Uncertainty Propagation in Calphad Calculations

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Background

Calculation of Phase Diagrams (CalPhad) is a method of using thermodynamic models obtained from experimental data to perform thermodynamic calculations. It has been a proven method integral to reducing the time and resources required for developing alloys in research and industry.[1] The next step to advancing this methodology is to account for the inconsistency or lack of data when assessing thermodynamic systems.[2] As proof of concept, a generalized framework made in Python was implemented to perform equilibrium calculations and handle model uncertainty. This framework includes the storage and handling of elemental and phase data, and the implementation of Newton's method to perform Gibbs free energy minimization to create step and phase diagrams and determine the confidence intervals of the results. The Mg-Si system was assessed using a Bayesian approach as a case study for this framework.

Objective

To produce a general framework to perform thermodynamic calculations using the CalPhaD method and propagate uncertainty through the results of these calculations

CalPhaD Modeling

Thermodynamic modeling consists of modeling both the pure elements (as reference states) and the phases. For the pure elements, the Gibbs free energy comes from a temperature, pressure and magnetic contribution, with the model parameters obtained from the STGE database.[3, 4] For phases, the Gibbs free energy comes from a reference, ideal mixing and excess mixing contribution. For example, the typical model for a solid solution phase is given in equation 3.[3]

$$G_A = G_{A,Temp} + G_{A,Pres} + G_{A,Mag} \quad (1) \qquad G_M^{\alpha} = G_{ref} + G_{ideal} + G_{excess} \quad (2)$$

$$G_M^{\alpha} = \sum_A x_A G_A + RT \sum_A x_A \ln(x_A) + \sum_i \sum_j x_i x_j \sum_n (x_i - x_j)^n \quad (3)$$

Minimization Procedure

At equilibrium, the Gibbs free energy of a system is at its lowest. Therefore, to perform equilibrium calculations, one must find the minimum of the Gibbs free energy subjected to mass balance, charge balance and summation constraints. This leads to the objective function in equation 4. To minimize the Gibbs free energy (G), the system is first sampled to find starting points, after which, the Newton-Raphson method is used to find the solution.[5]

$$minimize\ L = \sum_{\alpha} n^{\alpha} G_M^{\alpha} + \sum_A \mu_A \left(N_A - \sum_{\alpha} n^{\alpha} M_A^{\alpha} \right) + \sum_{\alpha} \sum_s \lambda^{\alpha,s} \left(1 - \sum_A y_A^{\alpha,s}\right) \quad (4)$$

$$\frac{\partial L}{\partial y_i^{\alpha,s}} = n^{\alpha} G_M^{\alpha} - \sum_A \mu_A n^{\alpha} \frac{\partial M_A^{\alpha}}{\partial y_i^{\alpha,s}} - \lambda^{\alpha,s} = 0 \quad (5) \qquad \frac{\partial L}{\partial n^{\alpha}} = G_M^{\alpha} - \sum_A \mu_A M_A^{\alpha} = 0 \quad (6)$$

$$\frac{\partial L}{\partial \lambda^{\alpha,s}} = 1 - \sum_A y_A^{\alpha,s} = 0 \quad (7) \qquad \frac{\partial L}{\partial \mu_A} = N_A - \sum_{\alpha} n^{\alpha} M_A^{\alpha} = 0 \quad (8)$$

$$\frac{\partial L}{\partial T} = \sum_{\alpha} n^{\alpha} \frac{\partial G_M^{\alpha}}{\partial T} = 0 \quad (9)$$

Bayesian Regression

To retain the uncertainty of the model parameters, a Bayesian approach was used to assess the Mg-Si system. A previous assessment of the Mg-Si system was used as the prior.[6] The posterior was sampled using a Monte-Carlo Markov Chain (MCMC) generated using the Metropolis Hastings algorithm. The MCMC was used the generate the average model parameters along with their covariance matrix.

$$P(Model \mid Data) = \frac{P(Data \mid Model)\, P(Model)}{P(Data)} \quad (10)$$

Uncertainty Propagation

Once the results are calculated using the minimization procedure, confidence intervals for the results can be calculated from the covariance matrix by the procedure proposed by Malakhov.[7]

$$\begin{aligned} f_1(z_1, z_2, \ldots, z_N; \vec{C}) &= 0 \\ f_2(z_1, z_2, \ldots, z_N; \vec{C}) &= 0 \\ &\vdots \\ f_N(z_1, z_2, \ldots, z_N; \vec{C}) &= 0 \end{aligned} \quad (11)$$

