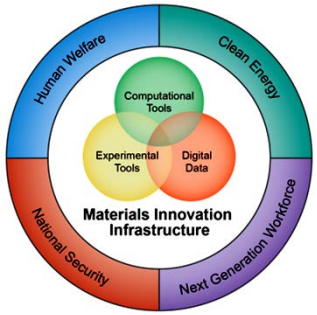
Thermo-Calc Software

CALPHAD and Beyond - The True Story of Materials Genome

Qing Chen

Thermo-Calc Software AB, Stockholm, Sweden

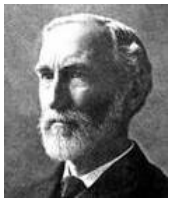


IFAM 2016, Nanjing, China, Sept 24-26, 2016

CALPHAD - Materials Genome

Thermo-Calc Software

Pre-CALPHAD 1908



Gibbs

van Laar

Kaufman

1973 CALPHAD

Thermo-Calc 1981

Hillert

Sundman

Jansson

Ågren

1990 DICTRA

Materials Genome® 2002

ZK Liu

Ceder

2006 Materials Genome Project

Materials Genome Initiative 2011

Obama

What is CALPHAD?

Thermo-Calc Software

Phase-based description

$$G_m = \sum {}^{o}G_{end} \prod y_j^s + RT \sum\sum n^s y_j^s \ln(y_j^s)$$
$$+ \prod y_j^s \sum y_B^t L_{A,B:D:G} + \ldots + \prod y_j^s \sum y_B^t y_D^u L_{A,B:D,E:G} + \ldots$$

Method

Journal

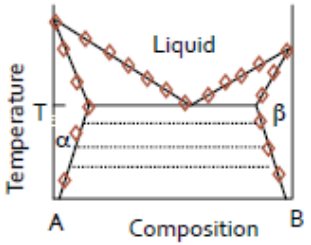
Conference

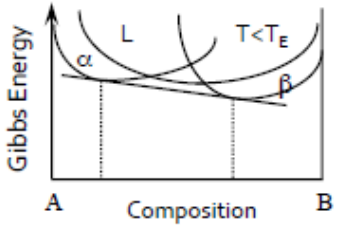
CALPHAD Method

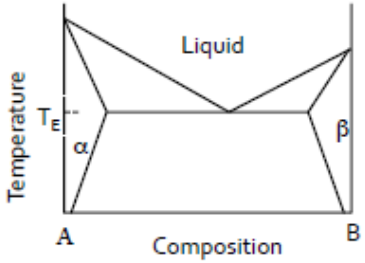
Thermo-Calc Software

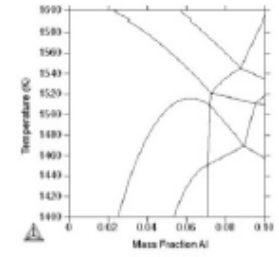
- Collected experimental and computational data are used to fit functions.
- Functions are used to calculate phase equilibria, including phase diagrams.

Experimental phase diagram and thermochemical data → Determine Gibbs energy functions for each phase: $G = f(x,T,P)$ → Calculated phase diagram → Combine binaries and ternaries to predict multi-component systems









Al isopleth for 8 component system

$$G^{\phi} = G^{0} + G^{ideal} + G^{excess}$$

Binaries → Ternaries → Quaternaries → n^{th} Order Systems

- True quaternary compounds are rare in metallic systems
- Assessment of ternary systems is usually sufficient for the description of a multicomponent system
- Same methodology can be applied to the description of other property data

From Dr. C. Campbell, NIST, USA

Big idea – lattice stability

Thermo-Calc Software

G_{Fe}^{fcc} G_{Fe}^{bcc} G_{Ni}^{fcc} G_{Ni}^{bcc}

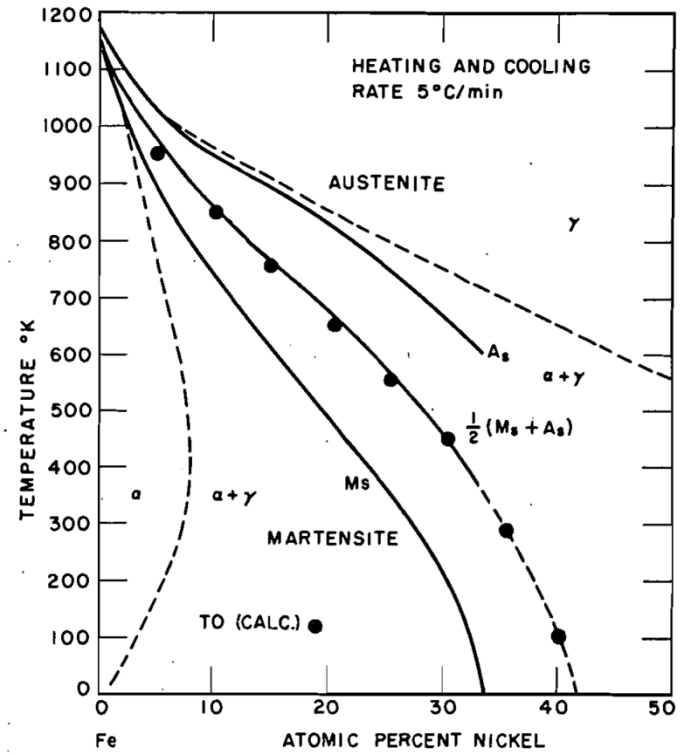


Fig. 1—The M_s-A_s diagram, determined by resistance measurements. The dashed lines are the $\alpha/\alpha+\gamma$ and $\alpha+\gamma/\gamma$ phase boundaries of the equilibrium diagram.

