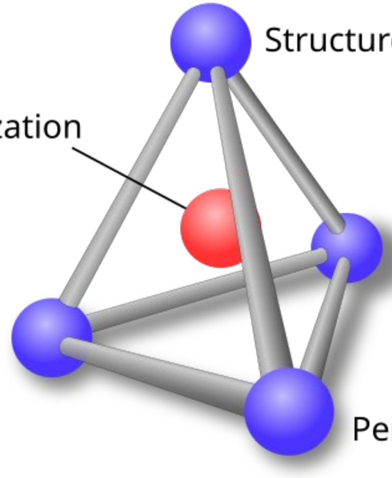
FS 2024/25

MSE-422 – Advanced Metallurgy

3- Fundamentals of Computational Materials Science/CALPHAD

Christian Leinenbach

How to design high-performance alloys?



How to design high-performance alloys?

EPFL

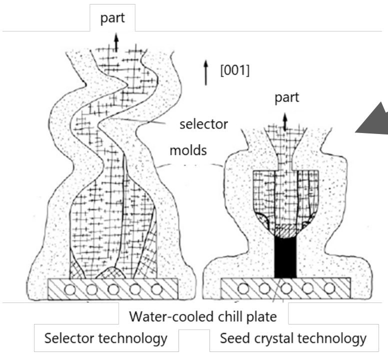
Composition

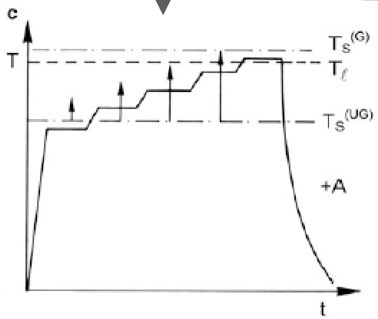
	C	Si	Mn	Cr	Mo	Ni	Ta	Ti	W	Co	Fe	Al	Hf	V	Zr
CM 247	0.074	< 0.03	< 0.03	8.16	0.43	Bal.	3.21	0.68	9.55	9.364	0.03	5.63	1.42	< 0.03	0.015

	Cu	B	P	S	Pb	Ag	Bi	Te	Tl	Sb	Sn	Zn	Cd
	< 0.03	0.0155	< 0.005	6 ppm	< 2 ppm	< 2 ppm	< 0.3 ppm	< 1 ppm	< 1 ppm	< 3 ppm	< 3 ppm	< 2 ppm	< 0.5 ppm

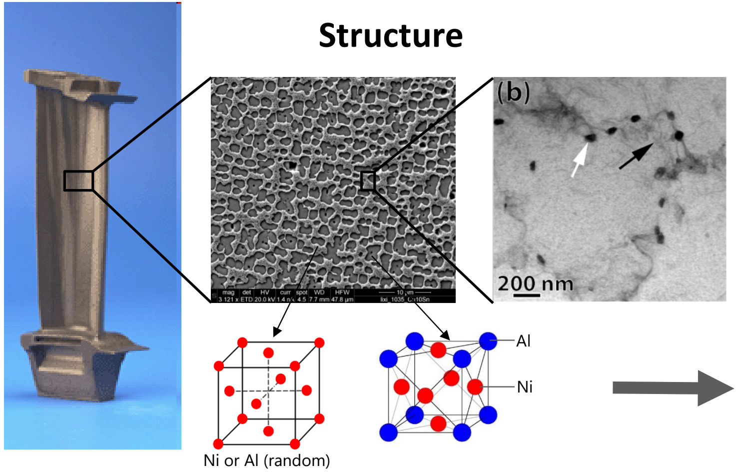
Performance

Processing

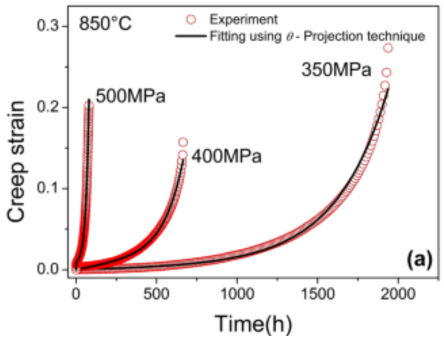




Structure

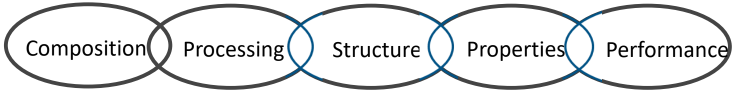


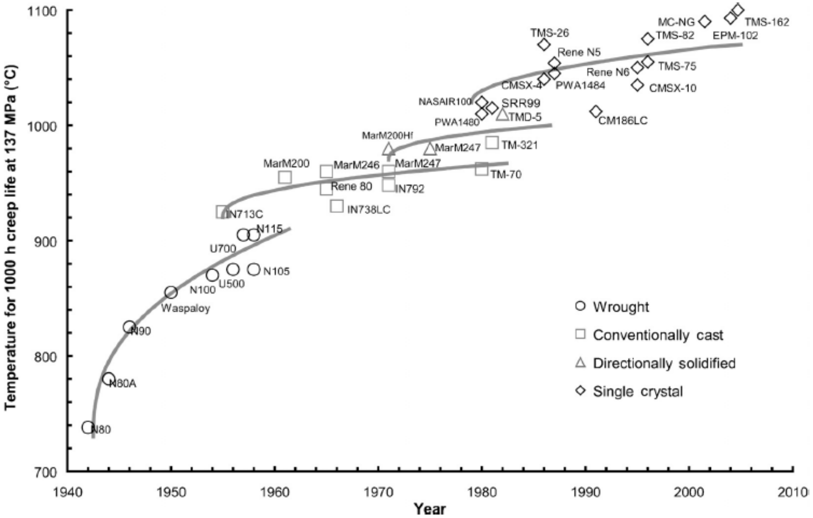
Properties



The alloy development process

- Modern high performance alloys are designed to fulfill a particular purpose
- The materials development process is usually rather slow; the duration from the first studies until the market entry is often 10-15 years
- Initially, alloys have been «designed» in a tedious trial-and-error experimental approach («cook and look»)





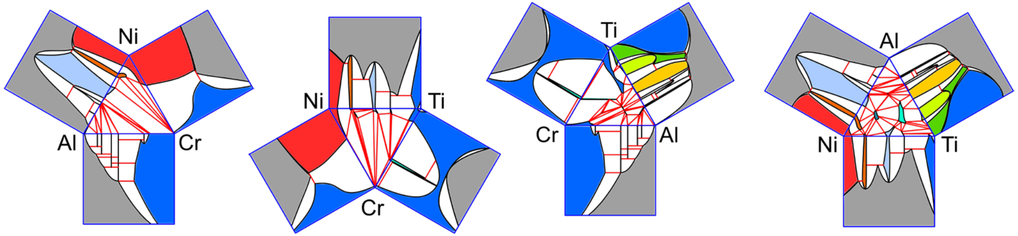
Evolution of the high-temperature capability of the superalloys over a 60 year period since their emergence in the 1940s.

