Computer lab tools - Thermodynamics

Python · Jupyter Notebook · pymatgen · ASE · pycalphad

Lab teacher: Souzan Hammadi

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1 Introduction

There are 118 known elements on earth, and these can be combined endlessly. Materials scientists have the challenge to combine these elements and design processing methods in order to achieve properties fit for certain applications. The properties (mechanical, electrical etc.) of materials in turn, are heavily dependent on their phase and microstructure. The type of phase we may have in a system depends on parameters such as concentrations of different elements, temperature etc. Now, you can imagine that testing all possible combinations experimentally would be an impossibly tiring and long task, and in order to accelerate materials development we need computational tools that can guide us in the right direction.

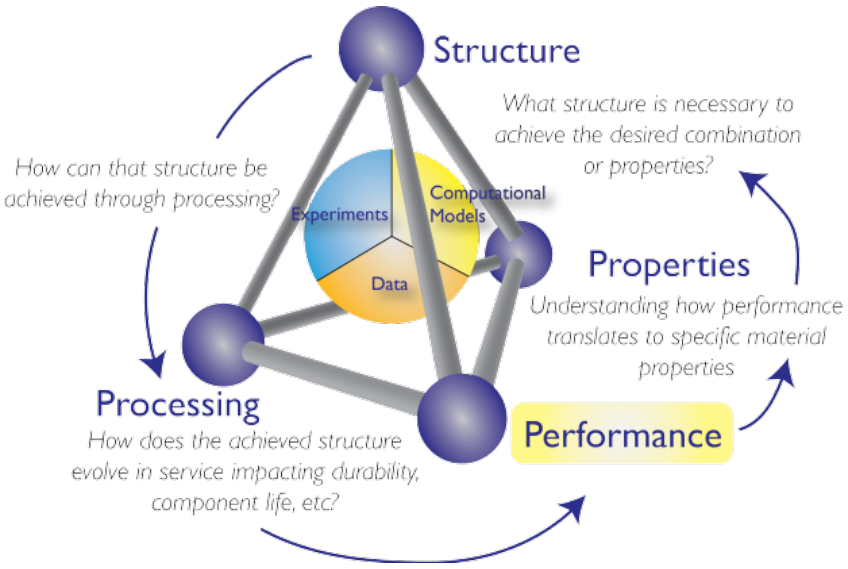

Figure 1: The framework of ICME (Integrated Computational Materials Engineering) where one combines computations and experiments in order to accelerate materials discovery. Taken from https://gems.matse.illinois.edu/educators/

In order to start knowing our materials, we need to probe their phase space i.e. we need to predict possible crystal structures. For that, thermodynamics will tell us what we may expect at equilibrium conditions and this will guide us far in our investigations. This tutorial aims at introducing concepts and python based tools that can be used for this.

At the end of this tutorial you will have learned:

- how to extract simple elemental properties from databases
- how to visualize structures
- how to read a thermodynamic database for CALPHAD
- how to predict phases
- how to draw Pourbaix diagrams

2 Part 1: Phase predictions

The first part of this tutorial will introduce pymatgen, materials project and ASE. At the end of this section you will be able to quickly access properties of elements and compounds (such as atomic mass, melting points etc), visualize structures and predict possible phases using first principle data. The tools will be demonstrated with the $Cu - Al$ system, but feel free to play around.

1: Basic properties of elements

To get warm fingers, we will start by extracting some elemental properties using pymatgen (https://pymatgen.org/).

2: Use ASE to visualize a compound

ASE (Atomic Simulation Environment, https://wiki.fysik.dtu.dk/ase/) has very handy tools and Python modules that one can use for setting up, running and analyzing atomistic simulations. In his part, we will only be using it to build and visualize an atomic structure.

3: Explore the phase space of Al-Cu

In this section, you will be interfacing with materials project in order to do your own calculations.

- Create an account at materialsproject.org
- Go to Dashboard
- Generate API key
- Copy your key and add it to the object MPRester as MPRester(KEY)

Question: which phases could we possibly have in the $Al - Cu$ system?