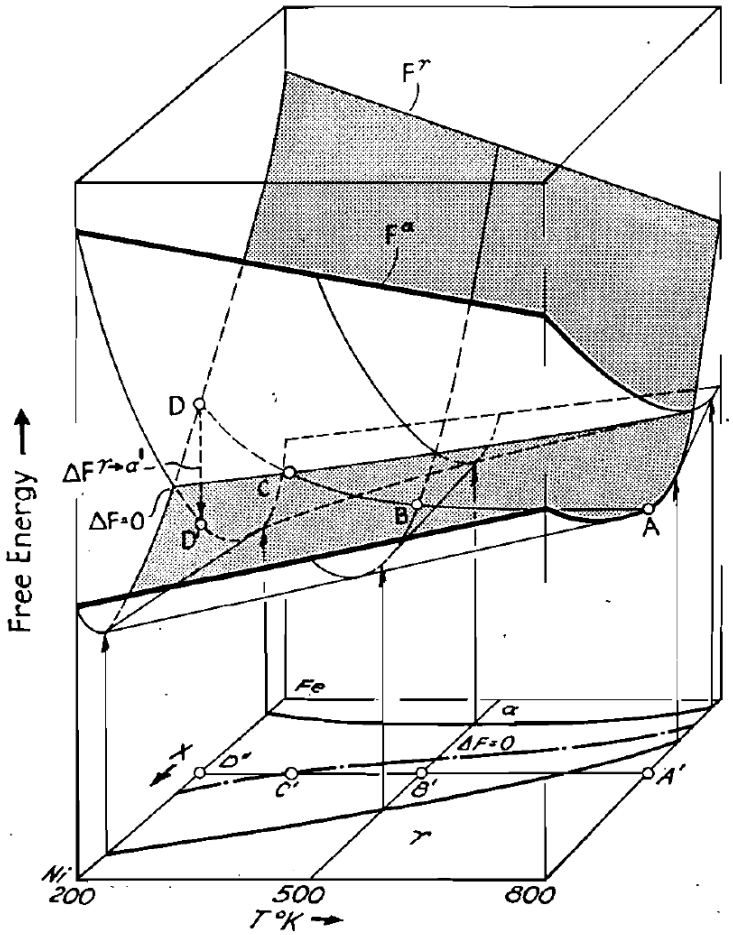


Fig. 6—Schematic representation of F^γ and F^α surfaces as a function of x and T.

by Larry Kaufman and Morris Cohen

Multicomponent systems for practical industrial application

$$G_m^{\alpha} = \sum_i x_i^{\alpha\, o}G_i^{\alpha} - TS_m^{ideal\,\alpha} + {}^{E}G_m^{\alpha}$$

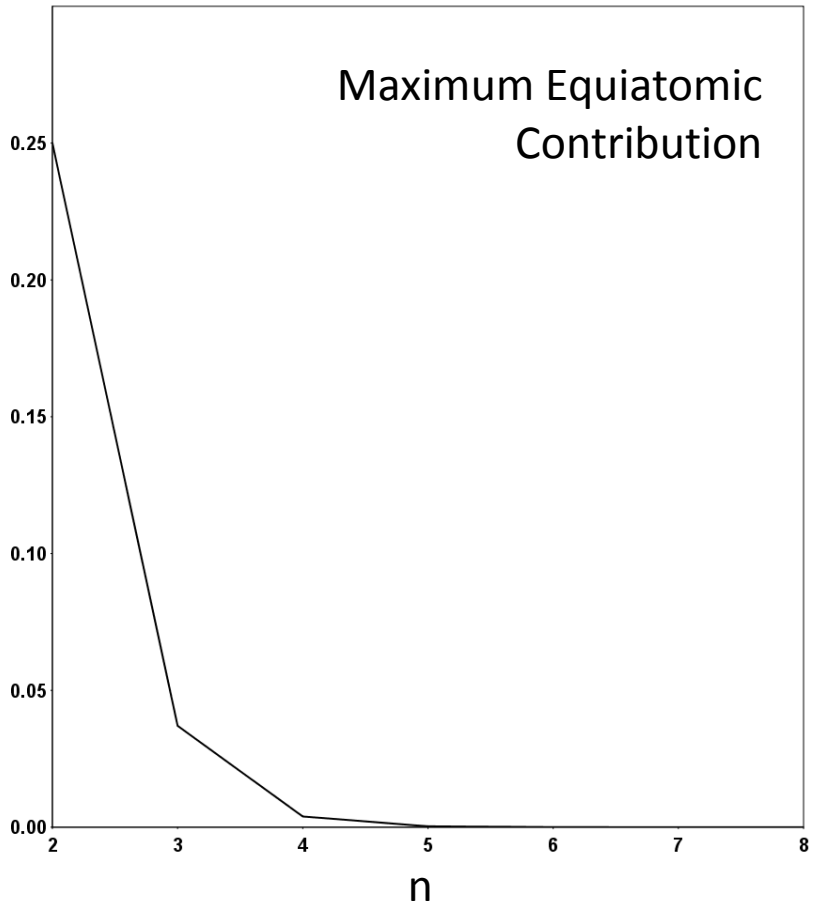
$${}^{E}G_m^{\alpha} = \sum_{i\neq j} x_i x_j L_{i,j}^{\alpha}$$

$$+ \sum_{i\neq j\neq k} x_i x_j x_k L_{i,j,k}^{\alpha}$$

$$+ \sum_{i\neq j\neq k\neq l} x_i x_j x_k x_l L_{i,j,k,l}^{\alpha}$$

$$+ \cdots$$

$$\prod_{i=2}^{n} x_i$$



What is a CALPHAD Database?

Thermo-Calc Software

- Different from conventional materials property databases where various property data are stored as specifications for engineering materials

MatWeb

- Does not store thermodynamic or phase diagram data

JANAF

ASM INTERNATIONAL Alloy Phase Diagram Database™

Home | Explore | Search | Tools | Help

- Stores Gibbs energy model parameters for **individual phases**

$$G_m = \sum {}^{o}G_{end} \prod y_j^s + RT \sum\sum n^s y_j^s \ln(y_j^s)$$
$$+ \prod y_j^s \sum y_B^t L_{A,B:D:G} + \ldots + \prod y_j^s \sum y_B^t y_D^u L_{A,B:D,E:G} + \ldots$$

Advantages of CALPHAD Database

Thermo-Calc Software

- Efficient and versatile
- Self-consistent and elimination of data of error. Data curation done!
- Prediction for regions where data is not available or difficult/impossible to obtain.
- **Based on unary, binary, and ternary data, we can predict properties of multicomponent systems that were not even measured.**

Table I. *Summary of parameters (in SI units and with R=8.31448) obtained by optimizing the representation of experimental data for the Fe–C system.*

Element	stable element reference	Mass	$H_{298}-H_0$	S_{298}
Va	Vacuum	0.00	0.00	0.00
C	Graphite at 298.15 K	12.011	1054.0	5.74
Fe	bcc at 298.15 K	55.847	4489.0	27.28

bcc
Excess model is Redlich-Kister
Additional contribution from magnetic ordering
2 sublattices, sites 1:3
Constituents: Fe:C,Va

$${}^{o}G^{hbcc}_{Fe:C} - {}^{o}G^{hbcc}_{Fe:Va} - 3\ G^{gra}_{C} = +322050 + 75.667\ T$$

$${}^{o}L^{bcc}_{Fe:Va,C} = -190\ T$$

fcc
Excess model is Redlich-Kister
2 sublatticies, sites 1:1
Constituents: Fe:C,Va

$${}^{o}G^{fcc}_{Fe:C} - {}^{o}G^{fcc}_{Fe:Va} - {}^{o}G^{gra}_{C} = +77207 - 15.877\ T$$

$${}^{o}L^{fcc}_{Fe:Va,C} = -34671$$

LIQUID
Excess model is Redlich-Kister
Constituents: C,Fe

$${}^{0}L^{liq}_{Fe,C} = -124320 + 28.5\ T$$

$${}^{1}L^{liq}_{Fe,C} = +19300$$

$${}^{2}L^{liq}_{Fe,C} = +49260 - 19\ T$$

CEMENTITE
2 sublattices, sites 3:1
Constituents: Fe:C

$${}^{o}G^{cem}_{Fe:C} - H^{SER}_{C} - 3\ H^{SER}_{Fe} = -10745 + 706.04\ T - 120.6\ T\ \ln(T)$$