/R.C. Reed, The superalloys – fundamentals and applications, 2006/

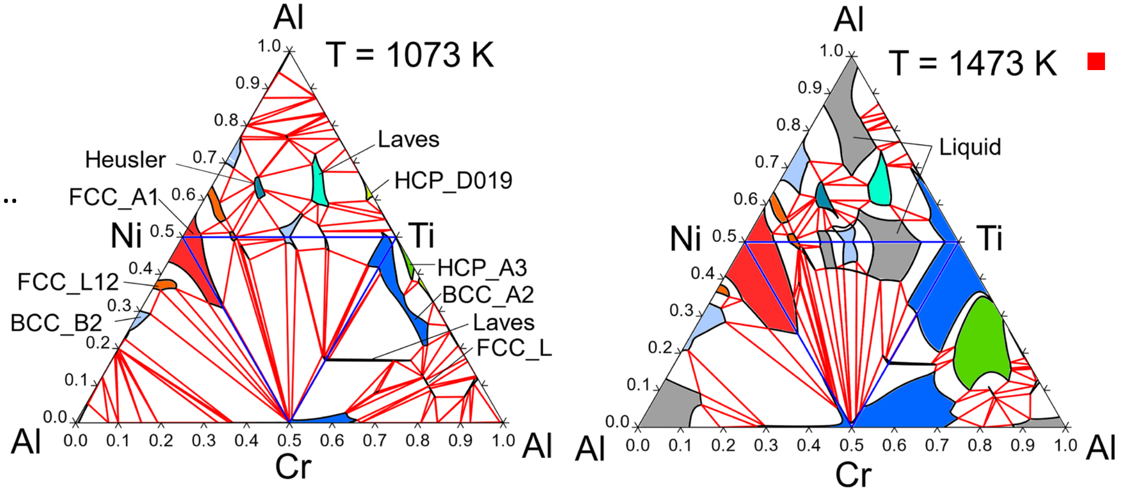
Materials Design

A multi-component problem

From binaries
To ternaries…



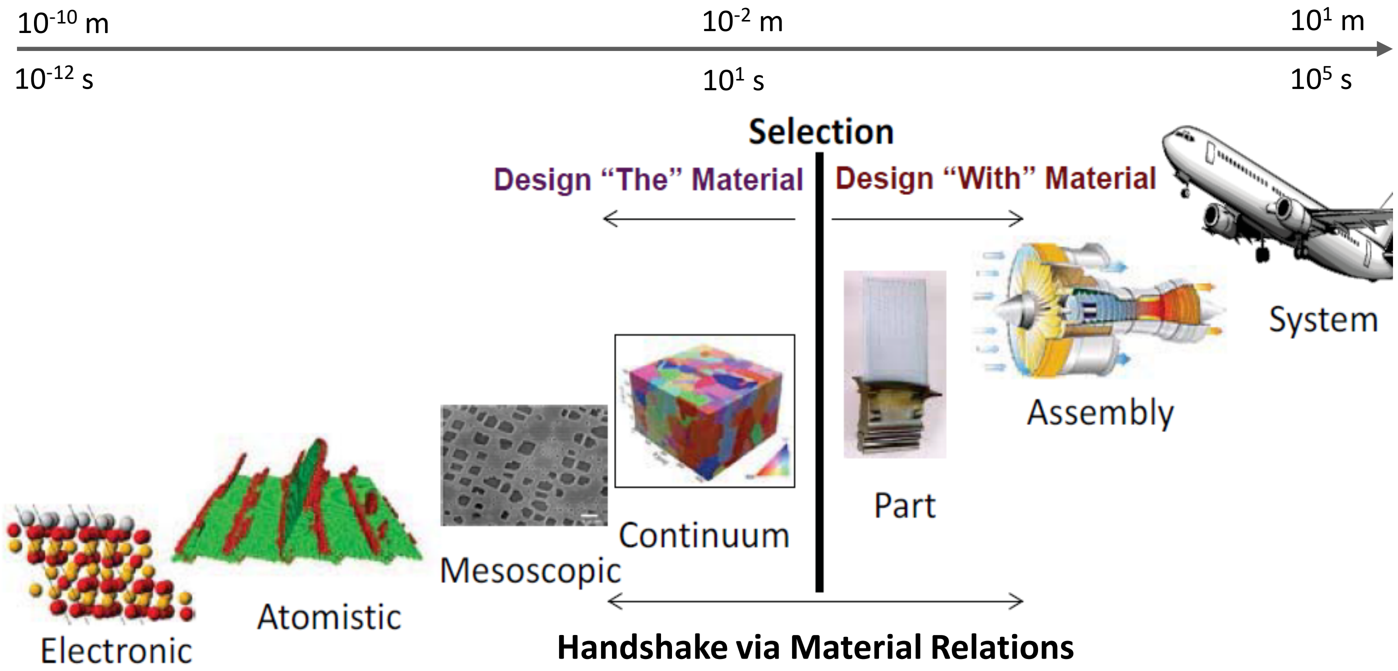
…to quaternaries…



- For example, modern Ni superalloys contain up to 12 elements
- How can we systematically study alloy systems with more than four elements?

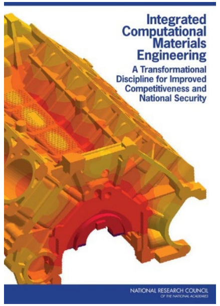
Materials Design

A multi-scale, multi-physics problem



ICME

Integrated Computational Materials Engineering



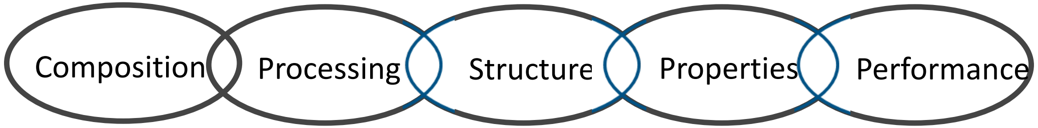
The National Academies Press, 2008

"Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security"

→ Materials Genome Initiative (Obama)

Moving beyond Materials Discovery…

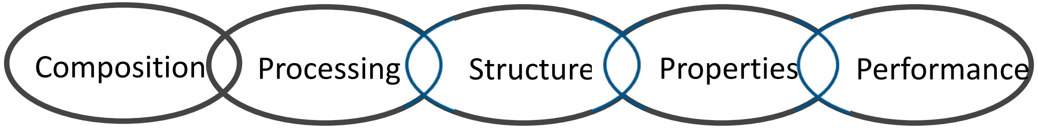
ICME: an approach to design products, the materials that comprise them, and their associated materials processing methods by linking materials models at multiple length scales.



