Calphad modeling of liquid phase models & ML support

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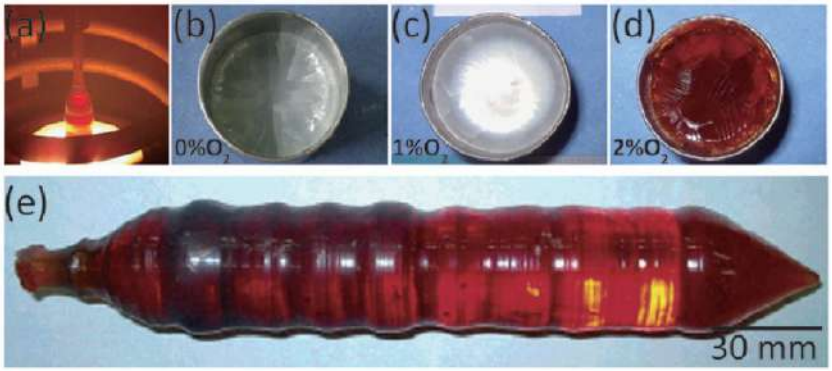
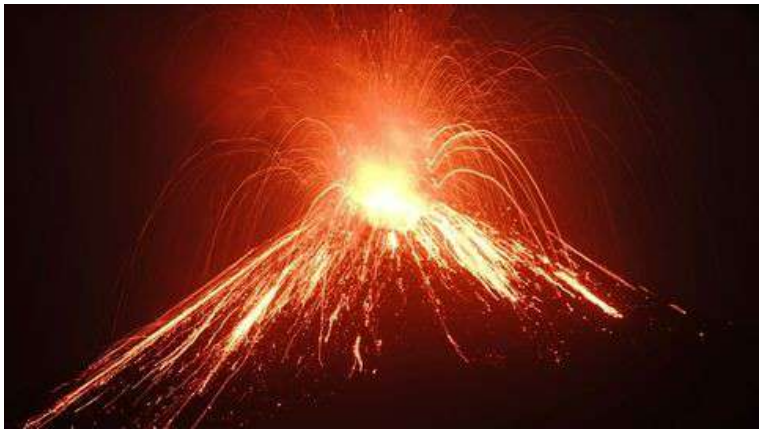
Motivation





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Outline

- The Calphad methodology
- Thermodynamic modeling of liquids
  - First generation - Kaufmann & Bernstein (1970)
  - Second generation - A. Dinsdale (1991)
  - Challenges
- Third generation modeling : adding more physics
  - Einstein model for heat capacity Cp
  - Two-state model for the liquid phase
- Modeling chemical interaction in the liquid phase
  - (Sub) regular solutions
  - Short range order – the ionic liquid model
- Machine learning on chemical interaction in the liquid
- Conclusions & Outlook

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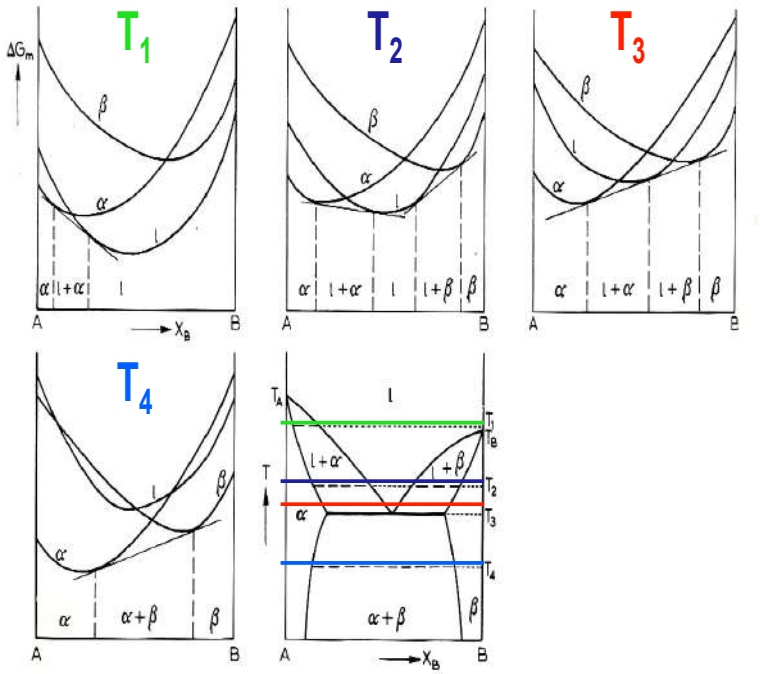
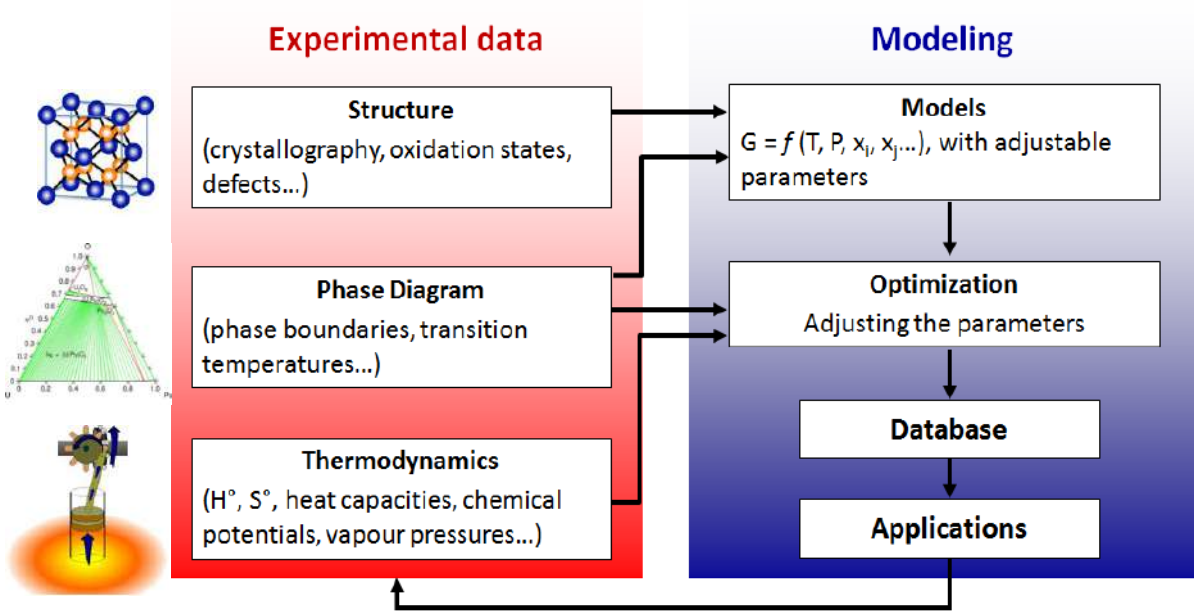
Modélisation thermodynamique : Méthode CALPHAD

⇨ Couplage entre énergies de Gibbs et diagramme de phase





$$\min(G) = \min\left(\sum_{\alpha} m^{\alpha} G_m^{\alpha}(T, p, x_i^{\alpha} or\ y_k^{(l,\alpha)})\right)$$

$$x_i = \sum_{\alpha} m^{\alpha} . x_i^{\alpha}$$

Les fonctions d'énergie de Gibbs des phases sont ajustées par une méthode aux moindres carrés pour reproduire les données exp. (thermodynamiques et de diagramme de phase)

The Calphad method

Calphad allows to

- calculate stable and metastable equilibria in multicomponent systems
- evaluate the coherence of experimental & theoretical data
- Extrapolate to unknown areas in the composition / temperature / pressure space
- link multicomponent thermodynamics to engineering codes : Aspen, ...
- Cover the full temperature range from 0K to (at least) 6000K

Many databases are available

- general purpose databases : SGTE solution, SGTE substance, FTPs,
- databases by chemistry : alloys (ferrous, Al, Mg …), oxides, salts,...
- databases by application : HEA, light metal, solders…
- aqueous solutions

Calphad can not

- Predict unknown compounds & phases
- Give physical meaning to the model parameters

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Modeling of liquid phase -1st generation

L. Kaufman & Bernstein (1970) "Computer Calculation of Phase Diagrams"

- Focus on Refractory metals
- Relative Gibbs energies
  => lattice stabilities

SUMMARY OF FREE ENERGY DIFFEREN

Metal	Free energy difference (cal/g-atom)	Temperature (°K)
Zr	$\Delta F^{\beta \to L} = 4250 - 2.0T$	$\bar{T}^{\beta} = 2125$
	$\Delta F^{\epsilon \to L} = 5280 - 2.9T$	$\bar{T}^{\epsilon} = 1820$
	$\Delta F^{\alpha \to L} = 4480 - 2.9T$	$\bar{T}^{\alpha} = 1544$
	$\Delta F^{\beta \to \epsilon} = -1030 + 0.90T$	$T_0^{\beta\epsilon} = 1144$
	$\Delta F^{\alpha \to \epsilon} = -800$	
	$\Delta F^{\alpha \to \beta} = +230 - 0.90T$	$T_0^{\alpha\beta} = 255$
Hf	$\Delta F^{\beta \to L} = 4990 - 2.0T$	$\bar{T}^{\beta} = 2495$
	$\Delta F^{\epsilon \to L} = 6820 - 2.9T$	$\bar{T}^{\epsilon} = 2351$
	$\Delta F^{\alpha \to L} = 6020 - 2.9T$	$\bar{T}^{\alpha} = 2076$
	$\Delta F^{\beta \to \epsilon} = -1830 + 0.90T$	$T_0^{\beta\epsilon} = 2033$
	$\Delta F^{\alpha \to \epsilon} = -800$	
	$\Delta F^{\alpha \to \beta} = +1030 - 0.90T$	$T_0^{\alpha\beta} = 1144$

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Modeling of liquid phase -2nd generation

CALPHAD Vol. 15, No. 4, pp. 317-425, 1991
Printed in the USA.