$$CI(z_i) = \begin{bmatrix} \frac{\partial z_i}{\partial C_1} & \frac{\partial z_i}{\partial C_2} & \ldots & \frac{\partial z_i}{\partial C_M} \end{bmatrix} \times \boldsymbol{cov}(\vec{C}) \times \begin{bmatrix} \frac{\partial z_i}{\partial C_1} \\ \frac{\partial z_i}{\partial C_2} \\ \vdots \\ \frac{\partial z_i}{\partial C_M} \end{bmatrix} \quad (12)$$

$$\begin{bmatrix} \frac{\partial f_1}{\partial z_1} & \cdots & \frac{\partial f_1}{\partial z_N} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_N}{\partial z_1} & \cdots & \frac{\partial f_N}{\partial z_N} \end{bmatrix} \begin{bmatrix} \frac{\partial z_1}{\partial C_j} \\ \vdots \\ \frac{\partial z_N}{\partial C_j} \end{bmatrix} = \begin{bmatrix} -\frac{\partial f_1}{\partial C_j} \\ \vdots \\ -\frac{\partial f_N}{\partial C_j} \end{bmatrix} \quad (13)$$

Results

Table 1: Model parameters obtained from MCMC

La0Liq	-73604.1
Lb0Liq	27.32199
La1Liq	-29986.9
Lb1Liq	21.41179
La2Liq	44419.32
Lb2Liq	-28.3432
La0HCP	-7150.88
Lb0HCP	0.894044
aMG2SI	-64808.4
bMG2SI	14.86437

Table 2: Covariance matrix of model parameters obtained from MCMC

	La0Liq	Lb0Liq	La1Liq	Lb1Liq	La2Liq	Lb2Liq	La0HCP	Lb0HCP	aMG2SI	bMG2SI
La0Liq	253292.2									
Lb0Liq	5.663641	0.030792								
La1Liq	-1783.33	0.30823	40829.38							
Lb1Liq	4.858458	0.001248	0.576773	0.022908						
La2Liq	4398.62	1.398977	-2827.86	-0.70703	99707.89					
Lb2Liq	-10.1021	-0.00184	-2.40031	-0.00036	-0.5457	0.036166				
La0HCP	-364.719	-0.19274	-11.6907	0.100934	-61.3984	-0.04039	2648.264			
Lb0HCP	-0.03908	1.02E-05	0.016078	-8.24E-06	0.00098	2.00E-05	-0.00059	5.16E-05		
aMG2SI	8456.775	-3.55557	827.1644	-3.76562	-2845.31	14.73861	281.3879	-0.00617	182401.3	
bMG2SI	-3.94481	-0.00023	-1.41644	0.000155	0.871084	0.001505	0.053944	-5.40E-06	-1.63824	0.011375

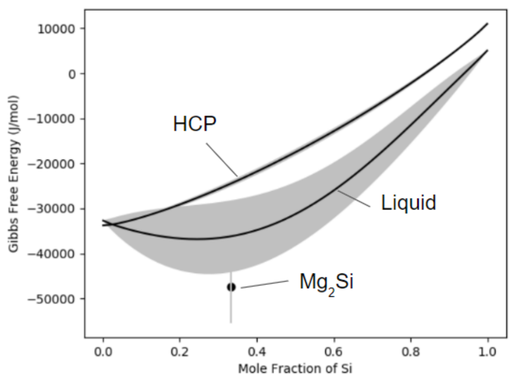

Figure 1: Gibbs free energy of phases in Mg-Si system with 95% confidence intervals at 850 K

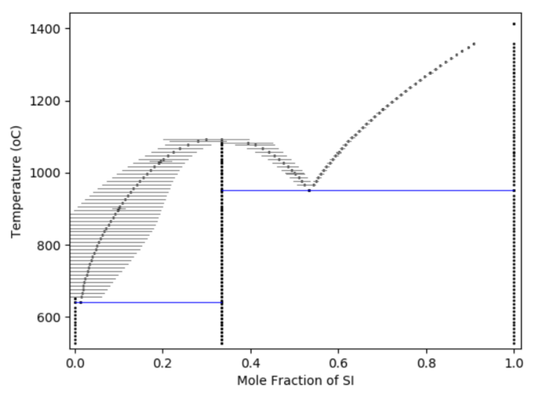

Figure 2: Calculated Mg-Si phase diagram with 95% confidence intervals

Summary and Conclusions

Thermodynamic calculations were performed and uncertainty was propagated through the system by constructing a Python library. The Mg-Si system was assessed as a proof a concept. Using the models and covariance matrix obtained from the assessment, the Mg-Si phase diagram was constructed with 95% confidence intervals.

Suggestions for Future Work

- Implement the calculation of temperature uncertainty
- Implement support for multicomponent systems and ordered solution models
- Assess a more complex system (either multicomponent and/or systems with more complex models) and propagate uncertainty through calculations on that system

References

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