Introduction to thermodynamic modeling

MatSE 501 recitation

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CALPHAD theory

The CALPHAD method

- **CAL**culation of **PH**ase **D**iagrams (CALPHAD)
- Pioneered by Larry Kaufman in the early 1970s
- What is it?
    - Parameterize the Gibbs free energy of individual phases
    - Calculate phase equilibria and thermodynamics properties
- Read more: Spencer A brief history of CALPHAD. Calphad 32, 1–8 (2008).

Parameterizing Gibbs free energies

Each phase (α, ice, water, liquid, fcc, perovskite) is assigned a Gibbs free energy

$$\begin{aligned}\underbrace{G^\alpha}_{\text{Energy of }\alpha\text{ phase}} &= \sum_i x_i {^\circ}G_i^\alpha \\ &+ RT\sum_i x_i \ln x_i \\ &+ {^E}G^\alpha\end{aligned}$$

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Excess mixing energy

- *Excess* mixing is somewhat nebulous
- Encountered excess mixing energy as enthalpy of mixing
    - ${}^{E}G^{\alpha} = x_A x_B \Omega = x_A x_B H_{\mathrm{mix}}$
- Extended to multicomponent systems using so called *interaction parameters*
    - Binary: ${}^{E}G^{\alpha} = \sum_{i,j} x_i x_j \sum_m {}^{m}L_{i,j}(x_i - x_j)^m$
    - Ternary: ${}^{E}G^{\alpha} = \sum_{i,j,k} x_i x_j x_k \sum_m (x_i L_i^{i,j,k} + x_j L_j^{i,j,k} + x_k L_k^{i,j,k})^m$
    - Higher orders are possible, but are seldom used due to diminishing effects on the energy
    - Different orders, *m* are possible

Lattice stability

- Pure W is stable in a bcc crystal, but alloyed into fcc solution.
- What is the energy of pure fcc W?
  - Lattice stability attempts to answer this question
  - $G_{\mathrm{W}}^{\mathrm{fcc}} = G_{\mathrm{W}}^{\mathrm{bcc}} + \Delta G_{\mathrm{W}}^{\mathrm{fcc\,-\,bcc}}$
- Determining lattice stabilities
  - Estimate ones with reasonable values that give correct phase diagrams
  - Extrapolate from experimental alloys
  - Calculate with first-principles methods

Redlich-Kister polynomials

- We have seen all of the contributions to a phase's energy as functions of G and L
- No mention has been made to this point about what these actually look like
- Mostly parameterized via Redlich-Kister polynomials
    - $G = a + bT + cT \ln T + \sum_n d^n T^n$
    - $L = a + bT$
- Simple analytical temperature derivatives for H, S, C_P, ...

Databases

- Multicomponent databases are available in literature and commercially
- For practical calculations, it is not required to know how energies are modeled
- Model development, building new databases, and database maintenance are active research areas

Getting started with pycalphad

pycalphad

- Most common CALPHAD software
  - Commercial: Thermo-Calc, Pandat
  - Non-commercial: pycalphad, OpenCalphad
- pycalphad is a Python-based CALPHAD software developed by Dr. Liu's group at PSU
  - `https://pycalphad.org`
  - Initially released in April 2015
  - Developed in the open on GitHub: `https://github.com/pycalphad/pycalphad`
  - Lead developer is Richard Otis at NASA JPL

Installing pycalphad

(Once per computer)

1. Install Anaconda (`https://anaconda.com/downloads`) (already done on PSU computers)
2. `Start -> Anaconda -> Anaconda Prompt`
3. Run `conda install pycalphad`

That's it!

Running pycalphad

- Any way you can run Python code, you can run pycalphad
- Recommend to use Jupyter Notebooks, which run in the browser
- `Start -> Anaconda -> Juypter Notebook`
- A browser Window will open

Download the files from `https://github.com/bocklund/notebooks/tree/master/MatSE501`