0364-5916/91 $3.00 +.00
1991 Pergamon Press plc

SGTE DATA FOR PURE ELEMENTS

A T Dinsdale

Division of Materials Metrology, National Physical Laboratory,
Teddington, Middlesex, TW11 0LW, UK

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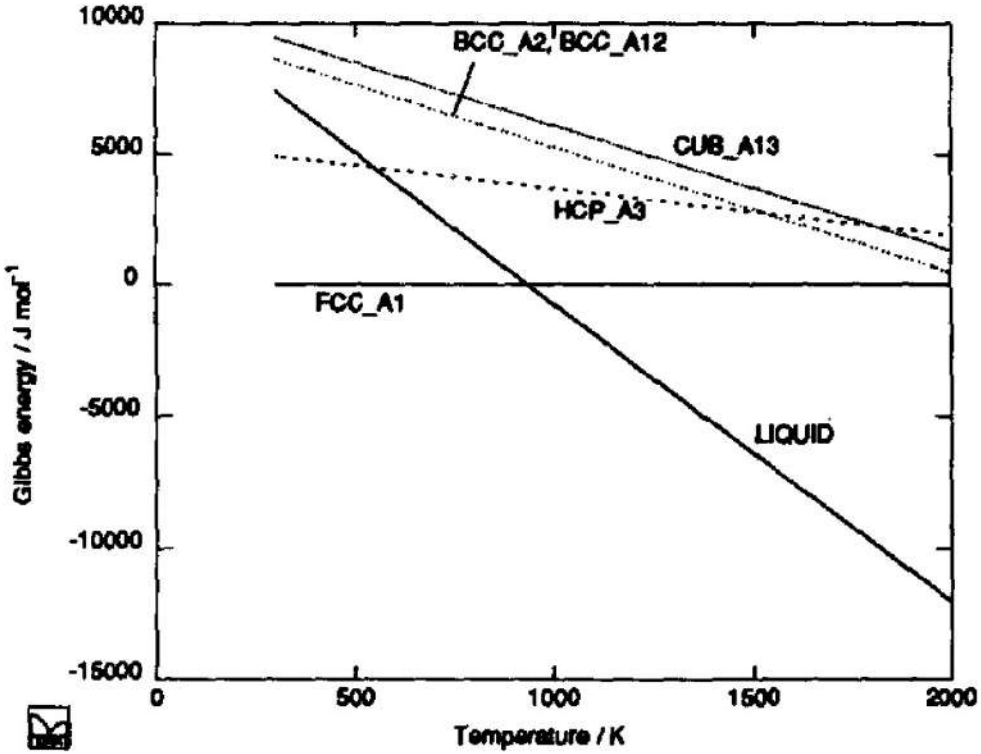
Modeling of liquid phase -2nd generation

$$G = a + b\,T + c\,T\ln(T) + \sum d\,T^{n}$$

$$S = -b - c - c\ln(T) - \sum n\,d\,T^{n-1}$$

$$H = a - c\,T - \sum (n-1)\,d\,T^{n}$$

$$Cp = -c - \sum n\,(n-1)\,d\,T^{n-1}$$



Gibbs energy of phases of Al relative to FCC_A1

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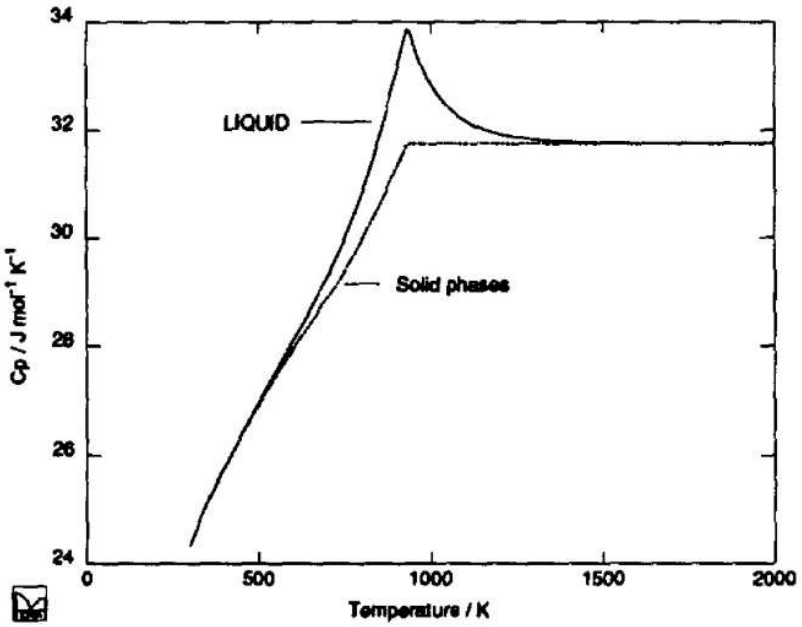
Modeling of liquid phase -2nd generation



Heat capacity of Al

FCC_A1

-7976.15 + 137.093038 T - 24.3671976 T ln(T) - 1.884662E-3 T^2 - 0.877664E-6 T^3 + 74092 T^{-1} *(298.15 < T < 700)*
-11276.24 + 223.048446 T - 38.5844296 T ln(T) + 18.531982E-3 T^2 - 5.764227E-6 T^3 + 74092 T^{-1} *(700 < T < 933.47)*
-11278.378 + 188.684153 T - 31.748192 T ln(T) - 1.231E28 T^9 *(933.47 < T < 2900)*

LIQUID

3028.879 + 125.251171 T - 24.3671976 T ln(T) - 1.884662E-3 T^2 - 0.877664E-6 T^3 + 74092 T^{-1} + 7.934E-20 T^7 *(298.15 < T < 700)*
-271.21 + 211.206579 T - 38.5844296 T ln(T) + 18.531982E-3 T^2 - 5.764227E-6 T^3 + 74092 T^{-1} + 7.934E-20 T^7 *(700 < T < 933.47)*
-795.996 + 177.430178 T - 31.748192 T ln(T) *(933.47 < T < 2900)*

LIQUID relative to FCC

11005.029 - 11.841867 T + **7.934E-20 T^7**
10482.382 - 11.253974 T + **1.231E28 T^9**

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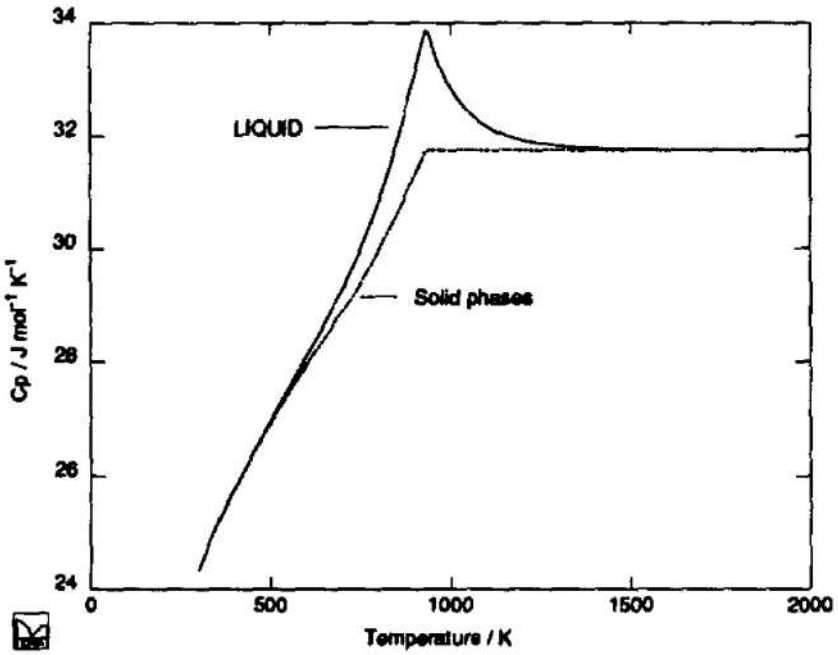
Modeling of the liquid phase - Challenges



Heat capacity of Al

- Break points at melting are unphysical
  - 1st & 2nd derivative are not continuous
  - leads to unwanted kinks in Cp when combined in solid / liquid solutions
- Constant heat capacity for liquid is unphysical, especially at very high T (influence of density)

