“Fundamentals of Thermodynamic Modelling of Materials”

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Extrapolations from thermodynamic models

[03004]

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Extrapolations from Thermodynamic Models

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Lattice stabilities
Metastable regions
Use in other applications
Extrapolations from Thermodynamic Models

why ab initio

scientific insight stems from the ability to extrapolate our understanding from simple models to a very complex physical world

no extrapolation is possible if our knowledge of the models is

- unfeasable
- irreproducible
- irrelevant
- inaccurate
- biased

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Extrapolations from Thermodynamic Models

Liquidus extrapolations for Cr

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Extrapolations from Thermodynamic Models

Jean-Marc Joubert

Extrapolations from Thermodynamic Models - Starts from what is known
Extrapolations from Thermodynamic Models – Models to train...

Gibbs energy \[ G = G(T, p, N_i) \]

entropy \[ S = -\left(\frac{\partial G}{\partial T}\right)_p N_i \]

enthalpy \[ H = G + TS = G - T \left(\frac{\partial G}{\partial T}\right)_p N_i \]

volume \[ V = \left(\frac{\partial G}{\partial p}\right)_{T, N_i} \]

Chemical potential of component \( i \) \[ \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T, N_{ij}} \]

heat capacity \[ C_p = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_{p, N_i} \]

thermal expansion \[ \alpha = \frac{1}{V} \left(\frac{\partial^2 G}{\partial p^2}\right)_{N_i} \]

isothermal compressibility \[ \kappa = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial p^2}\right)_{T, N_i} \]

bulk modulus \[ B = \frac{1}{V} \]

Elastic constants

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Extrapolations from Thermodynamic Models

Open field: Models can be improved.
More quantities are modelled, higher the consistency for applications

The general Gibbs energy expression is

\[ G_m = G^{rf}_m - TS_m^{com} + G^{ex}_m \]

The surface of reference for the model is the sum of Gibbs energies of all configurations with atom \( i \), on each sublattice, \( \sigma \), weighted by the site fractions \( y^{(\sigma)}_i \). The \( \sigma \) phase has five sublattices with different numbers of sites and coordinations and can be described as

\[ \{ \text{Re}, W_i \}_{1}, \{ \text{Re}, W_i \}_{2}, \{ \text{Re}, W_i \}_{3}, \{ \text{Re}, W_i \}_{4}, \{ \text{Re}, W_i \}_{5}, \text{sites 1-5} \], respectively. This gives \( 2^{5} \approx 32 \) ordered configurations. Thus, the surface of reference becomes

\[ G^{rf}_m = \sum_{ijklm} y^{(1)}_i y^{(2)}_j y^{(3)}_k y^{(4)}_l y^{(5)}_m G_{ijklm} \]

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These compound energies, \( {\omega G}_{ijklm} \), are exactly the same FP energies calculated in the paper by Berne et al.

The only additional term necessary to calculate the Gibbs energy at any temperature is the entropy of mixing which is assumed to be ideal in CEF:

\[
S^{conf} = -R \sum_s \alpha^{(s)} \sum_{i=Rc,W} y_i^{(s)} \ln(y_i^{(s)})
\]

\[
\left( \frac{\partial G_m}{\partial T} \right)_{p,x_i} = \left( \frac{\partial G_m}{\partial T} \right)_{p,y_j} + \sum_j \left( \frac{\partial G_m}{\partial y_j} \right)_{T,p,y_k} \cdot \left( \frac{d y_j}{dT} \right)_{p,y_k} \quad (k \neq j)
\]

The second derivative of the Gibbs energy with respect to mole fractions is

\[
\Omega_{ij} = \left( \frac{\partial^2 G}{\partial x_i \partial x_j} \right)_{T,p,x_k} \quad (k \neq i, k \neq j)
\]
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Ag-Sn-Cu

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## Assessments evolution

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**Calphad Database**

- Thermodynamic database
- Phase diagram generation
- High-temperature phase stability
- Kinetic simulation
- Modelling of phase transformation rates

**ThermoCalc**

- Thermodynamic property calculation
- Phase diagram construction
- Kinetic simulation
- Modelling of phase transformation rates

**MICRESS**

- Nucleation model
- Multi-phase-field solver
- Multicomponent diffusion solver
- Temperature solver

**Assessment evolution**

- From experimental phase diagrams to modelled Gibbs energies
- From modelled Gibbs energies to calculated phase diagrams
Re-W: only VASP total energies and a Bragg-Williams ideal entropy

Calculated diagram using CEF

Dft energies from T. Hammerschmidt et al.

CALPHAD assessment.
On going work by Arthur Bialon

\[ G' = H'_{\text{ref}} - TS'_{\text{conf}} \]

\[ H'_{\text{ref}} = \sum_{ijklm} y_{ij}^{(1)} y_{ji}^{(2)} y_{im}^{(3)} y_{mi}^{(4)} y_{mn}^{(5)} H_{jklm} \]

**Computational Thermodynamics**

**What is it CALPHAD?**

It is not a software!

It is a method!

Gibbs energies for all the stable phases of a system are described by parametric models. These parameters are obtained in such a way that the Gibbs energy and its derivatives reproduce the experimental corresponding value at its best.

When this is done, by Gibbs energy minimization the phase diagram can be calculated! CALculated PHAse Diagrams

Big advantages: interpolations and extrapolations can be done. Less experiments are need. Even some antecipation of higher order systems can be done!

Interpolations are so good as the description...Extrapolations too and they are not truly predictable. It there is a ternary compound that is not in the description it can not be guessed by the extrapolation from the binaries.
Computational Thermodynamics
An overview

A puzzle to be solved till the end of the week:
to which lecture is each one of the images related?

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