ICME

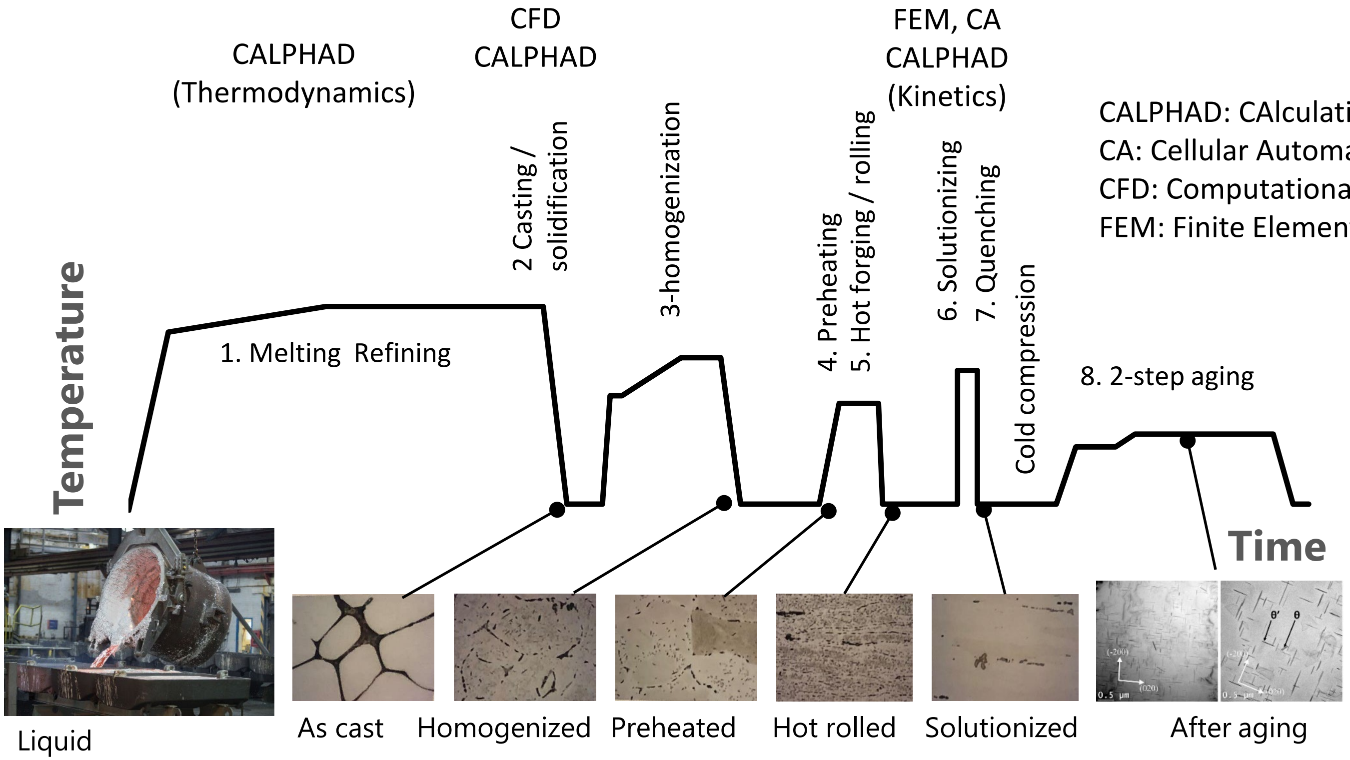
Integrated Computational Materials Engineering

- ICME is the bridging of information from two or more experimentally validated models or simulation codes in which structure–property information passes from one code to another
  - “Horizontal ICME”: the simulation codes connect the sequential materials processes with their associated multiscale structures to their mechanical properties that can be used in the performance life-cycle evaluation so the heterogeneities of the multiscale structures and history are embedded into the simulation codes
  - “Vertical ICME”: the simulation codes connect the multiple length scale cause-effect relationships that are heterogeneous in nature and embedded into the simulation codes
  - “Hybrid ICME”: both Horizontal ICME and Vertical ICME are integrated



Horizontal ICME

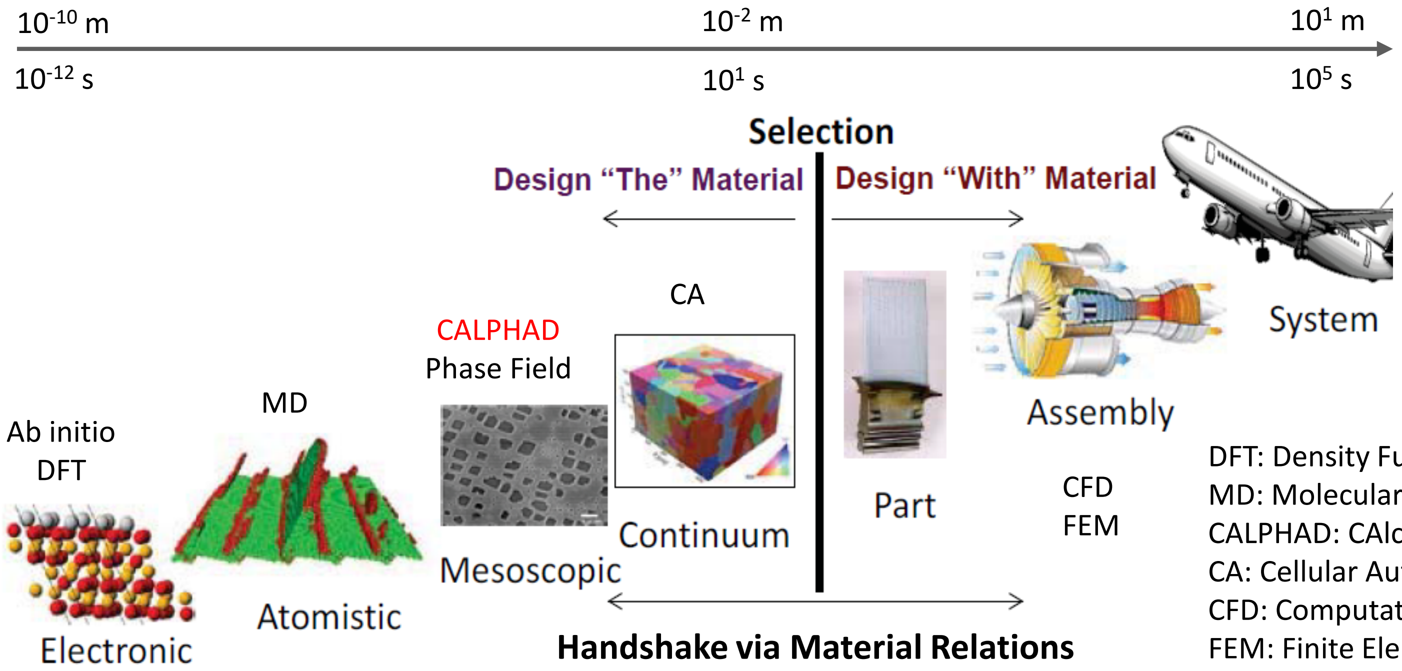
Through-process modeling of metallurgical processes