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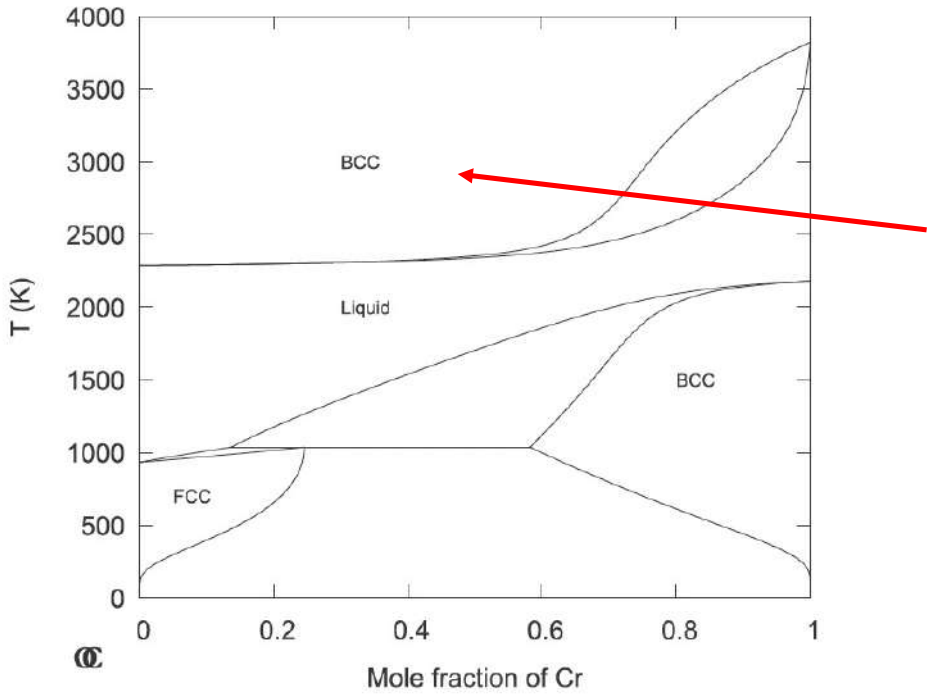
Modeling of the liquid phase - Challenges

No breakpoint at melting point



(a) Al-Cr no break points, no EEC

B. Sundman et al. Calphad 68 (2020): 101737

Stabilization of solid phases at high temperature !

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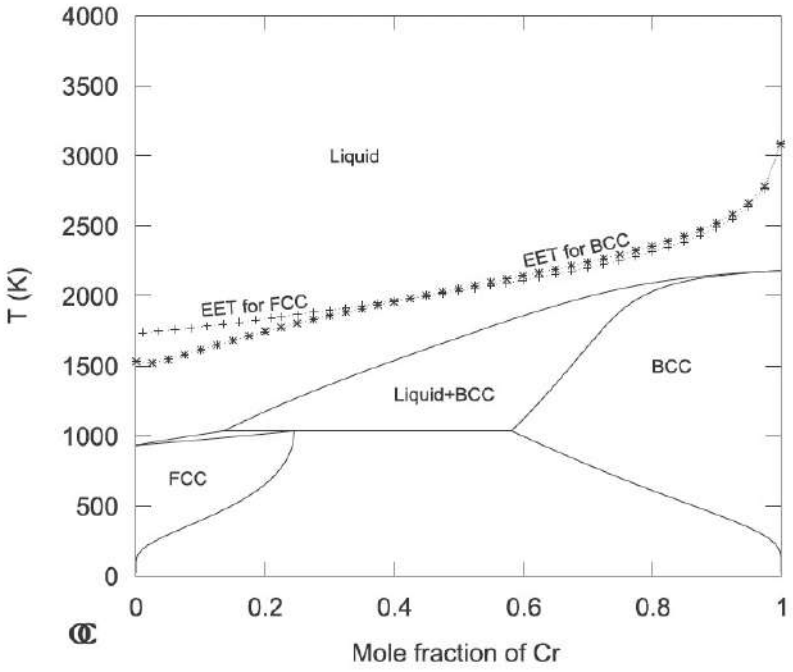
Thermodynamic modeling of the liquid phase - Challenges

Solution I : Equal Entropy Criteria EEC



(b) Al-Cr no break points, with EEC

B. Sundman et al. Calphad 68 (2020): 101737

Gibbs energy minimizer software related

1. Gibbs energy & entropy are checked prior to equilibrium calculation in the full temperature range
2. If S(solid) > S(liquid), the solid phase is withdrawn from the equilibrium calculation

EEC is programmed in OpenCalphad & ThermoCalc

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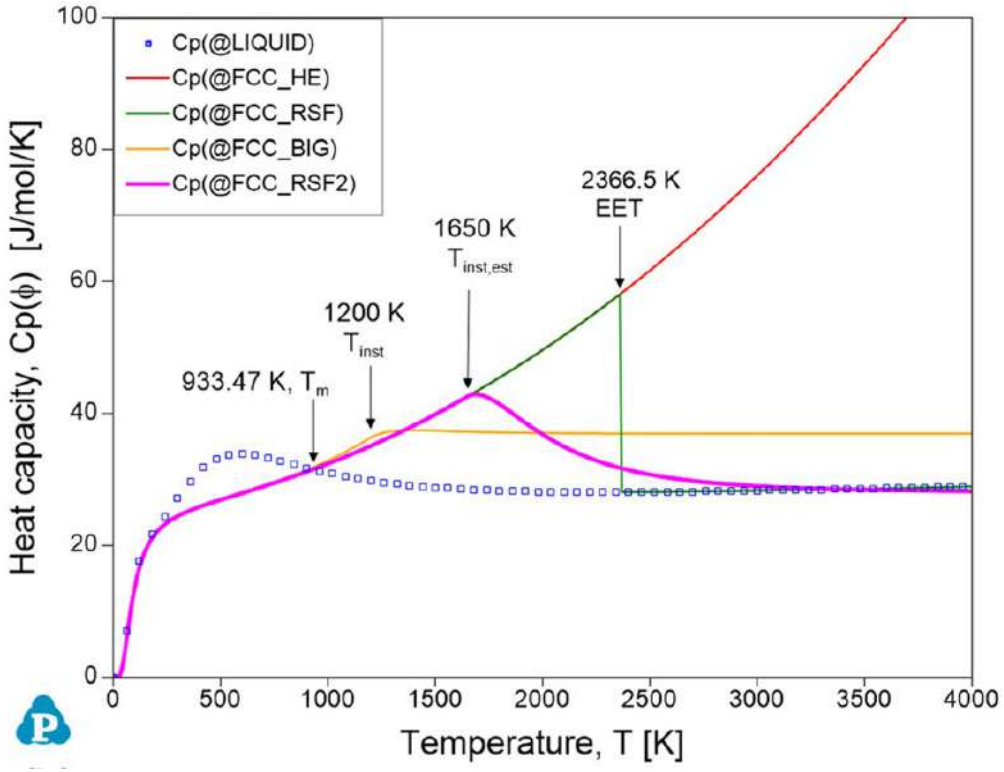
Thermodynamic modeling of the liquid phase - Challenges

Solution II : Extend solid above T_f + change in slope



R. Schmid-Fetzer, JPED 43(3) (2022): 304-316.

Slope change above fusion

- better for solution phases : no/less kinks in Cp curves
- implemented in all softwares
- drawback of 1st and 2nd derivative of G (solid) remains

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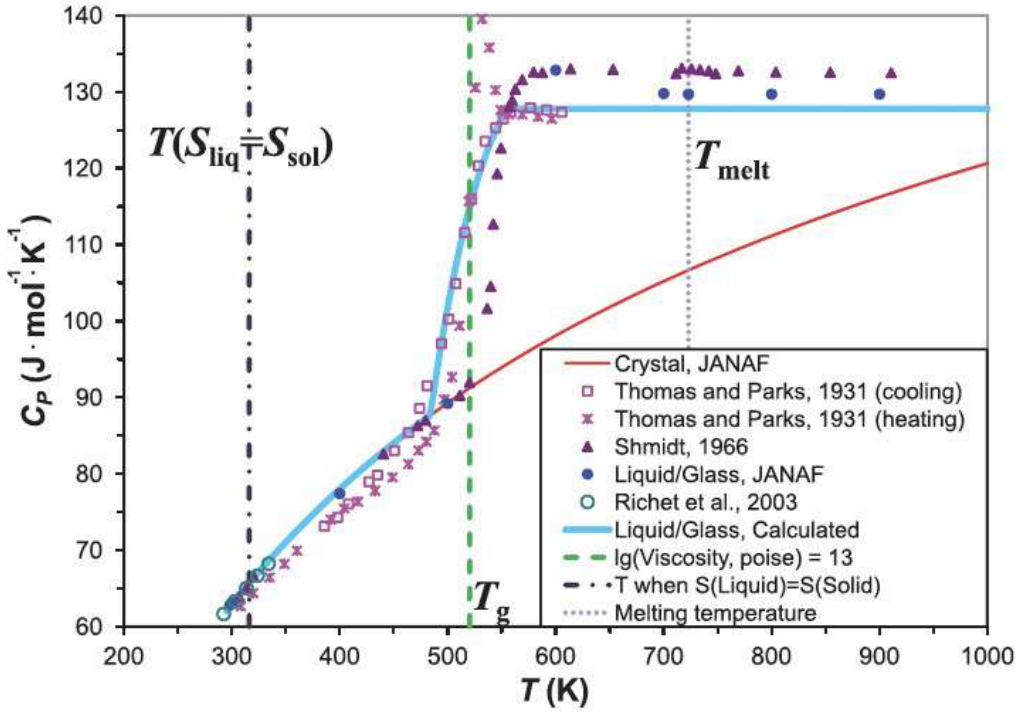
Modeling of the liquid phase - Challenges