14 parameters

Thermo-Calc Software

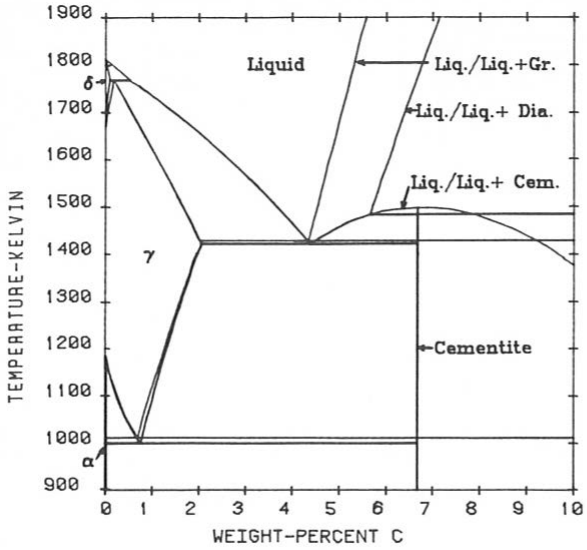


Fig. 1. *The stable and metastable Fe–C phase diagram according to the present evaluation.*

Scandinavian Journal of Metallurgy 14 (1985) 259–267

A Thermodynamic Evaluation of the Fe–C System

Per Gustafson

Physical Metallurgy, Royal Institute of Technology, S-100 44 Stockholm, Sweden

>1000 experimental data

Thermo-Calc Software

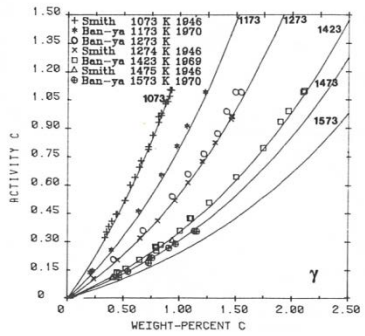


Fig. 3. *Calculated C activities in fcc phase in comparison with experimental data.*

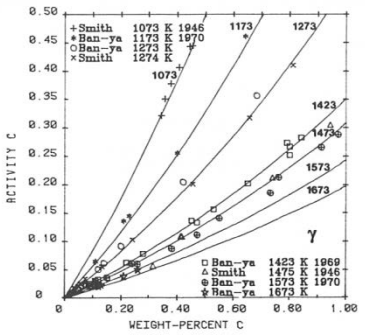


Fig. 4. *Calculated C activities in fcc phase in comparison with experimental data.*

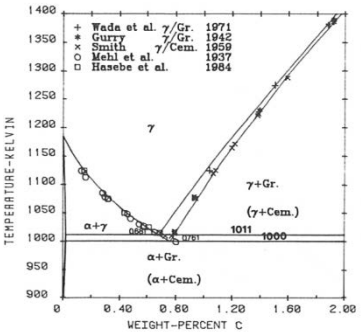


Fig. 5. *The eutectoid part of the stable and the metastable ph diagram according to the present evaluation together with experimental information*

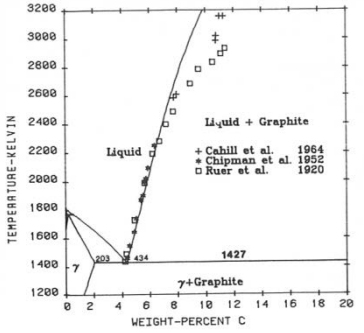


Fig. 6. *Calculated C activities in liquid phase in comparison with experimental data.*

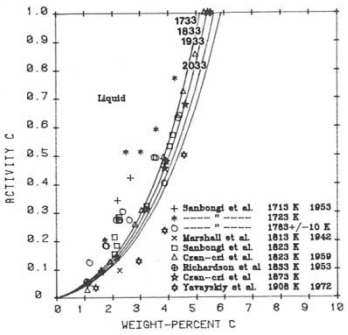


Fig. 7. *Calculated C activities in liquid phase in comparison with experimental data.*

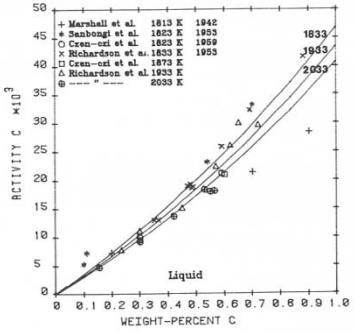


Fig. 8. *The calculated solubility of graphite in liquid Fe at high temperatures in comparison with experimental data.*

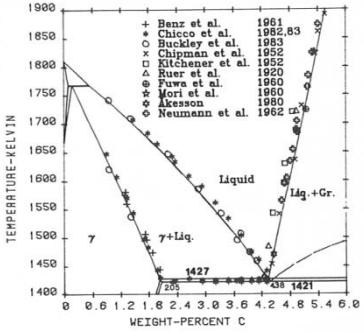


Fig. 9. *The eutectic part of the stable and the metastable phase diagram according to the present evaluation together with some experimental data.*

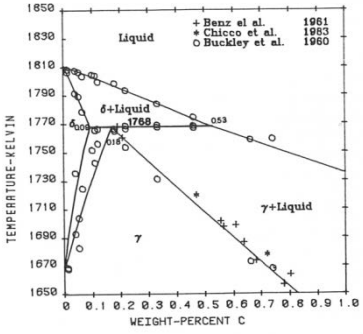


Fig. 10. *The peritectic part of the phase diagram according to the present evaluation together with some experimental data*

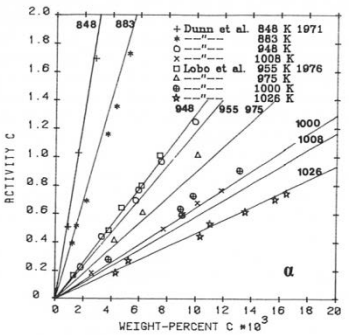


Fig. 11. *Calculated C activities in bcc phase in comparison with experimental ata.*