CALPHAD: CAlculation of PHAse Diagrams
CA: Cellular Automata
CFD: Computational Fluid Dynamics
FEM: Finite Element Methods

Vertical ICME

Multi-scale, multi-physics modeling and simulation

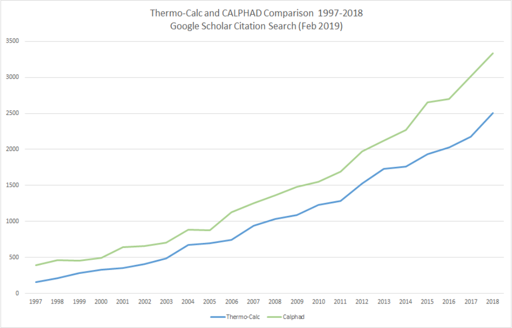


DFT: Density Functional Theory
MD: Molecular Dynamics
CALPHAD: CAlculation of PHAse Diagrams
CA: Cellular Automata
CFD: Computational Fluid Dynamics
FEM: Finite Element Methods

What is CALPHAD?

- What does CALPHAD stand for?
  - Originally «**CAL**culation of **PHA**se **D**iagrams»
  - Now: computer coupling of phase diagrams and thermodynamics

- What is CALPHAD?
  - A phase based approach to modeling the underlying thermodynamics and phase equilibria of a system through a self consistent framework that allows extrapolation to multicomponent systems
  - Captures the composition, temperature and pressure dependence
  - A journal published quarterly by Elsevier Ltd.
  - An international community, and conference held each year with 150-300 active participants from around the world

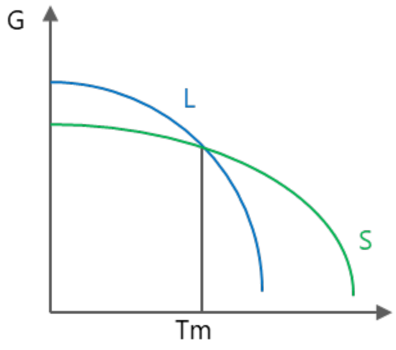


Reminder: Construction of binary phase diagrams

- Binary phase diagrams describe the state of a materials system in **thermodynamic equilibrium** as a function of temperature, pressure and composition

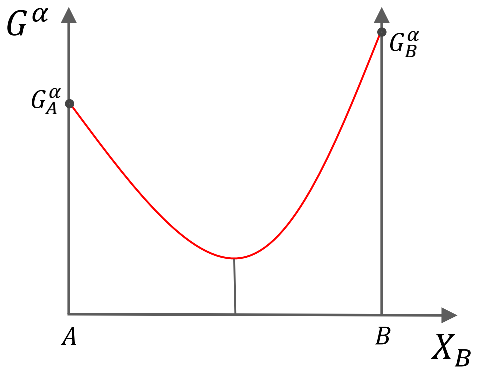
Unary system

- $G = H - TS$



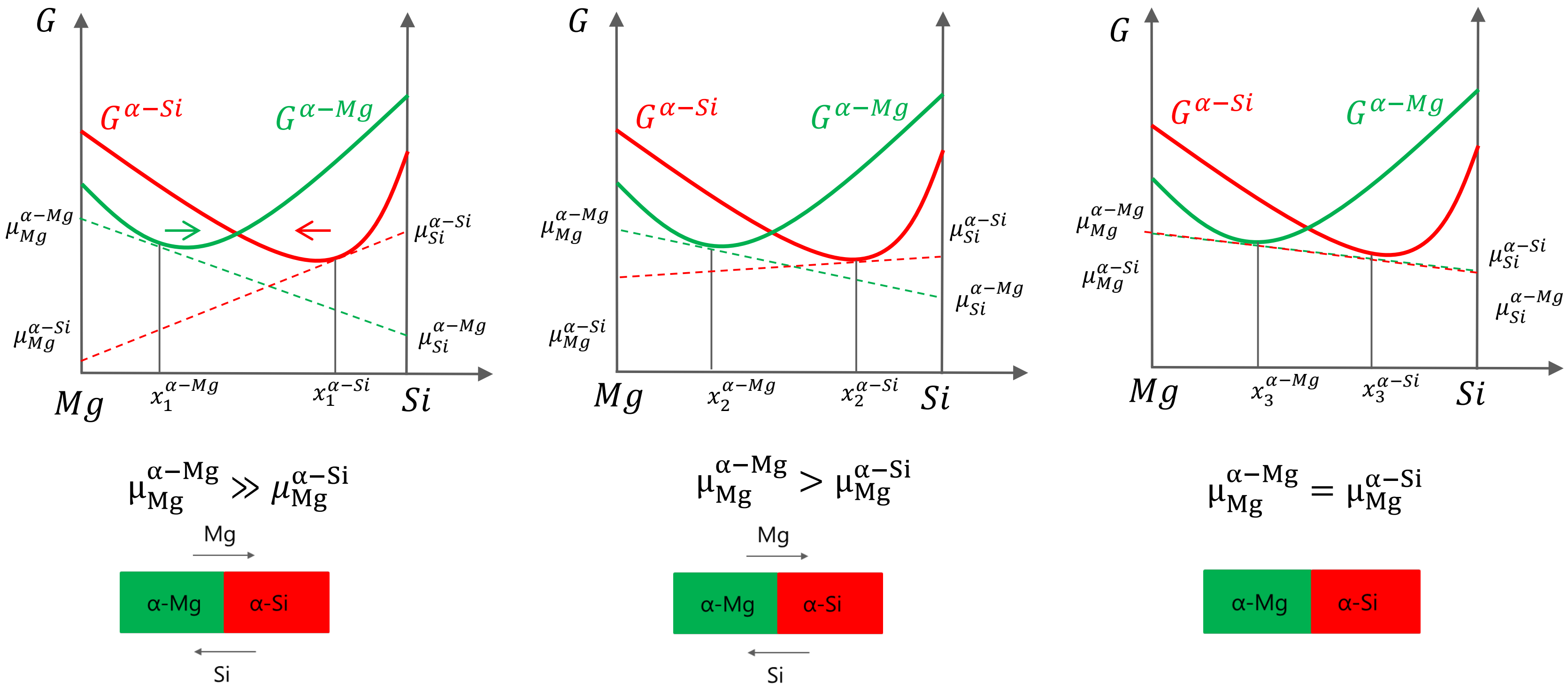
Binary system

- $G_{\alpha} = X_A G_A + X_B G_B + \Delta \boldsymbol{G}_{\mathbf{mix}}$



Reminder: Construction of binary phase diagrams

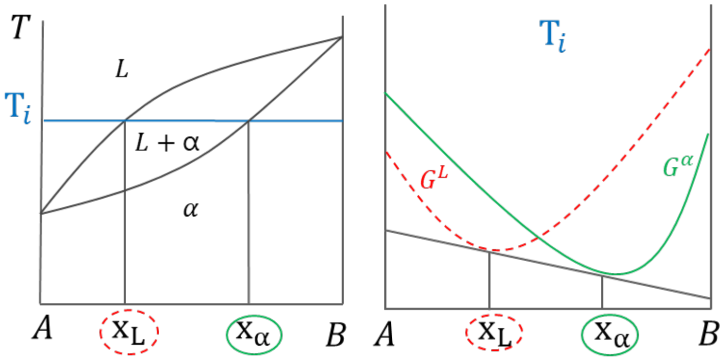
- Binary system (e.g. Si-Mg) → formation of α-Mg and α-Si phases