Extrapolation of liquid down to RT -> glass transition

B_2O_3



C.A. Becker et al. Physica Status Solidi (b) 251 (2014): 33–52

2nd generation approach

- fitting the glass transition with three polynomial functions
- problem for 1st & 2nd derivative of the Gibbs energy
- problem on extrapolation in multicomponent systems

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Modélisation CALPHAD 3ème génération des liquides unaires

P. Benigni

AFTherMat
Association Française de Thermodynamique des Matériaux

Journées des liquides hautes températures
Paris, 29 novembre 2024

Heat capacity of liquid metals

Stable liquid ($T > T_m$)

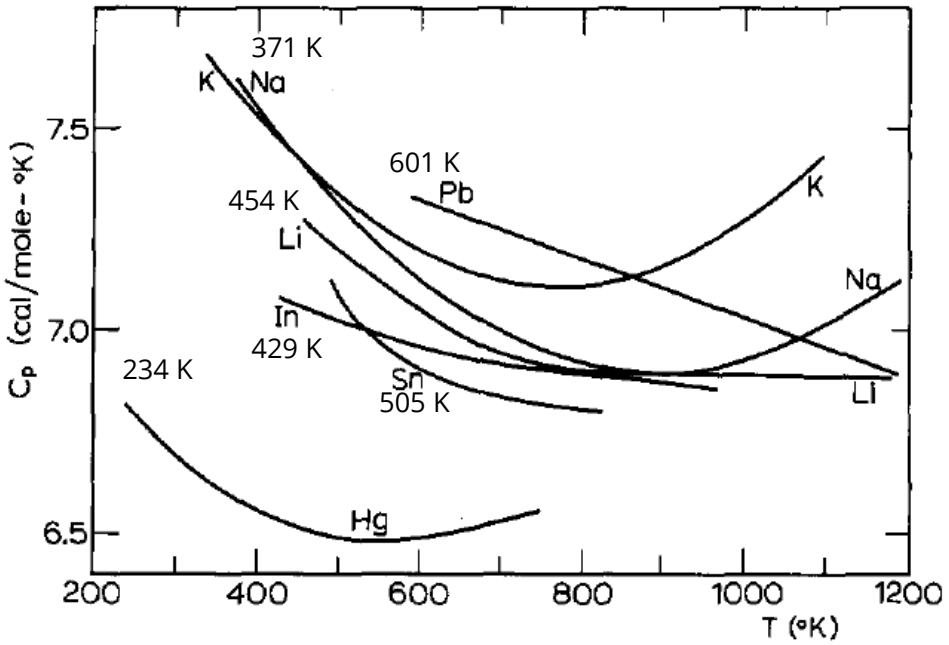


Fig. 1. Heat capacity at constant pressure of liquid metals

T.W. Chapman, The heat capacity of liquid metals, Mater. Sci. Eng. 1 (1966) 65–69

Stable ($T > T_m$) and supercooled liquid ($T < T_m$)

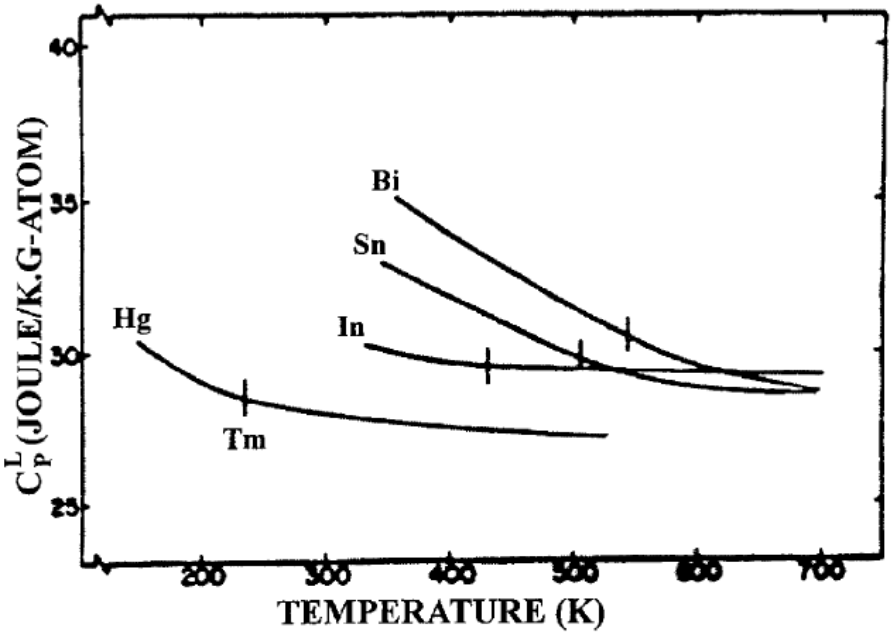
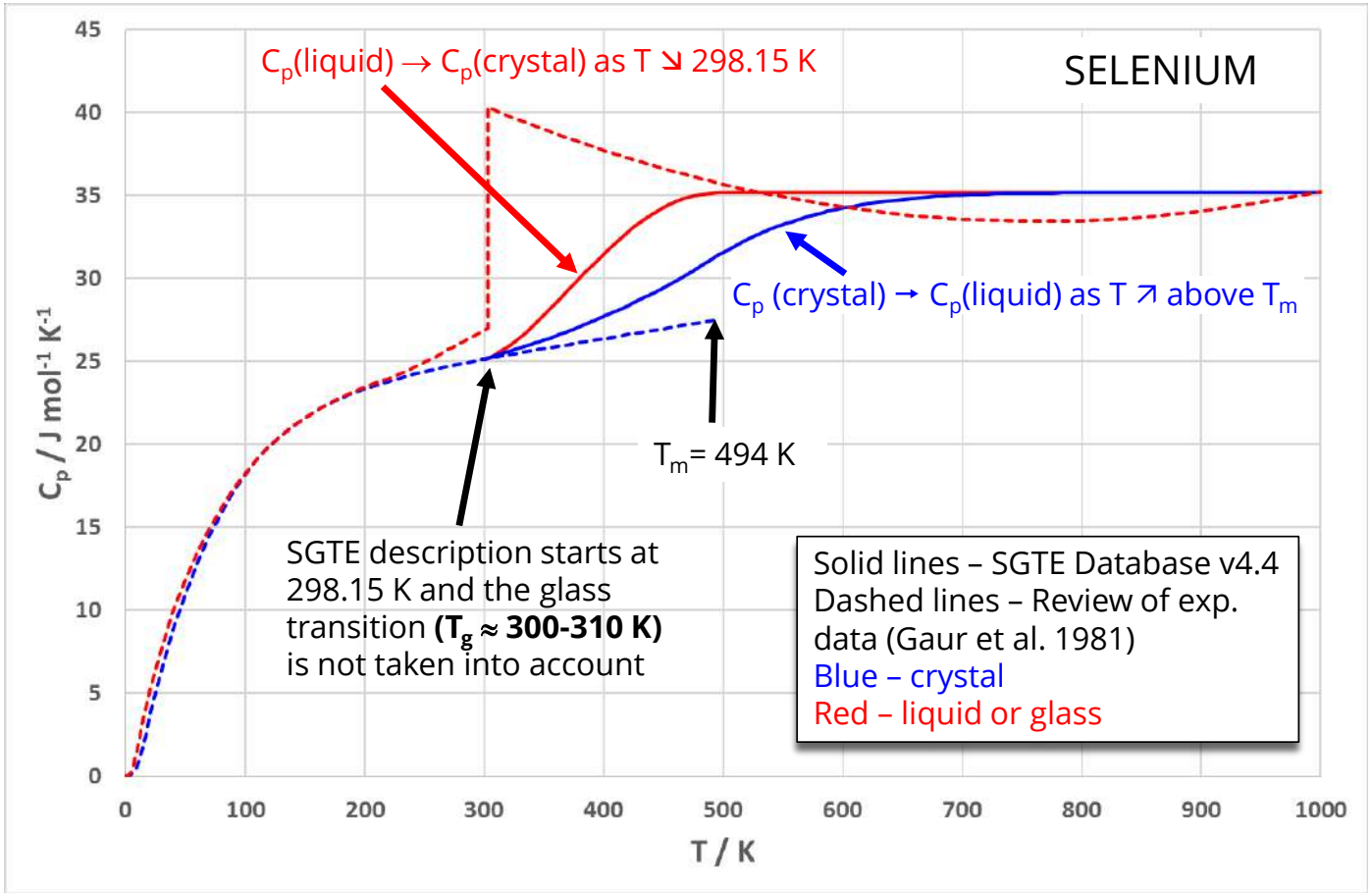


Fig. 3. Heat capacity of several liquid metals as a function of temperature. The vertical marks are the melting temperatures (after Perepezko and Paik [10]).