3 Part 2: Phase diagrams using CALPHAD

Temperature is a very important parameter in materials science, it affects both the thermodynamics and kinetics. It thus follows that we can have different phases at different conditions. Furthermore, materials of more technological use usually consist of more than one element. For so-called multi-component materials, steel is a good example where we can have tens of components. Simulating these type of materials using first-principle calculations would require too much computing power, and other type of approaches are thus required. One such popular approach is CALPHAD (CAlculation of PHase Diagrams).

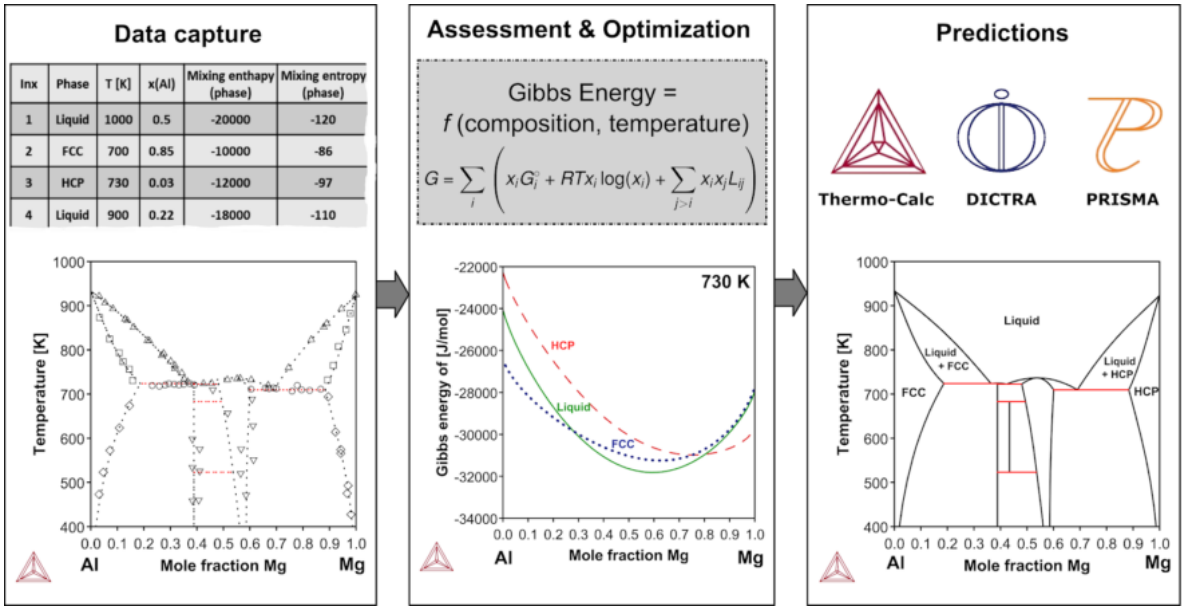

Figure 2: CALPHAD explained by Thermo-Calc. Experimental data is used to fit and optimize Gibbs energy models which then are used to predict different properties. Taken from: https://thermocalc.com/about-us/methodology/the-calphad-methodology/

In short, models of Gibbs energies are used to calculate thermodynamic properties and simulate phase transformations. One such model is a model for solution phases (e.g. liquid), and it is a sum of different energy contributions.

Gibbs energy = Gibbs energy of pure elements + energy contributions from ideal entropy of mixing + excess Gibbs energy

The terms can be found in the lecture slide as well as in this article: https://www.sciencedirect.com/science/article/pii/S0925838809019537 - [Thermodynamic analysis of Al–Sc, Cu–Sc and Al–Cu–Sc system]

This technique has been quite successful due to the development of multi-component

databases. However, the construction of these databases require a lot of work and knowledge. One has to keep in mind that the models assume thermodynamic equilibrium, and that one has to be careful when extrapolating them to more unstable states.

Question: How would the Gibbs energy model look like for the liquid phase in a binary system with elements A and B? Write it down.

PYTHON TUTORIAL

1: Find a thermodynamic database

For this, the TDB DB (Thermodynamic DataBase DataBase) https://avdwgroup.engin.brown.edu/, is a good tool. However, it may not be recently updated so for more recent databases a literature search would be appropriate. Some scientific articles inlcude thir databases in the supplementary section.