Reminder: Construction of binary phase diagrams

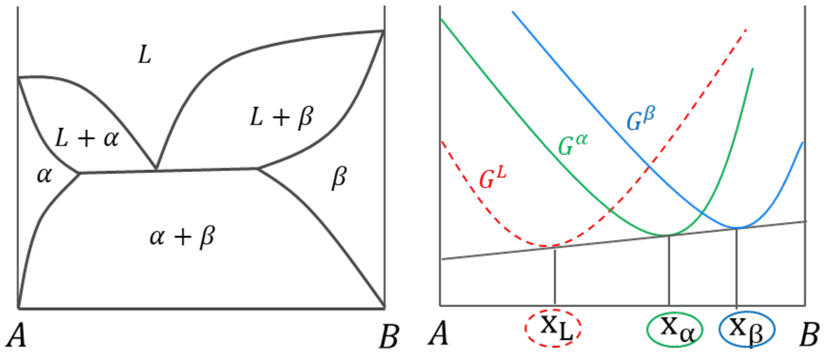
- Binary system (A, B)

  Isomorphous



- Binary system (A, B)

  Non - Isomorphous



What does CALPHAD do?

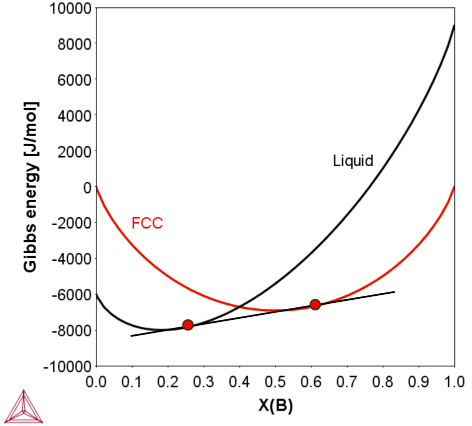
From Gibbs energies to phase diagrams

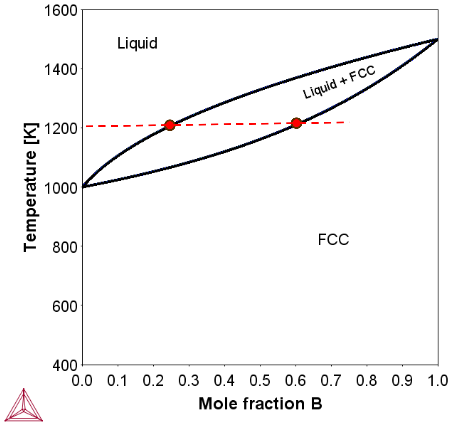
- Phase diagrams can be derived from the Gibbs energy of different phases, which are in equilibrium
- CALPHAD aims at calculating multi-component phase diagrams

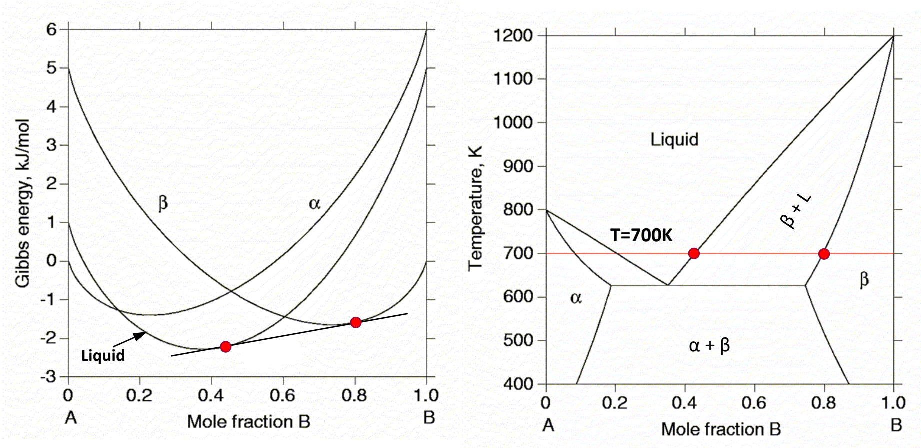
$$G_m^{\alpha}(x)_T = G_m^0 + G_m^{id} + G_m^E$$

$$G_m^{\alpha}(x)_T = x_{\mathrm{A}} G_A^{\alpha} + x_{\mathrm{B}} G_B^{\alpha} + \mathrm{R}T(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}) + x_A x_B \Omega$$

With Ω: interaction parameter



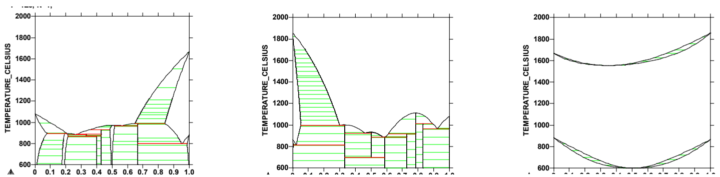




Quantities related to the Gibbs energy

Gibbs energy	$G = G(T, p, N_i)$	**State** of system in function of **T, p** and composition
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*	$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,N_{j\neq i}}$	
Heat capacity	$C_p = \frac{\partial H}{\partial T} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{T,N_i}$	
Thermal expansion	$\alpha = \frac{1}{V}\left(\frac{\partial^2 G}{\partial p\,\partial T}\right)_{N_i}$	
Isothermal compressibility	$\kappa = \frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N_i}$	
Bulk modulus	$B = 1/\kappa$	