Heat capacity of pure selenium, a glass forming element

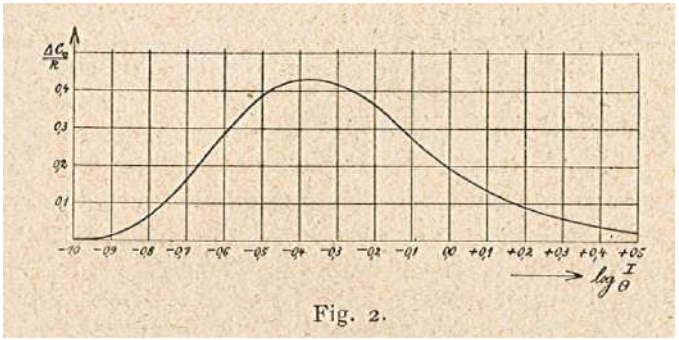
- For each phase, including the liquid, various G analytical expressions are used over different T ranges, with several drawbacks



The 2-state models, 100 years of history

- 2-level models have long been used in statistical physics
- In **crystals**
  - to describe **heat capacity anomalies** at low T (Schottky 1922) or explain some different kind of phase transitions (Strässler & Kittel 1965)
- The application to **liquids** consists in making the hypothesis that a pure substance at the liquid state is made up of 2 types of distinct structural entities
  - which may or may not form an ideal binary solution
- Within the CALPHAD community
  - In 1988, Agren proposed describing the liquid phase using an ideal 2-state model
  - **This choice is finally retained for the 3rd generation CALPHAD descriptions**
- In the glass community
  - 2-state models in various variants are used to describe the liquid phase by many authors: Macedo et al. (1966), Rapoport (1967), Angell & Rao (1972), Ponyatovsky et al. (1994), Moynihan (1997), Ojovan (2008), Holten et al. (2011)…

W. A. Schottky (1886-1976)

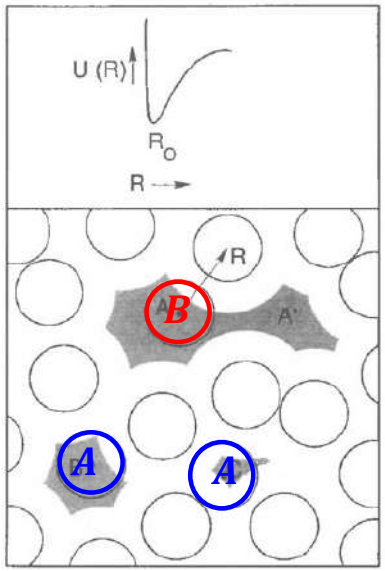


W. Schottky, Über die Drehung der Atomachsen in festen Körpen. (Mit magnetischen, thermischen und chemischen Beziehungen)., Phys. Zeitschrift. 23 (1922) 448–455

The ideal 2-state model

- Key assumption
  - liquid = ideal solution of 2 types of structural entities

(Fig. adapted from Debenedetti 1996 and Zallen 1983)



B = **liquid-like or gas-like** (translation + vibration) = excited state

A = **solid-like** (vibration) = ground state

  - that exchange through an equilibrium : $\boldsymbol{A \rightleftarrows B}$

- The mole fractions ξ_A and ξ_B of A and B vary with the external variable T
- Liquid Gibbs energy: $G_L = \underbrace{\xi_A G_A^\circ + \xi_B G_B^\circ}_{\text{Mechanical mixture}} + \underbrace{RT(\xi_A ln\xi_A + \xi_B ln\xi_B)}_{\text{Ideal entropy of mixing}}$
  - If $\boldsymbol{\xi = \xi_B}$ kept as the single **internal variable** = **non-conservative order parameter**

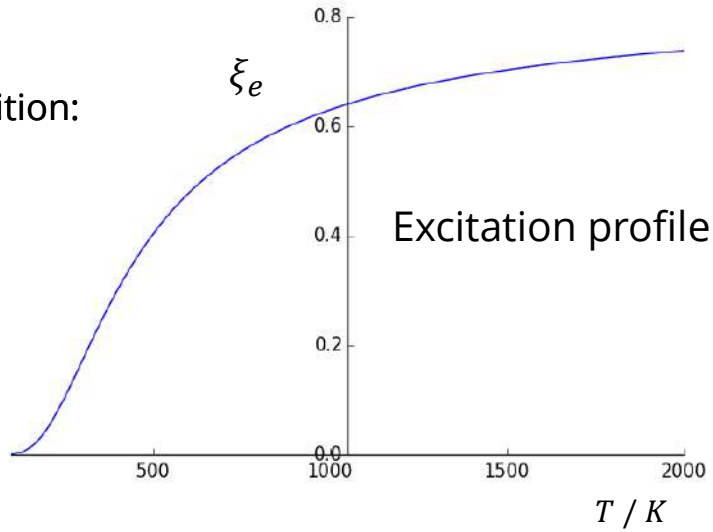
$$G_L = G_A^\circ + \xi \boldsymbol{\Delta G_d} + RT((1-\xi)\ln(1-\xi) + \xi \ln \xi)$$

  - With: $\boldsymbol{\Delta G_d} = G_B^\circ - G_A^\circ$

- The internal equilibrium condition:

$$\left(\frac{\partial G_L}{\partial \xi}\right)_{\xi=\xi_e} = 0$$

Gives: $\xi_e = \frac{1}{1 + exp\left(\frac{\Delta G_d}{RT}\right)}$



Excitation profile

Application to a real substance

- Liquid Gibbs energy : $G_L = G_A^{\circ} - RT\ln(1+\exp(-\Delta G_d/RT))$

- The 100% A phase = metastable liquid in internal equilibrium in which the structural entities only have vibrational degrees of freedom
  - Simple vibrational model based on a weighed sum of Einstein functions

$$C_p(T) = \sum_i 3R\alpha_i \left(\frac{\Theta_i}{T}\right)^2 \frac{e^{\Theta_i/T}}{(e^{\Theta_i/T}-1)^2}$$

$$S(T) = \sum_i 3R\alpha_i \left(\frac{\Theta_i}{T}\frac{e^{\Theta_i/T}}{e^{\Theta_i/T}-1} - \ln\left(e^{\Theta_i/T}-1\right)\right)$$

$$H(T) - H(0) = \sum_i \alpha_i \frac{3R\Theta_i}{e^{\Theta_i/T}-1}$$

  - The Einstein temperatures $\boldsymbol{\Theta_i}$ and corresponding weights $\boldsymbol{\alpha_i}$ are adjustable parameters to be fitted to experimental results

- Gibbs energy difference between the two states
  - CALPHAD type expansion : $\Delta G_d = A + BT + CT\ln T$
  - $A, B, C \ldots$ coefficients to be fitted to experimental results