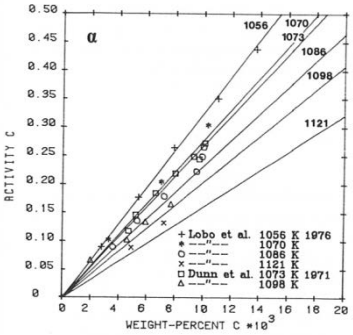


Fig. 12. *Calculated C activities in bcc phase in comparison with experimental ata.*

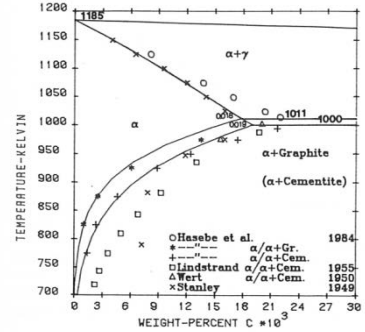


Fig. 13. *The solubility of carbon in bcc phase according to the present evaluation in comparison with experimental data.*

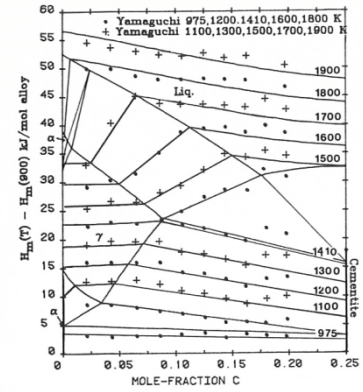
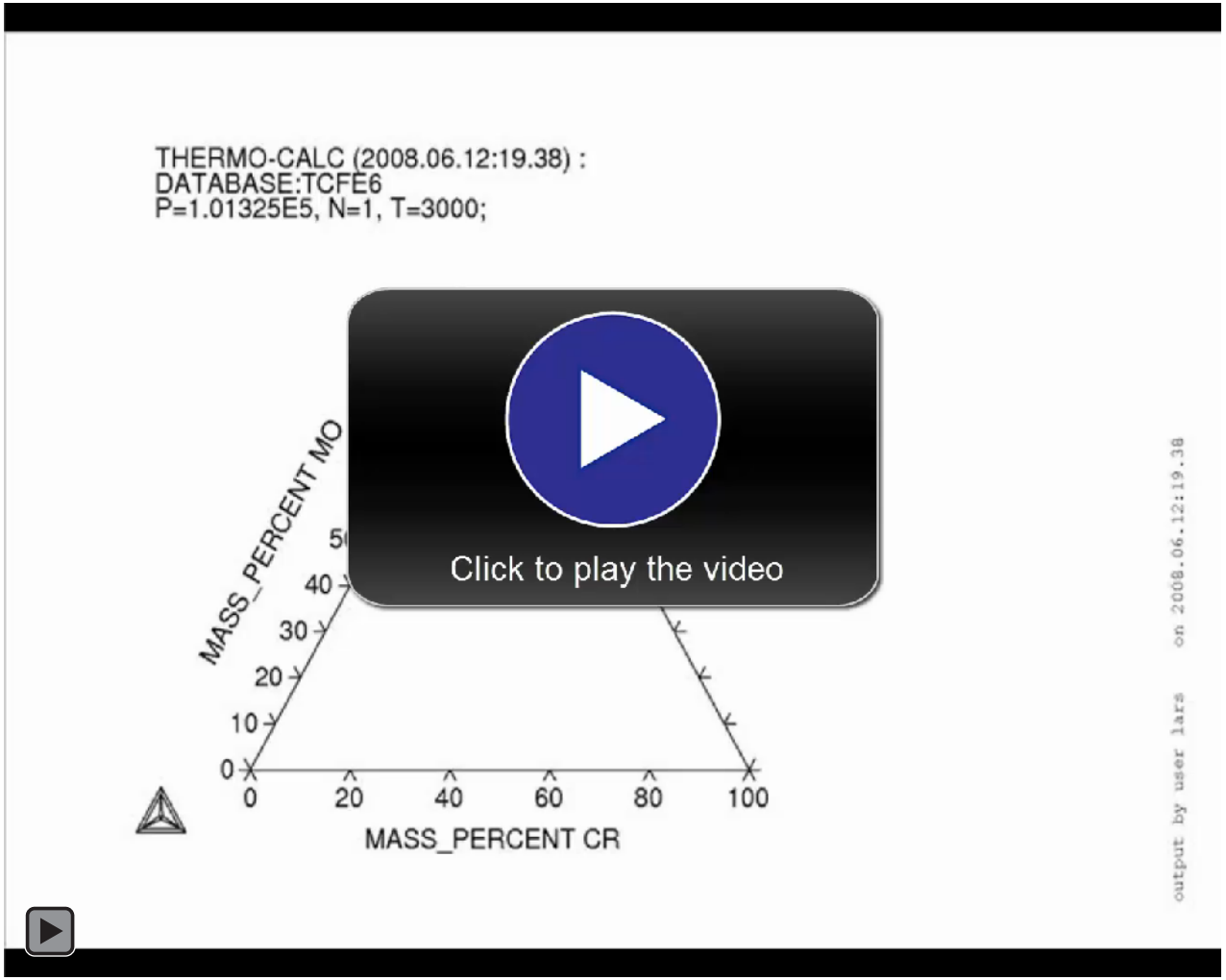
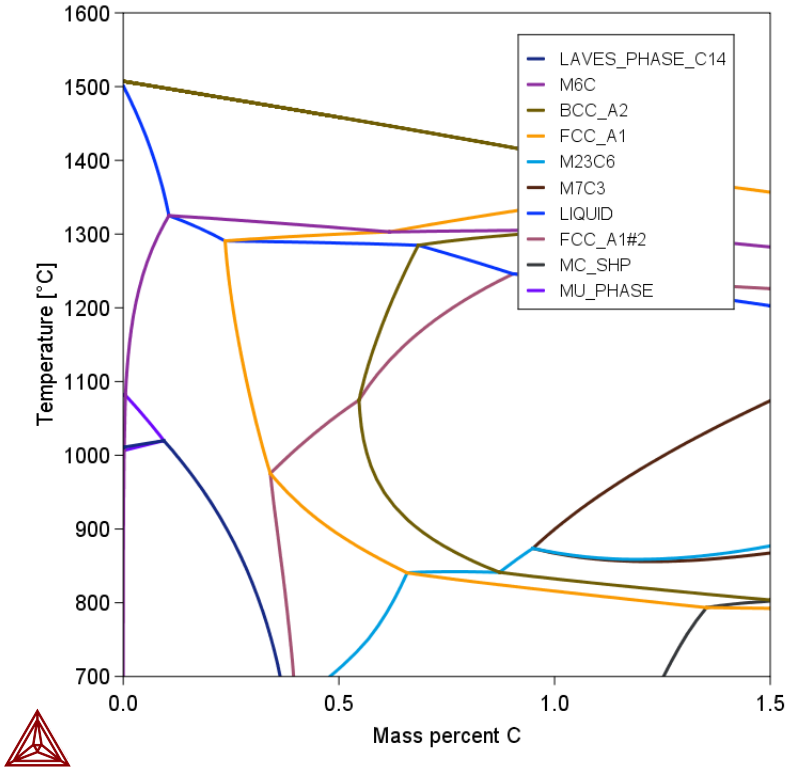