The CALPHAD approach



optimised A-B

optimised A-C

optimised B-C

extrapolated A-B-C

optimised A-B-C

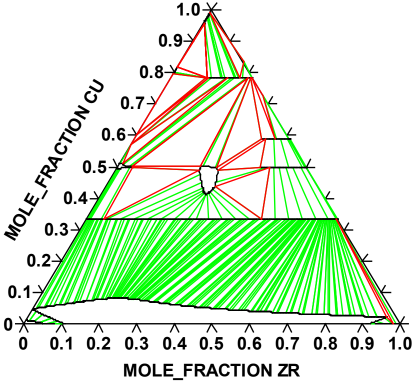
key experimental data estimation

$$G = \sum x_i G_i^0 + RT\, x_i \ln x_i + G^{ex}$$

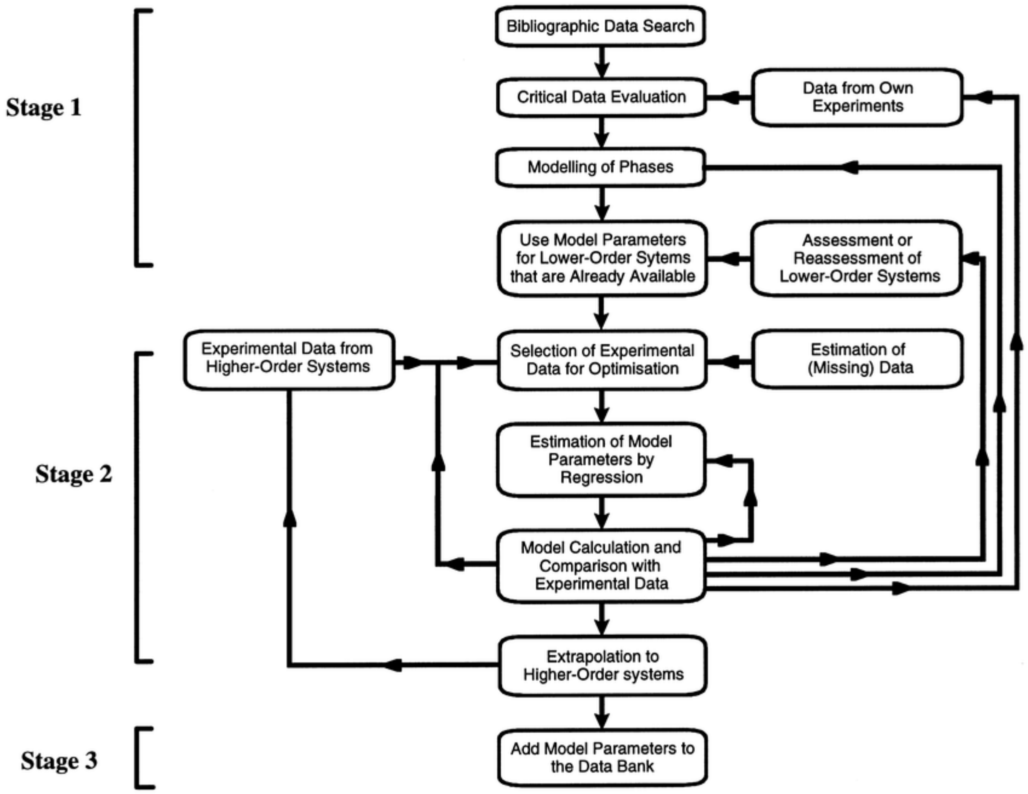
Binary Assessment: G^{ex}_{bin}

Extrapolation $(\sum G^{ex}_{bin})$

Ternary + Assessment: G^{ex}_{ter}



CALPHAD flowchart

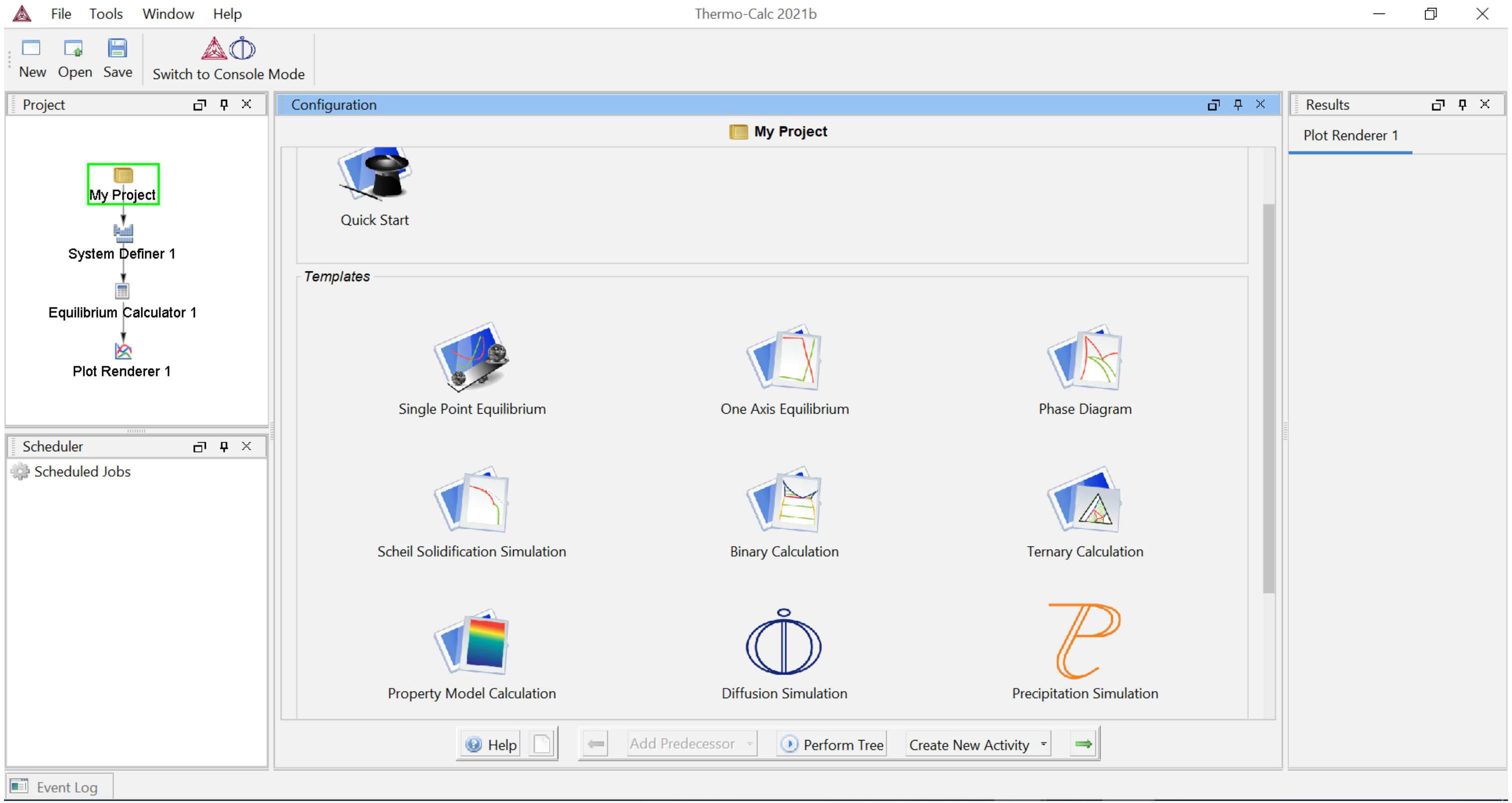


Thermodynamic simulation software

EPFL

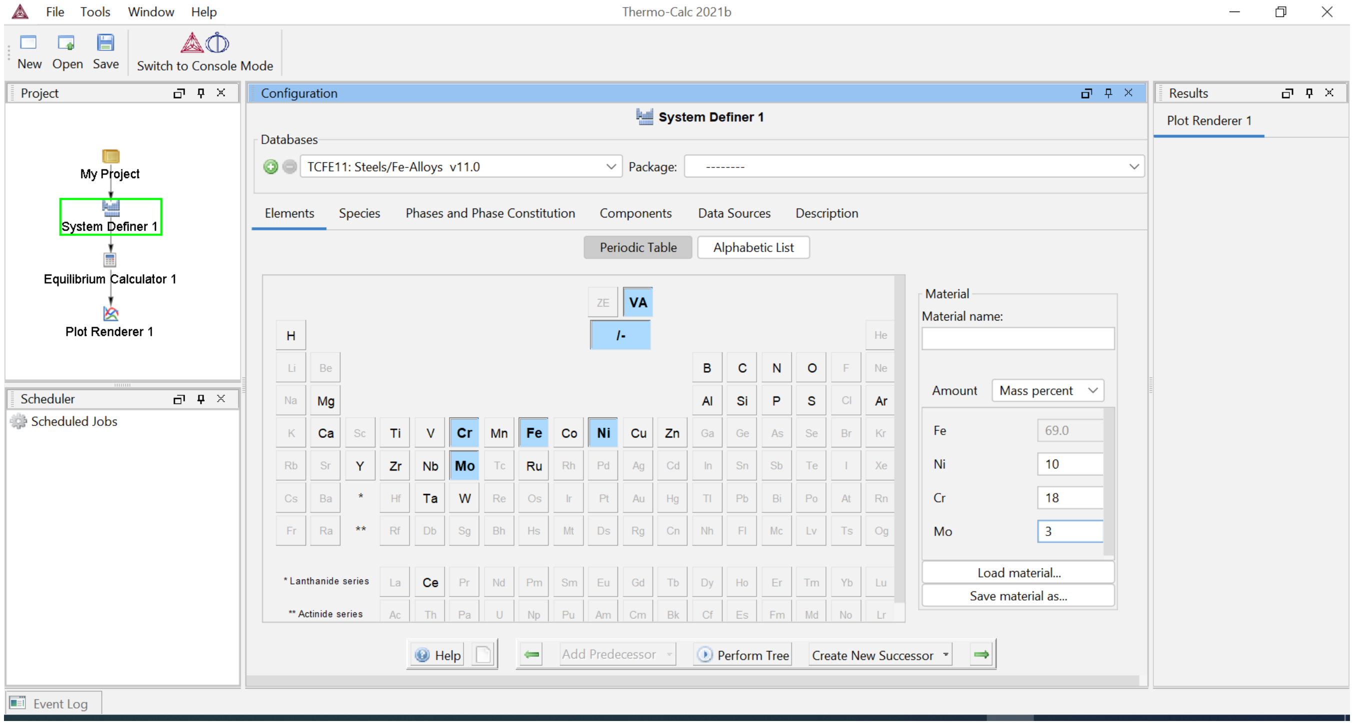
- Thermo-Calc
  / https:// thermocalc.com/
- FactSage
