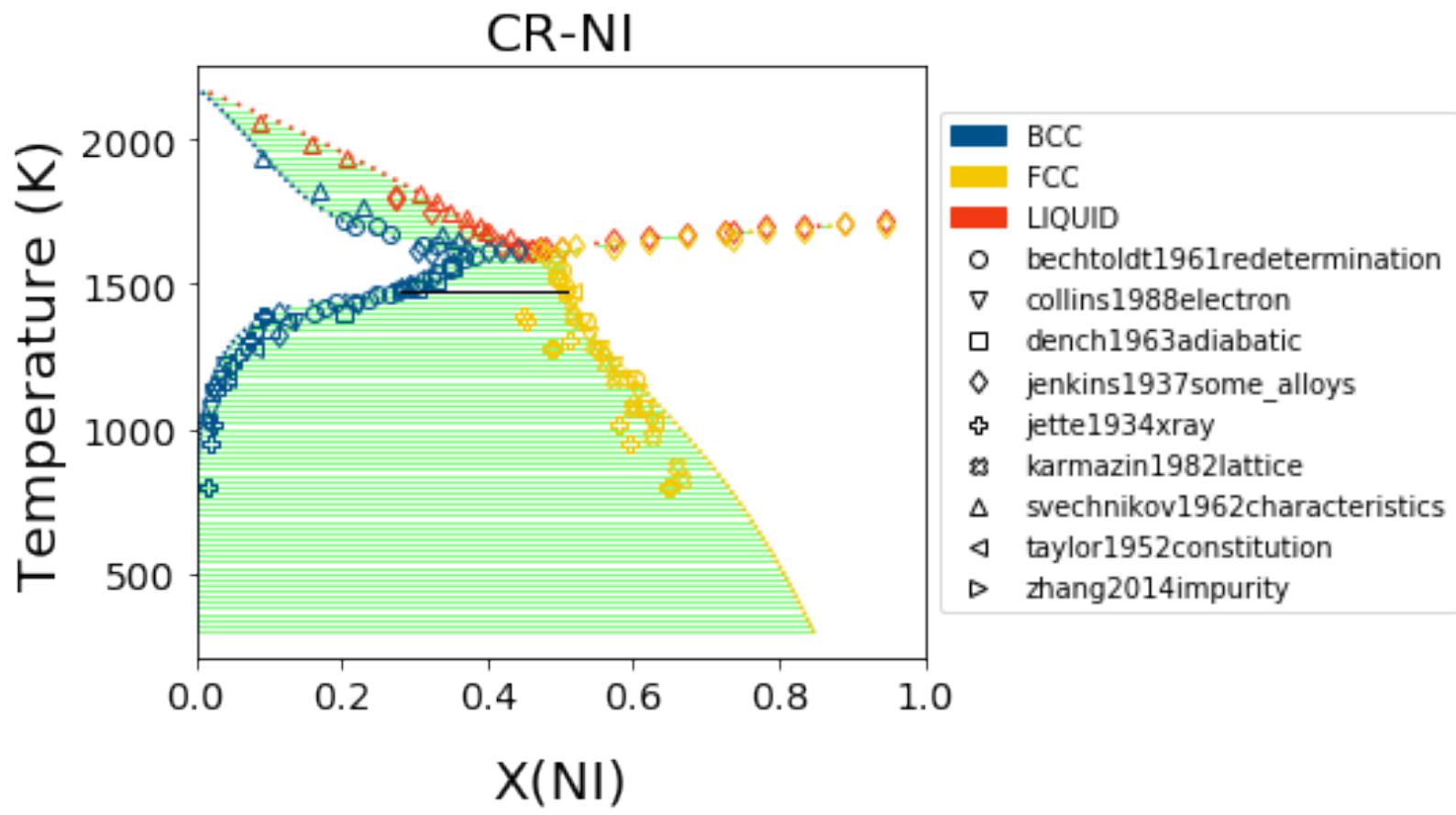


Marius Stan

Argonne National Lab

<https://pduq.readthedocs.io>

Cr-Ni Phase Diagram (2000 MCMC iterations)