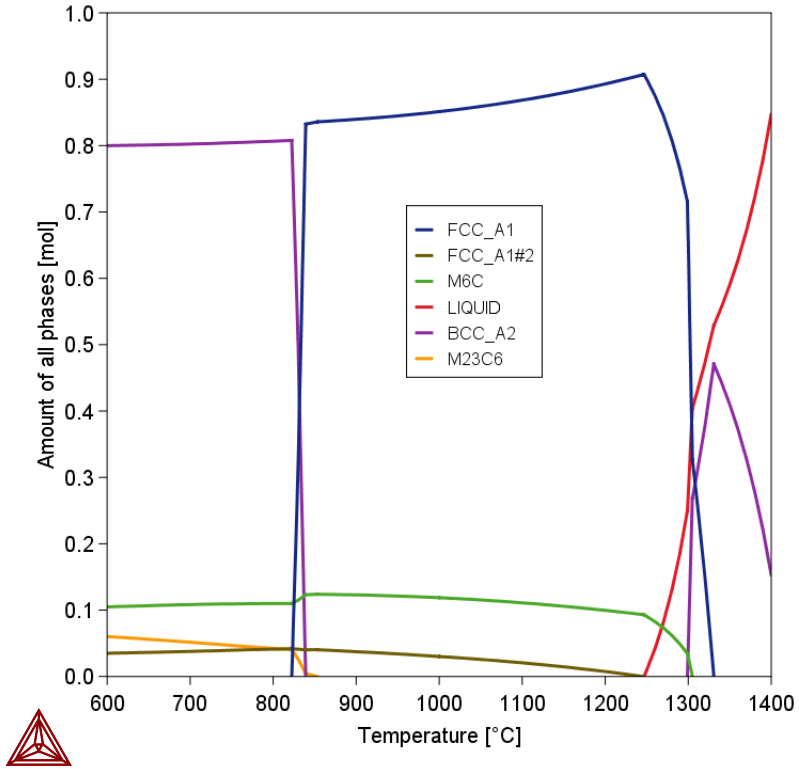
Fig. 15. *The metastable phase diagram plotted with an enthalpy axis instead of the temperature axis, compared with experimental*

Phase equilibria at all temperatures and compositions



Multicomponent industry alloys

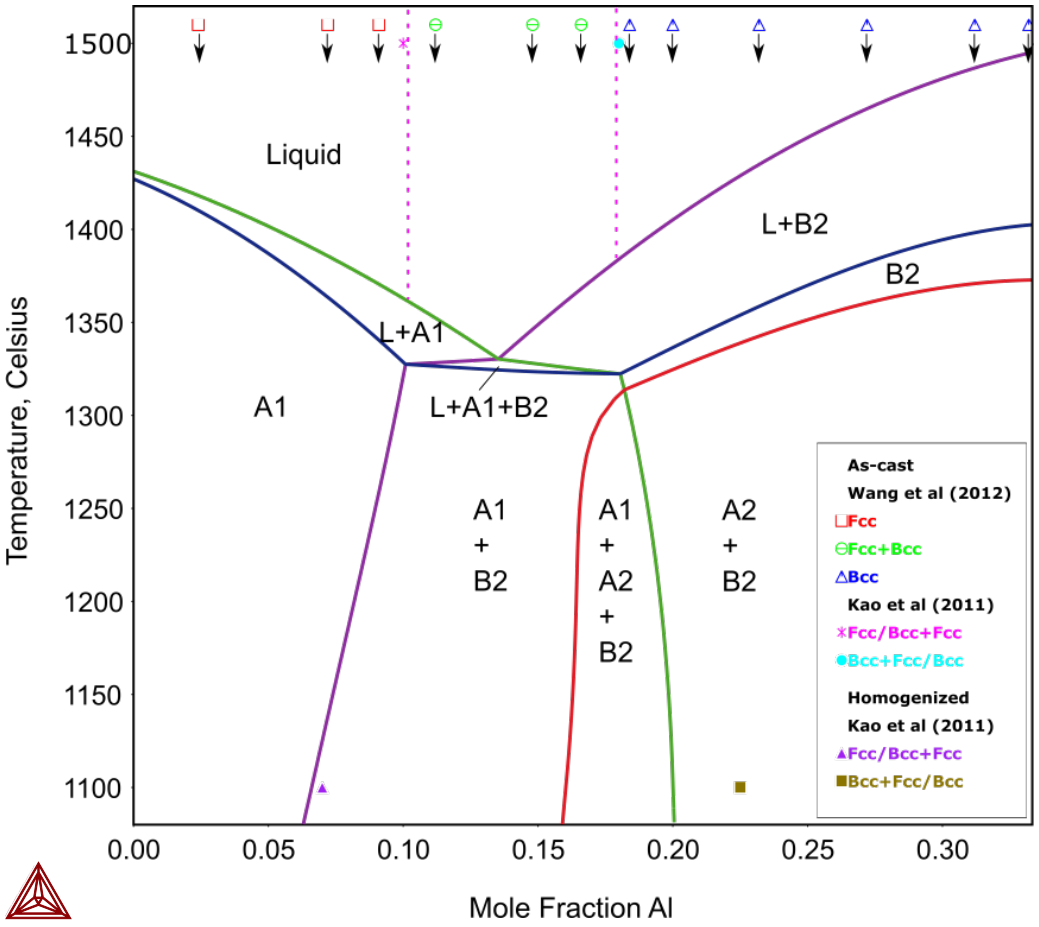




Phase diagram for a M42 high speed steel.
The lines represent where a phase appears or disappears, numbers show on which side of the line that phase is present. The alloy is Fe-4Cr-5Mo-8W-2V-0.3Mn-0.3Si-C(wt%).

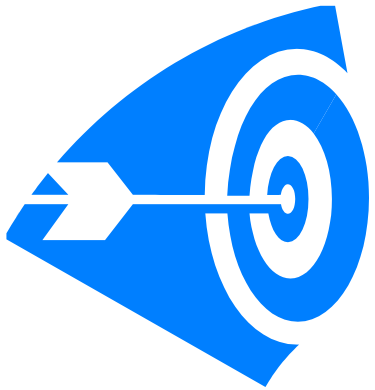
Property diagram for a M42 high speed steel.
Shows how the fractions of the phases in the system vary with temperature. The alloy is Fe-4Cr- 5Mo-8W-2V-0.3Mn-0.3Si-0.9C.