$$\Delta G_d = \Delta H_d - T\Delta S_d = A + BT + CT\ln T$$

$$\Delta S_d = -B - C(1+\ln T)$$

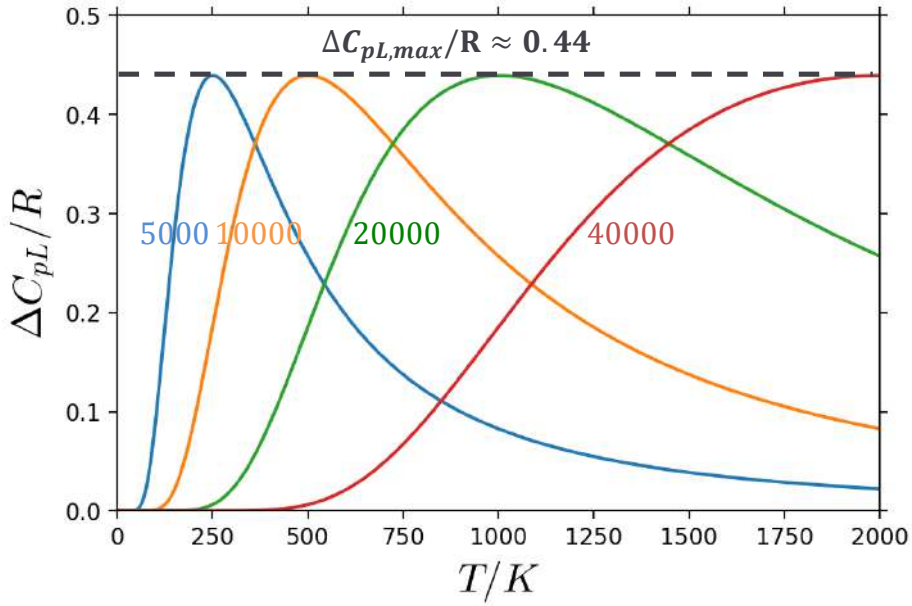
$$\Delta H_d = A - CT$$

$$\Delta C_{pd} = -C$$

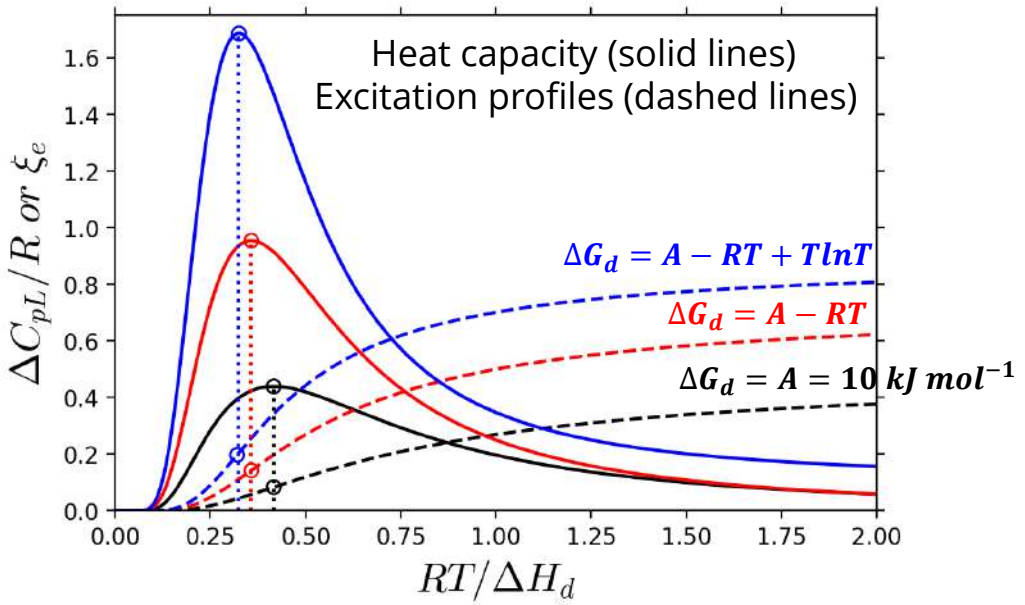
Configurational part (Δ) of the thermodynamic functions of the liquid

- Gibbs energy: $\Delta G_L = G_L - G_A^\circ = -RT\ \ln(1 + \exp(-\Delta G_d/RT))$
  - with: $\Delta G_d = \Delta \boldsymbol{H_d} - T\Delta \boldsymbol{S_d} = \boldsymbol{A} + \boldsymbol{B}T + \boldsymbol{C}T ln\ T$
- Heat capacity: $\Delta C_{pL} = \left(\frac{\partial \Delta H_d}{\partial T}\right)_p \xi_e + \frac{\Delta H_d^2}{RT^2}\xi_e(1-\xi_e)$

Effect of changing $\boldsymbol{A}$ ($J\ mol^{-1}$) with $\boldsymbol{B} = \boldsymbol{C} = \boldsymbol{0}$
Schottky heat capacity hump



Effect of adding $\boldsymbol{B}$ and $\boldsymbol{C}$

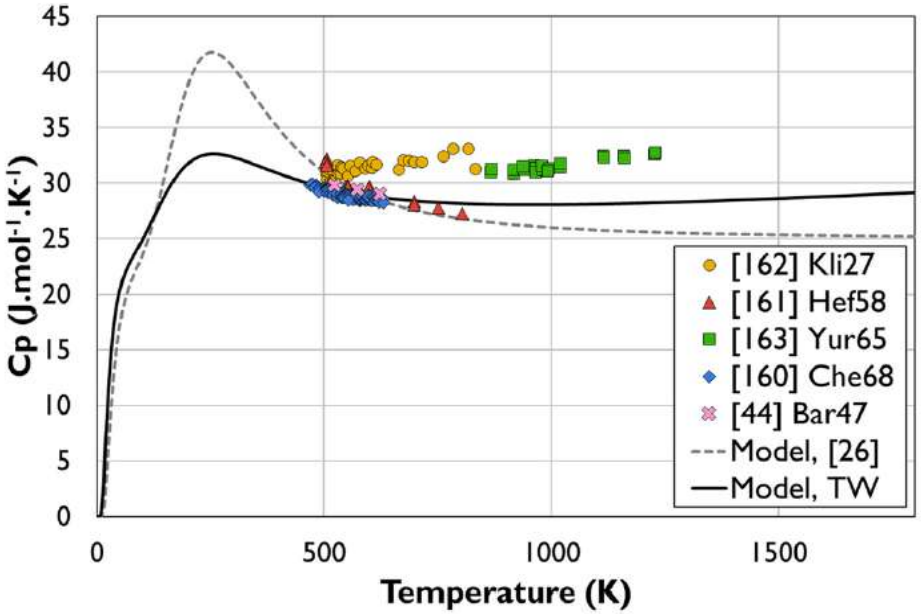


(Dimensionless temperature)

Examples of 3rd generation descriptions of unary liquids

Sn

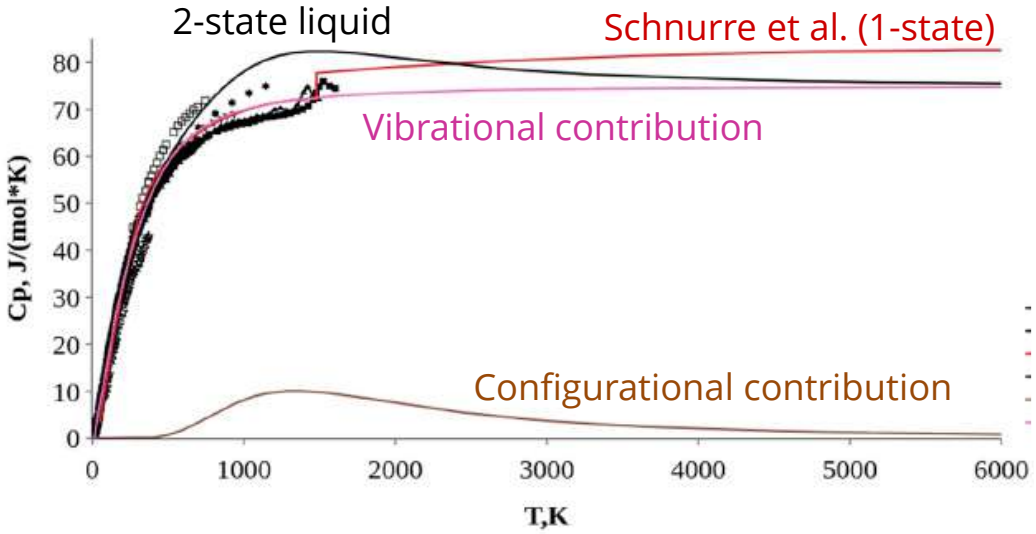
2 different descriptions



G. Deffrennes, P. Faure, F. Bottin, J.M. Joubert, B. Oudot, Tin (Sn) at high pressure: Review, X-ray diffraction, DFT calculations, and Gibbs energy modeling, J. Alloys Compd. 919 (2022) 165675.

SiO_2

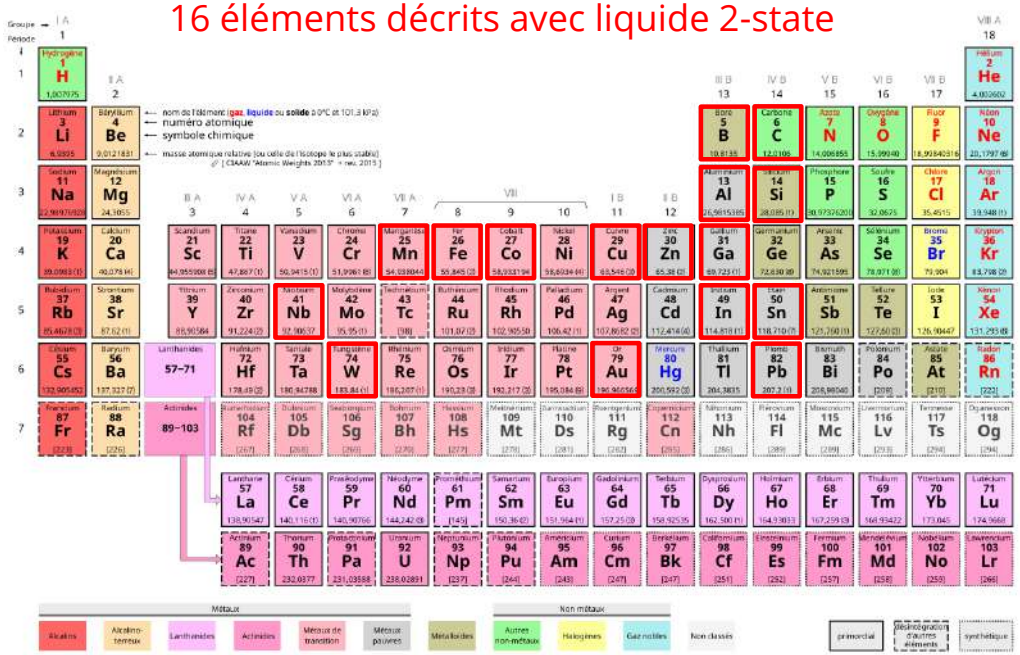
2-state liquid



- The parameters are adjusted so that the peak of the two-state liquid corresponds to the glass transition temperature (around 1480 K)

I. Bajenova, A. Khvan, A. Dinsdale, A. Kondratiev, Implementation of the extended Einstein and two-state liquid models for thermodynamic description of pure SiO_2 at 1 atm, Calphad Comput. Coupling Phase Diagrams Thermochem. 68 (2020) 101716