<https://doi.org/10.1557/jmr.2020.269>

Sensitivity estimation for calculated phase equilibria

Richard Otis^{1,a)} , Brandon Bocklund² , Zi-Kui Liu²

¹*Engineering and Science Directorate, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA*

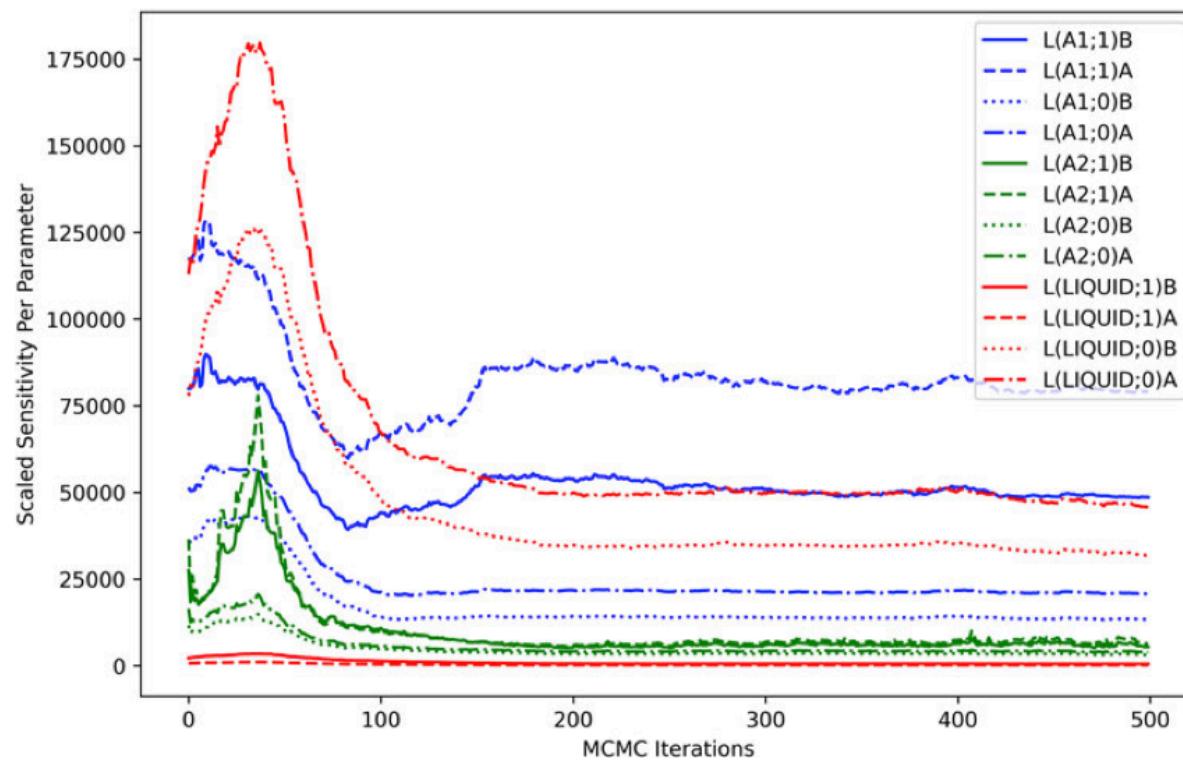
²*Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA*

^{a)}Address all correspondence to this author. e-mail: richard.otis@jpl.nasa.gov