High Entropy Alloys



Calculated phase diagram of CoCrFeNi-Al by using TCHEA1

- 216 alloys in literature
- Predictions by using TCHEA1
- 70% on target

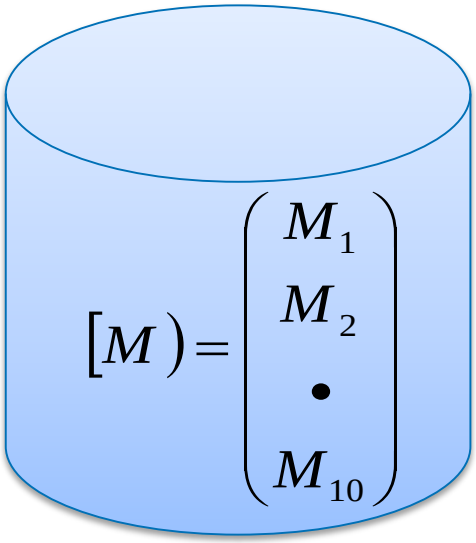


To be published, Prof. R. Arroyave, et al, Texas A & M Univ., 2016

Mobility and Diffusivity

- ($\mathbf{n}$-1)^2 elements in the inter-diffusion matrix. All depending on composition and temperature.
- **n** mobilities depending on composition and temperature.

Atomic mobility Database



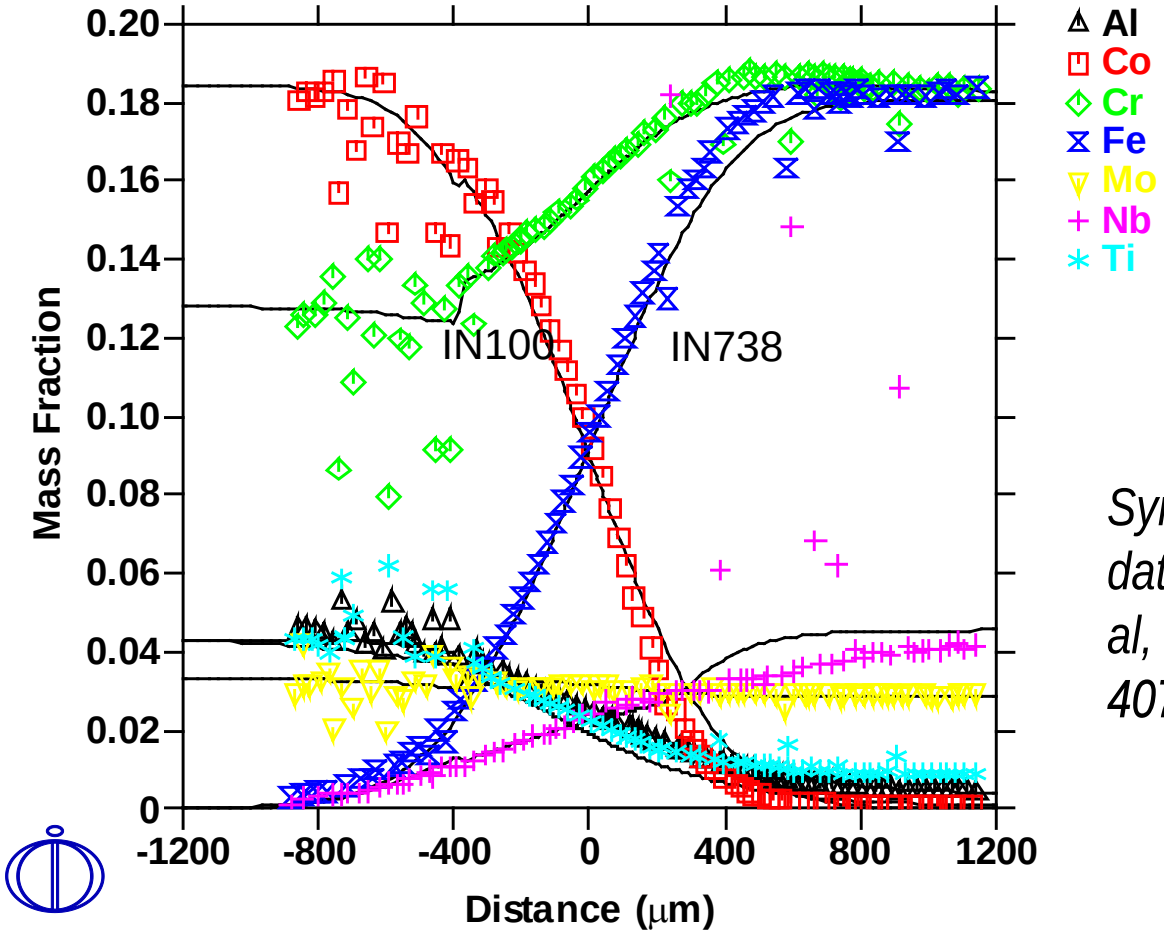
Chemical Diffusivity

$$[D] = \begin{bmatrix} D_{11} & D_{12} & \bullet & D_{19} \\ \bullet & \bullet & & \\ \bullet & & \bullet & \\ D_{91} & & & D_{99} \end{bmatrix}$$

Self-Diffusivity
Impurity Diffusivity
Intrinsic Diffusivity

J.O. Andersson and J. Ågren, J. Appl. Phys., 72 (1992) 1350.