Conclusions



- Quelques oxydes simples : B_2O_3, CaO, SiO_2, GeO_2
- Quelques systèmes multiconstitués
  - Binaires : Al-C, Al-Zn, B-Fe, Pb-Sn, C-W
  - Ternaire : B-Fe-Nb
- Certaines de ces descriptions adoptent des choix de modélisation ou de paramétrisation discutables
- L'utilisation d'un modèle à 2 états régulier a été proposée
  - pour améliorer la capacité du modèle à représenter les informations expérimentales disponibles
  - pour pouvoir modéliser le polymorphisme liquide

Modeling chemical interaction

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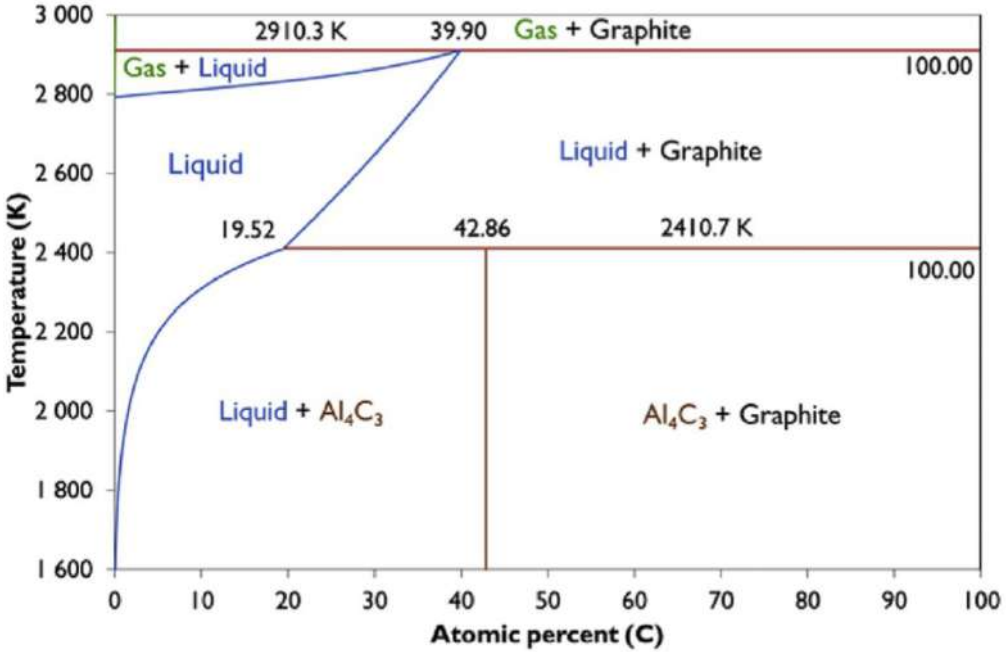
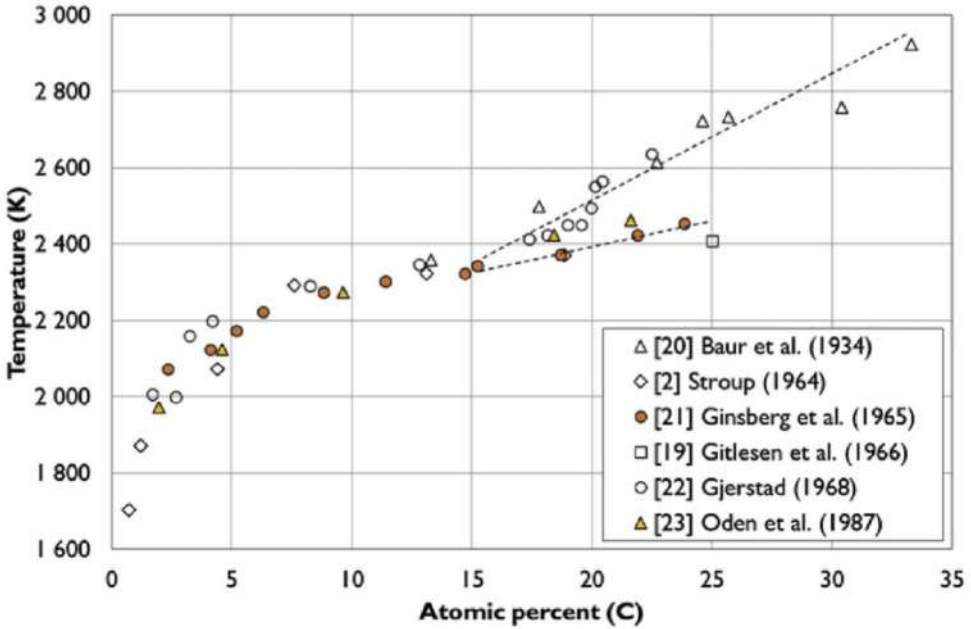
Modeling interaction : (Sub) regular solution





G. Deffrennes et al, Calphad 66 (2019) 101648.

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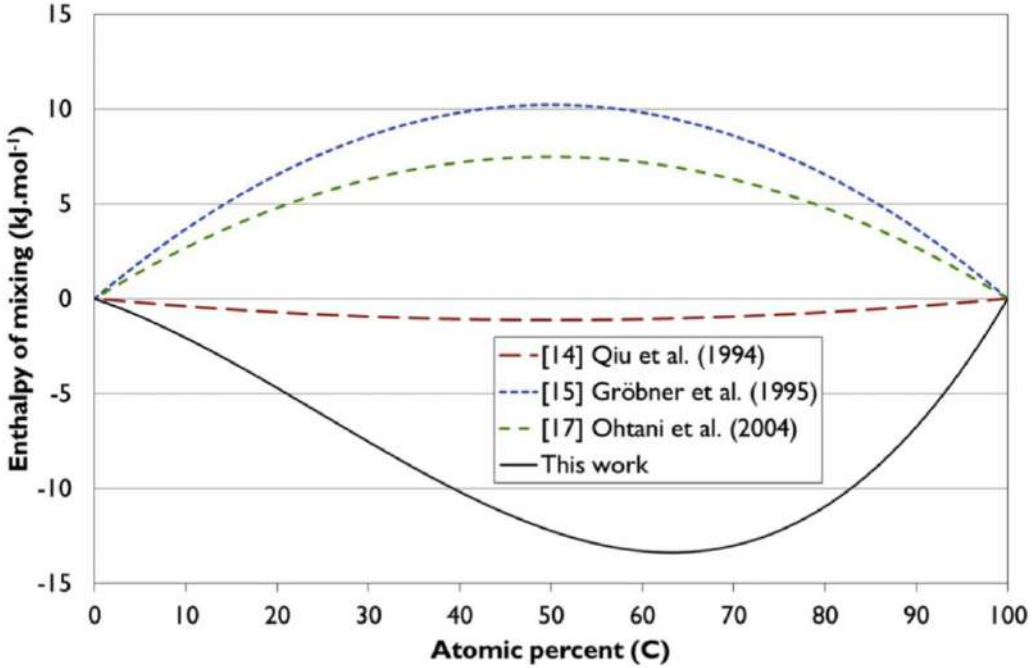
Modeling interaction : (Sub) regular solution

$$G^{Liq} = G^{ref} + G^{ideal} + G^{exc}$$

$$G_m^{Liq}{}_{ex} = x_{Al} x_C \left(L_{Al,C_0}^{Liq} + L_{Al,C_1}^{Liq} (x_{Al} - x_C) \right)$$

$${}^{0}L_{Al,C}^{Liq} = {}^{0}a_{Al,C}^{Liq} + {}^{0}b_{Al,C}^{Liq} T$$

$${}^{1}L_{Al,C}^{Liq} = {}^{1}a_{Al,C}^{Liq}$$



Liquid, Redlich-Kister, (Al, C)

${}^{0}L_{Al,C}^{Liq}$	[14] Qiu et al. (1994)	−4426	−11.1007
	[15] Gröbner et al. (1995)	+40861.02	−33.21138
	[17] Ohtani et al. (2004)	+29910	−25.586
	This Work	−48892	+1.15
${}^{1}L_{Al,C}^{Liq}$	This Work	+32543	–

G. Deffrennes et al, Calphad 66 (2019) 101648.

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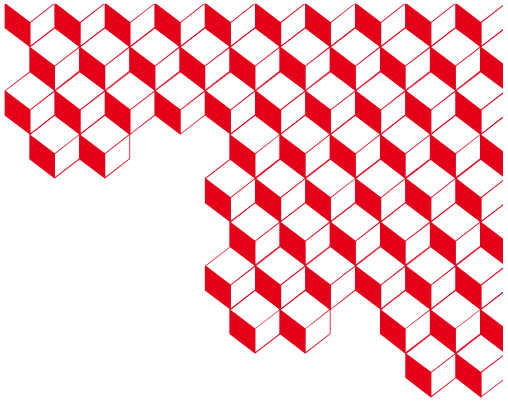


Modèle ionique pour décrire les liquides

Christine Guéneau

Université Paris-Saclay, CEA, Service de Recherche en Corrosion et Comportement des Matériaux
Gif-sur-Yvette, France

Partially ionic two sublattice model

✓ Possibilité de décrire des liquides métalliques et non métalliques (oxydes, sulfures, chlorures …)