Received: 29 June 2020; accepted: 4 September 2020

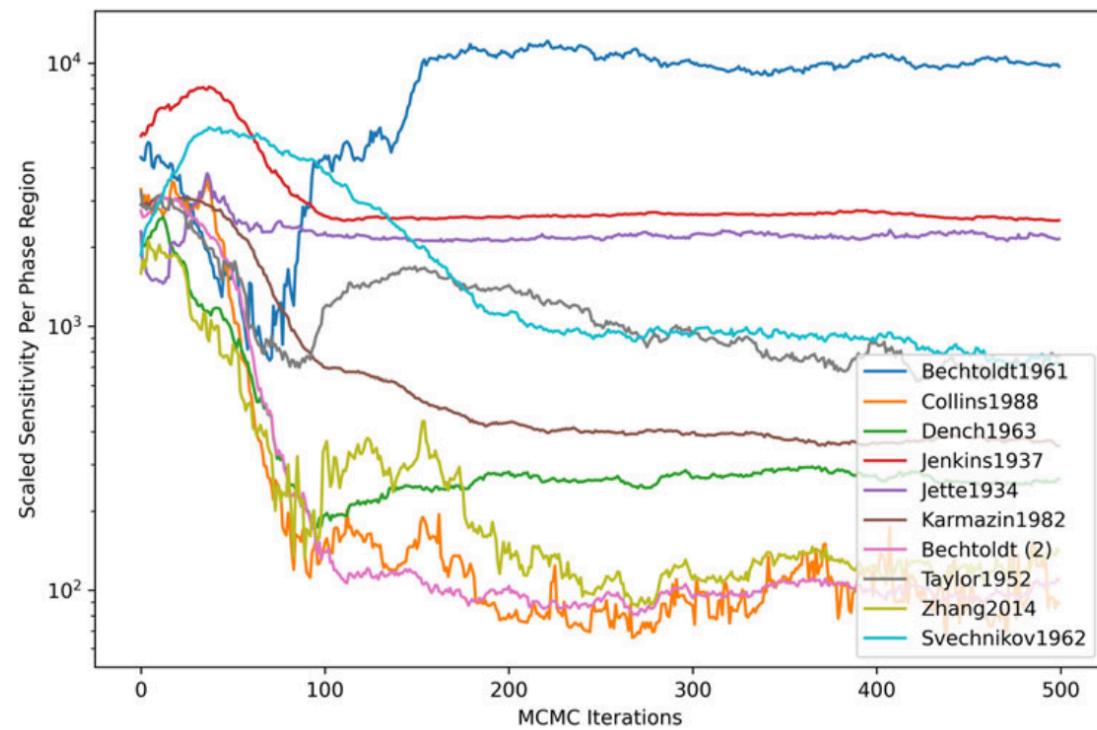
The development of a consistent framework for Calphad model sensitivity is necessary for the rational reduction of uncertainty via new models and experiments. In the present work, a sensitivity theory for Calphad was developed, and a closed-form expression for the log-likelihood gradient and Hessian of a multi-phase equilibrium measurement was presented. The inherent locality of the defined sensitivity metric was mitigated through the use of Monte Carlo averaging. A case study of the Cr–Ni system was used to demonstrate visualizations and analyses enabled by the developed theory. Criteria based on the classical Cramér–Rao bound were shown to be a useful diagnostic in assessing the accuracy of parameter covariance estimates from Markov Chain Monte Carlo. The developed sensitivity framework was applied to estimate the statistical value of phase equilibria measurements in comparison with thermochemical measurements, with implications for Calphad model uncertainty reduction.

Cr-Ni Parameter Sensitivity



Otis, JMR (2020)

Cr-Ni Dataset Sensitivity



Otis, JMR (2020)

Interactive Demo

Uncertainty Propagation



Summary of Notable Features

- Parameter generation
 - Generate multicomponent CEF models with Redlich-Kister polynomials from thermochemical data
 - Select optimal model forms based on statistical information criteria
- MCMC optimization, UQ, and UP
 - Optimize and quantify uncertainty for any PyCalphad model
 - Software infrastructure designed to be extendable to new types of data and different optimization and UQ backends
 - HPC capable
- Command line interface and interactive Python API are supported

Getting help

- PyCalphad

- <https://pycalphad.org>
- Gitter channel (chat)
 - <https://gitter.im/pycalphad/pycalphad>
- GitHub Discussions (forums)
 - <https://github.com/pycalphad/pycalphad/discussions>

- ESPEI

- <https://espei.org>
- Gitter channel (chat)
 - <https://gitter.im/PhasesResearchLab/ESPEI>
- GitHub Discussions (forums)
 - <https://github.com/phasesresearchlab/espei/discussions>





Materials
Genome
Foundation