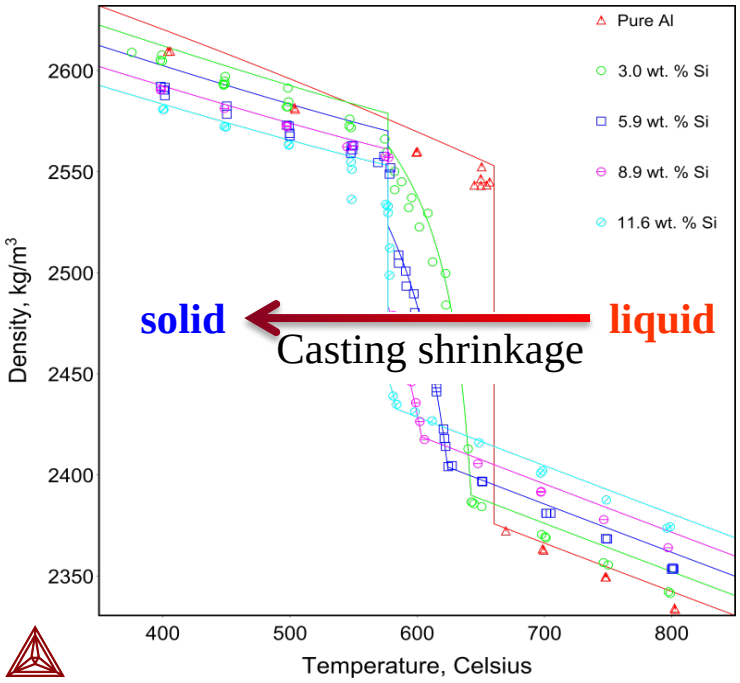
Mobility and Diffusivity



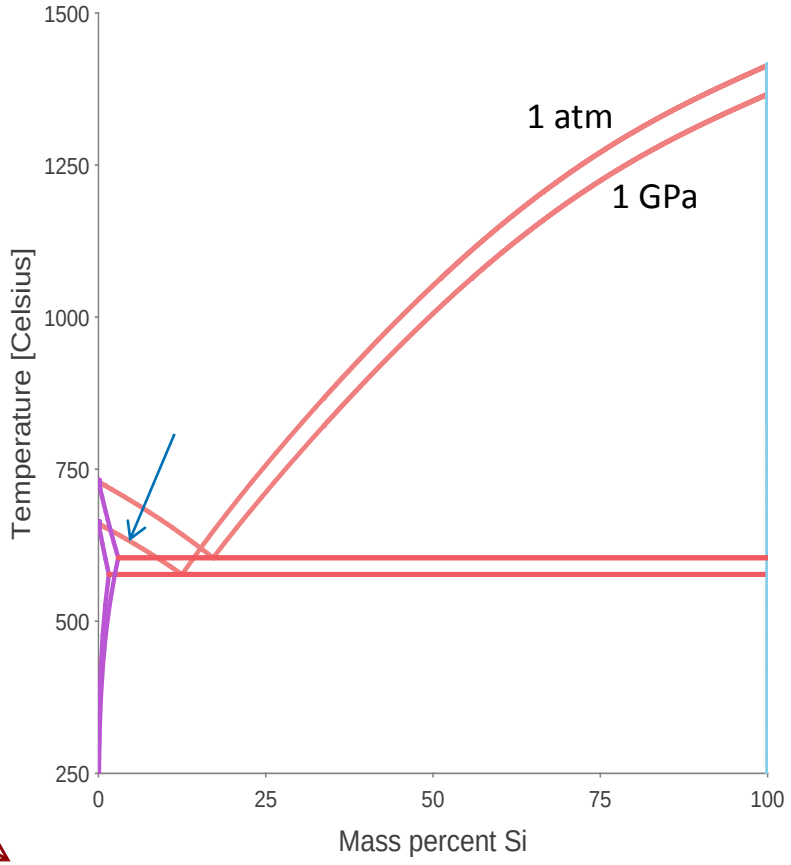
Symbols are experimental data taken from Campbell et al, Materials Sci & Eng A 407(2005), pp. 135-146.

Volume and bulk modulus – Pressure dependence

lattice parameter	molar volume	density	thermal expansion coefficient	relative length change	lattice mismatch



The effect of Si content on the densities of Al-Si alloys



Extensions

To facilitate linkage among thermodynamics, processing modelling and microstructure simulation, the following phase-based property data can be modelled in the CALPHAD-type fashion:

Elastisity

- Elastic constants
- Young's modulus
- Bulk modulus
- Shear modulus
- Possion's ratio

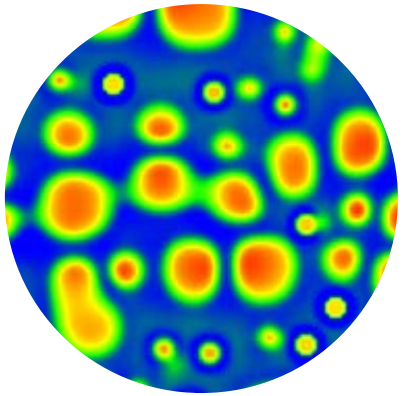
Viscosity (and diffusivity) in liquid

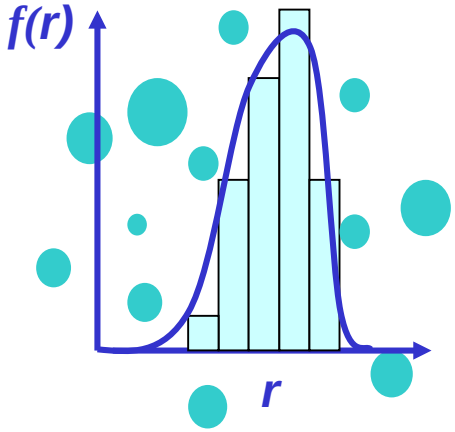
Thermal conductivity and diffusivity
Electric conductivity and resistivity

Thermal radiative properties: emissivity, adsorptivity, reflectivity, transmissivity