  /www.factsage.com
- Computherm Pandat
  /https://computherm.com/
- JMatPro
  /https://www.sentesoftware.co.uk/jmatpro/
- OpenCalphad
  /http://www.opencalphad.com/

The Thermo-Calc GUI



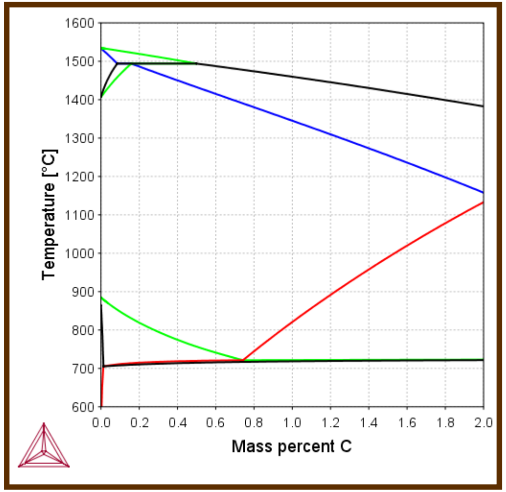
The Thermo-Calc GUI

EPFL



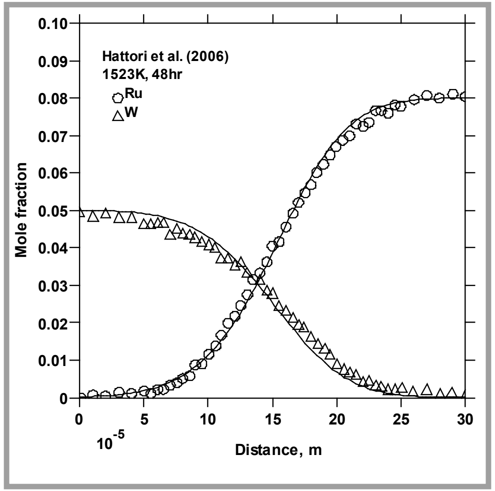
Extensions of CALPHAD

Kinetic simulations: diffusion and precipitation



Gibbs energy
= **Phase diagrams**
(equilibrium & metastable
also driving forces!)

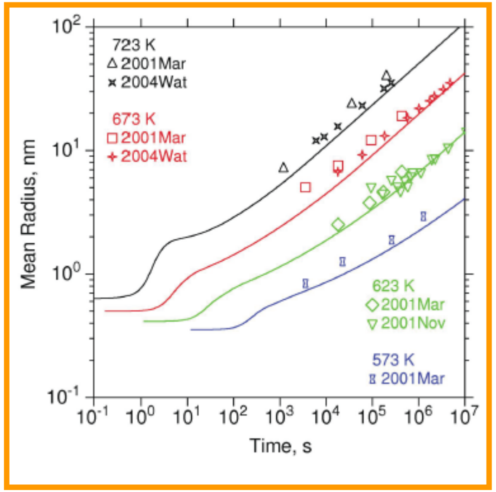
Thermo-Calc software
for thermodynamic properties and phase equilibria