Have a look at the database file and see if you can find some of the parameters for the Gibbs models. Save the file in the same folder as your Jupyter notebook.

2: Define the Gibbs module and the terms needed

We will do this for liquid and FCC, which are both solution phases. Define the terms in the Gibbs model for this type of phase.

3: Use pycalphad to plot the whole phase diagram

pycalphad (https://pycalphad.org/) is a python library for computational thermodynamics using the CALPHAD method.

We start by plotting the Gibbs energy curves for a few phases and then go ahead and plot the whole phase diagram.

Question: Compare the predictions of the CALPHAD phase diagram with the previous results from the atomistic calculations. What are the main differences?

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4 Part 3: Pourbaix diagrams

A Pourbaix diagram has axis of pH vs potential (E) and show the type of dominating chemical species we have in a system. As materials scientists, we need to know how our system will act at different pH values in order to avoid failures due to corrosion.

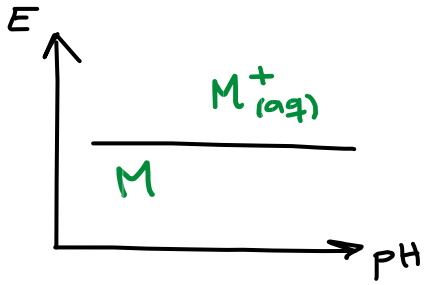

Figure 3: Schematic illustration of a pourbaix diagram.

The figure above shows a simple pourbaix diagram for metal M. At low potentials, we will have the metal $M_{(s)}$ dominating in our system. At higher potential, the dominating species will instead be the metal in its oxidized state M^{+}_{aq}. Both of these species will exist together along the line separating them ($M + M^{+}_{aq}$).

1: How to plot pourbaix diagrams

To demonstrate how pourbaix diagrams work, we will calculate a few lines for the copper system. It follows a straightforward procedure. First, we define the species, reaction and the equilibrium constant of the reaction.

Species	Cu, Cu^{2+} and e^{-}
Reaction	$Cu^{2+}_{aq} + 2e^{-} \rightleftharpoons Cu_{(s)}$
Equilibrium constant	$lg(K) = 11.5$

We set up the Nernst-equation:

$$E_e = E^0 - \frac{2.303RT}{zF} log\big(K\big) \tag{1}$$

, where the equilibrium constant is defined by our chemical reaction.

$$K = \frac{[Cu_{(s)}]}{[Cu^{2+}_{(aq)}][e^-]^2} \tag{2}$$

We use the tabulated value, which in this case is 11.5 for the logarithm.

$$lg(K) = lg\left(\frac{[Cu_{(s)}]}{[Cu^{2+}_{(aq)}][e^-]^2}\right) = 11.5 \tag{3}$$

$$E_e = E^0 - \frac{2.303RT}{zF} log\big(K\big) = 0.34 - \frac{2.303 \cdot 8.3145 \cdot 298}{1 \cdot 96485} \cdot 11.5 = 0.335 \tag{4}$$

This has to be done for every line in the pourbaix diagram, which can be become tedious if the system is more complicated. We may also not have any tabulated values for the equilibrium constants. We then need to use tools such as pymatgen, that calculates the values and directly generates the graph for us.

2: use pymatgen to generate pourbaix diagrams

As you saw from the previous section, in order to have a complete pourbaix diagram one has to first deduct which species are involved, the reactions between them and values for their equilibrium constant (which comes from the free energy as per $K = exp(-\Delta G^0/RT)$). Equilibrium constants for most common species and some simple alloys are tabulated, but it can get tricky when we investigate more advanced systems and combinations of them.

However, calculating free energies of both solid phases and ions is difficult and takes a long time. What pymatgen does is that it uses first principle calculations of free energies on solid phases and combines them with experimentally measured free energies of ions. More about the infrastructure can be found here and here.

5 References

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Persson, K. A., Waldwick, B., Lazic, P., Ceder, G. (2012). Prediction of solid-aqueous equilibria: Scheme to combine first-principles calculations of solids with experimental aqueous states. Physical Review B, 85(23), 235438.

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