Properties of interface

- essential for modelling of microstructure evolution

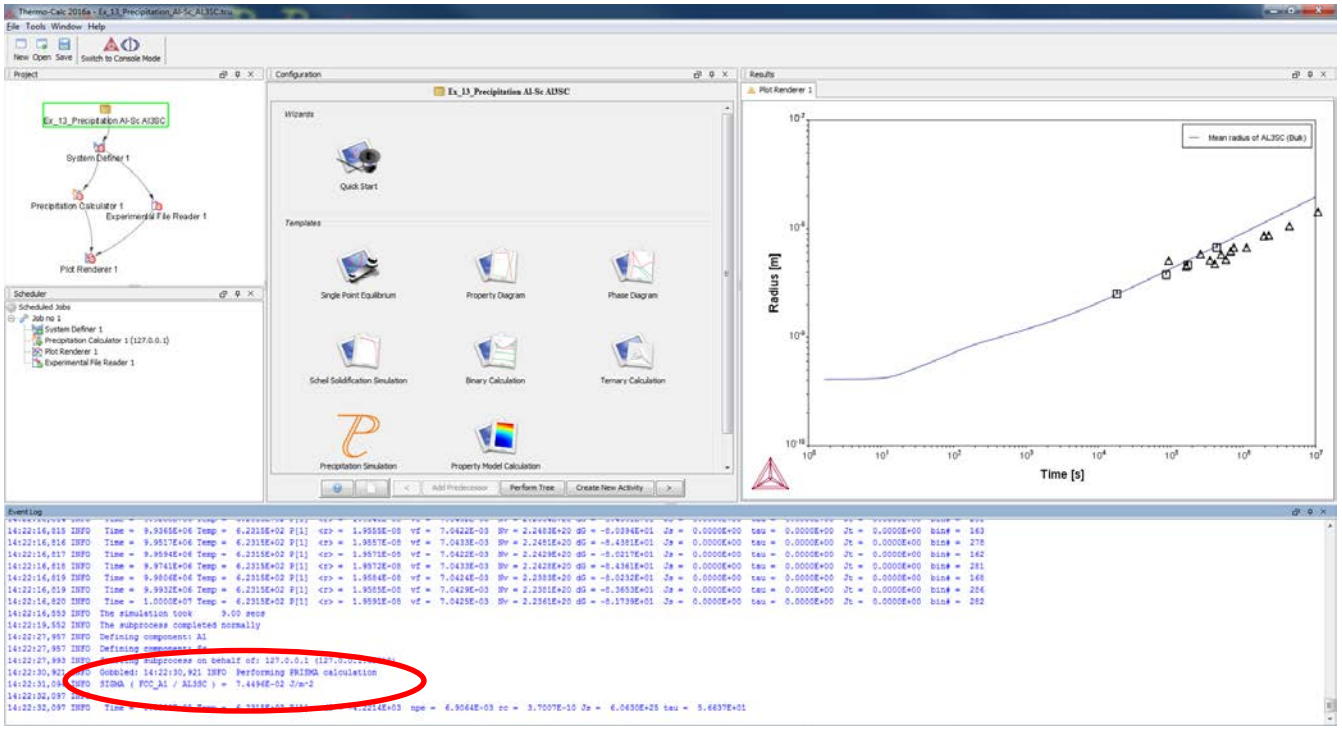




Interfacial energy
Grain boundary energy
Surface tension

Estimation of interfacial energy

System	Phases	Estimation (J/m^2)	Literature (J/m^2)
Al-Li	α/δ'	0.011	0.004 to 0.115
Cu-Ti	Cu/Cu4Ti	0.035	0.067, 0.031
Ni-Al-Cr	γ/γ'	0.022	0.023
Co-W-C	Co/WC	0.68	0.44 to 1.09



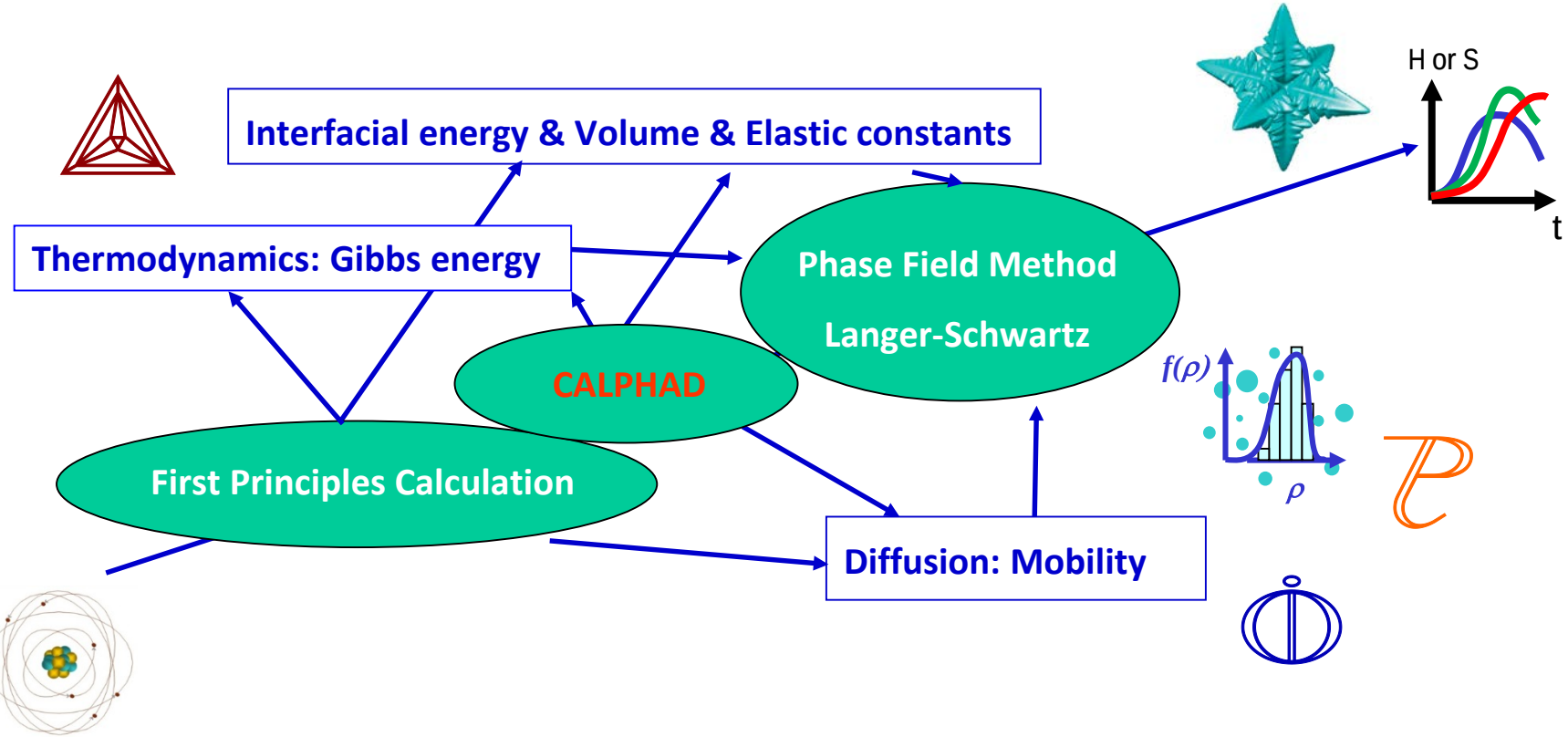
Limitations and Challenges

Thermo-Calc Software

- Relying on (at least key) experiments, which unfortunately are supported less and less. Quite often, facing not a big data problem, but few or no data problem.
- Requiring development of high-throughput experimental method and more accurate ab-initio calculation results
- Updating of existing CALPHAD database
- Thermodynamic properties for metastable and sometimes even unstable structures
- Anisotropy of inter-phase and grain boundary energy
- Self-consistent description of elastic properties by using Gibbs energy as a funciton of strains
- Uncertainty quantification

Summary

CALPHAD method is truly a materials genome method and it plays a central and fundamental role in materials design



CALPHAD-type genomic databases of thermodynamic and thermophysical as well as kinetic properties have been and will be the only feasible source to provide input data for simulation of materials processing and microstructure evolution in multicomponent systems.

Thermo-Calc Software

Thank You!

www.thermocalc.com

Save Time ♦ Reduce Costs ♦ Increase Innovation