\+ Mobility data
= **Diffusion**

Diffusion
module

DICTRA



\+ Interfacial energy
= **Precipitation**

Precipitation
module

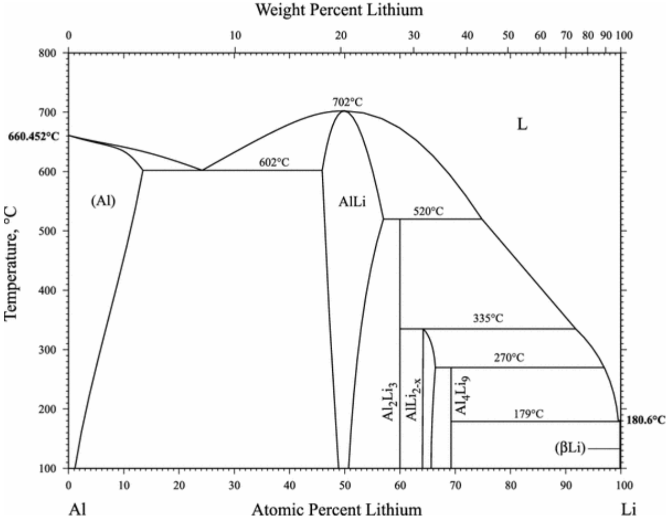
TC-PRISMA

Application of Thermo-Calc

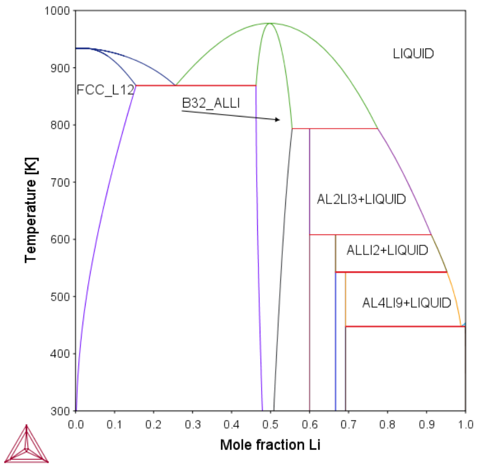
Example: Assessment of binary Al-Li

- Binary phase diagram with 6 phases
- Optimized considering >1000 experimental results + results from ab initio calculations

experimental



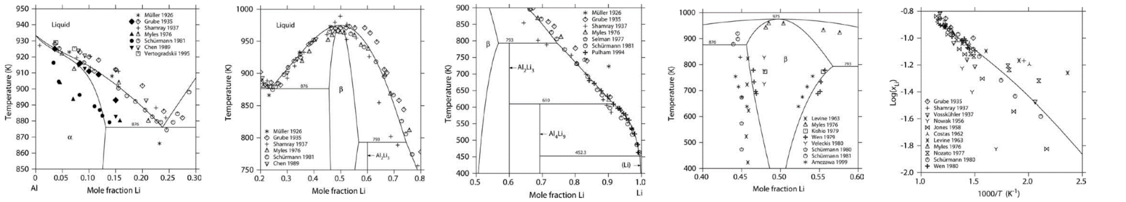
calculated



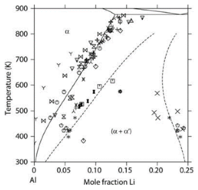
Application of Thermo-Calc

Example: Assessment of binary Al-Li

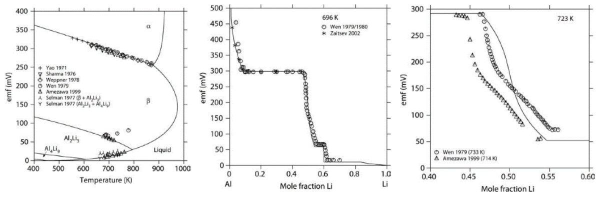
Phase diagram data



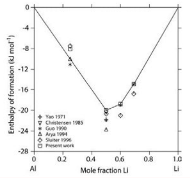
Metastable PD



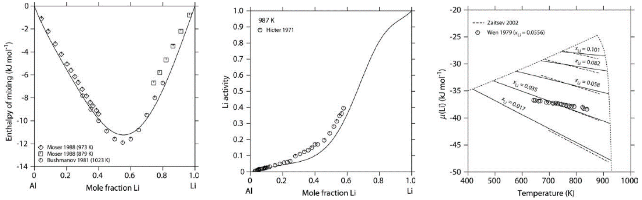
Enthalpy of formation



0 K Lattice stability
(Ab Initio)



Mixing enthalpy, activity data, chem. potential

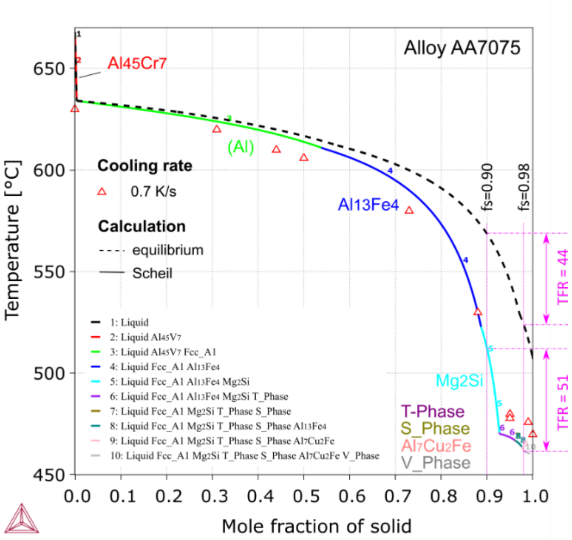


...More than just phase diagrams!

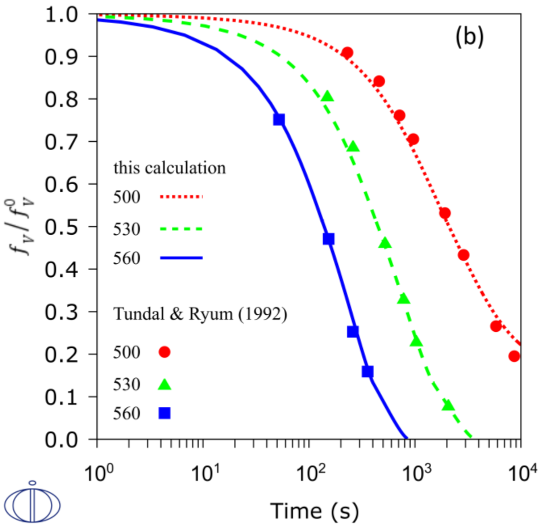
/B. Hallstedt and O. Kim, Int. J. Mat. Res. **98**(10) (2007) 961-969/

Application of Thermo-Calc

Example: Casting and age hardening of Al alloys

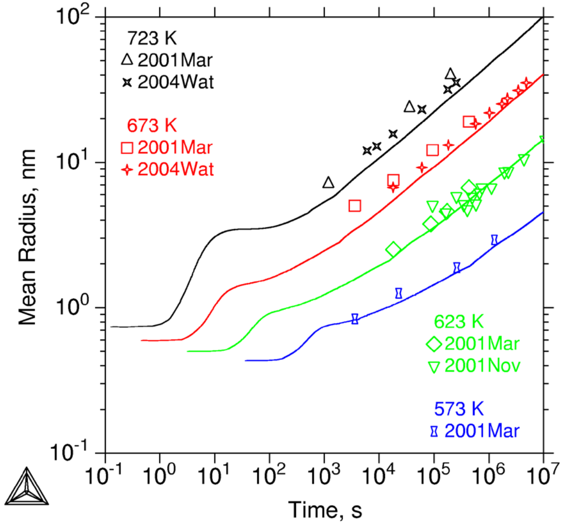


Non-equilibrium solidification of alloy AA7075
CASTING



Dissolution of particles

HOMOGENIZATION



Size distribution of precipitates In Al-Mg-Sc
ANNEALING / AGING