➡ **2 sous-réseaux $(C_i^{ci+})_P (A_j^{aj-}, Va^{-Q}, B_k^{0})_Q$**

cation anions lacunes espèces neutres

➡ Introduction de lacunes chargées (-Q) pour décrire le liquide métallique $(C_i^{ci+})_P (Va^{-Q})_Q$

➡ La charge des lacunes (-Q) varie avec la composition pour maintenir la relation d'eléctroneutralité

$$P = \sum a_j \, y_{A_j} + Q \, y_{Va}$$

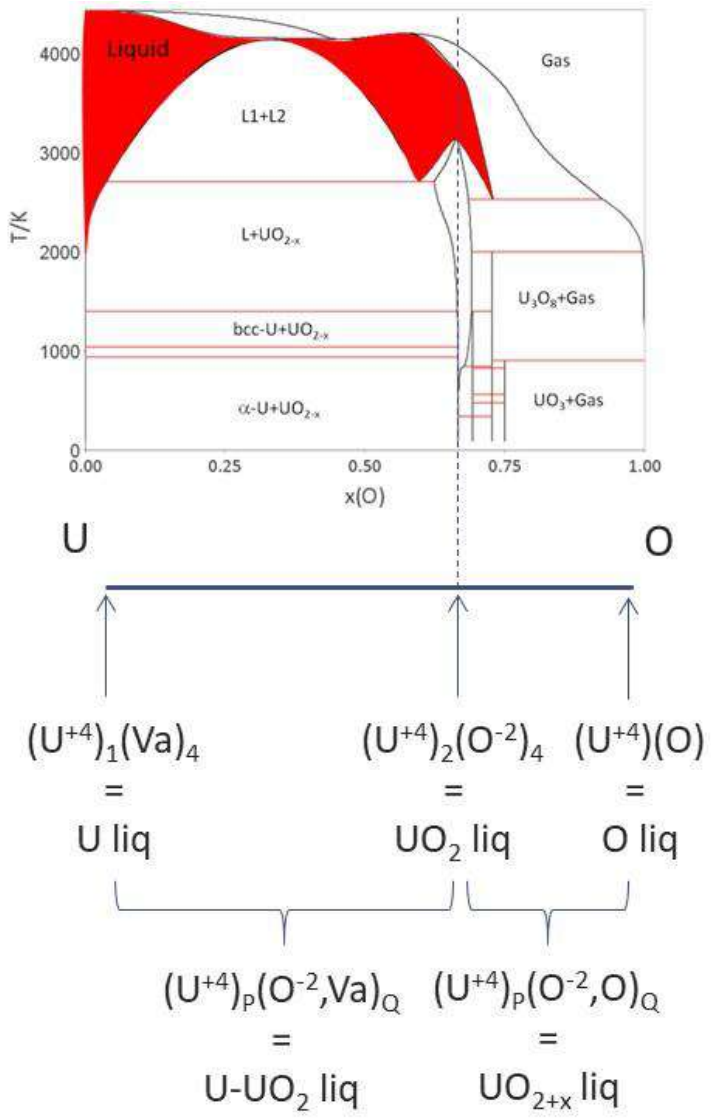
$$Q = \sum c_i \, y_{C_i}$$

➡ L'ordre à courte distance est pris en compte par l'introduction d'espèces chargées

Exemple: $(Ba^{+2})(MoO_4^{-2})$

[Hillert et al, Metall. Trans. A16 (1985) 261]

Exemple: Système U-O



➡ **Two ionic sublattice model $(U^{+4})_P(O^{-2},Va^{-Q},O)_Q$**

$$P = 2y_{O^{-2}} + Qy_{Va^{-Q}}$$
$$Q = 4$$

P = Charge moyenne du sous-réseau 2

Q = Charge moyenne du sous-réseau 1

$$G_m^{Liq} = y_{U^{+4}} y_{O^{-2}} G^0_{(U^{+4})_2(O^{-2})_4} + y_{U^{+4}} y_{Va} G^0_{(U^{+4})_1(Va)_4} + y_{U^{+4}} y_O G^0_O + QRT\left(y_{O^{-2}} \ln y_{O^{-2}} + y_{Va} \ln y_{Va} + y_O \ln y_O\right) + G_m^{Excess}$$

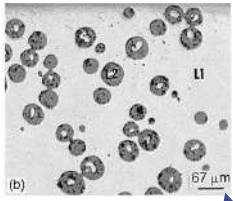
⬅ Endmembers

⬅ Paramètres d'interaction

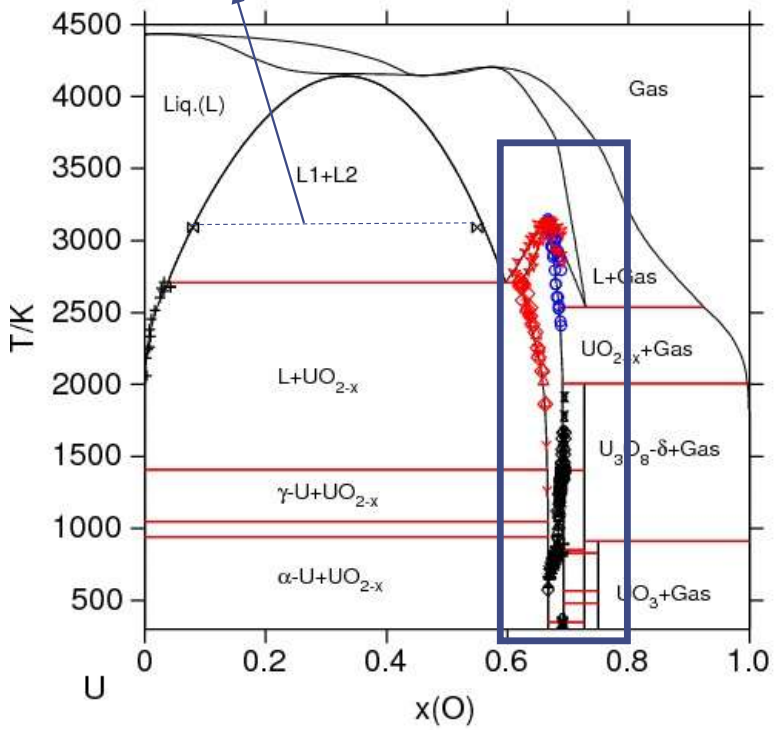
Aucune donnée sur le liquide
Excepté le Cp de UO_2 liquide

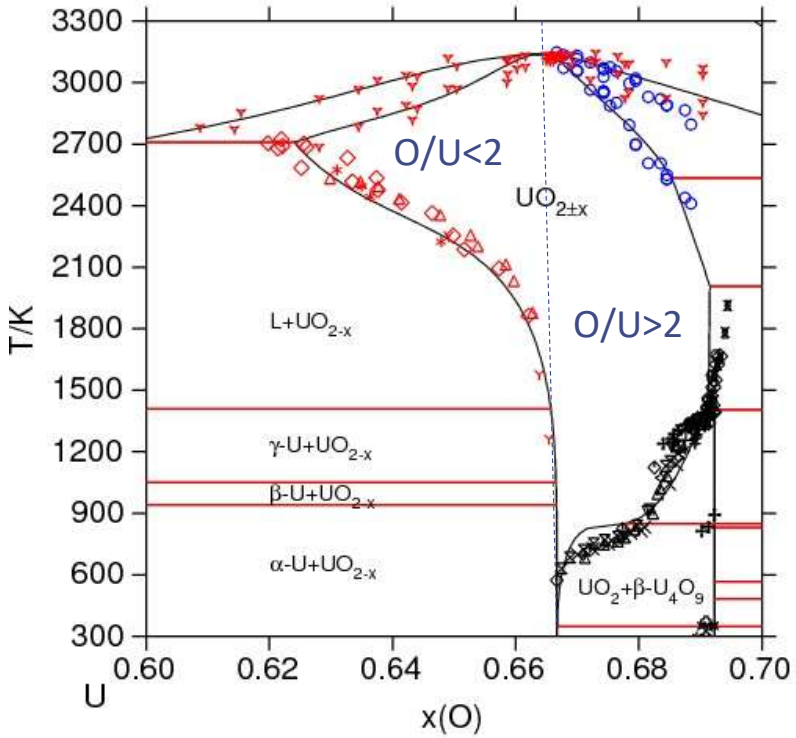
[Guéneau et al, JNM 419 (2011) 145]

Diagramme de phase U-O



L1+L2





⇨ T fusion de UO_2 très élevée = 3120 K

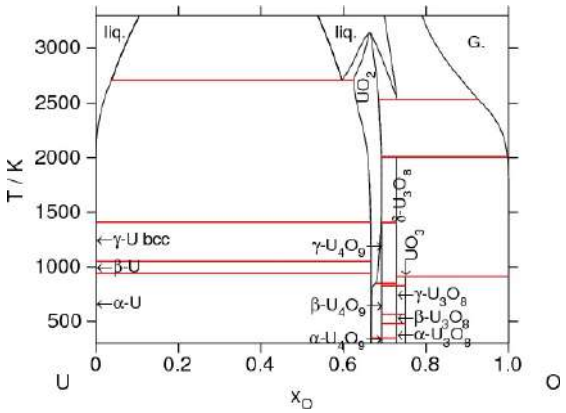
⇨ **T solidus / liquidus ↘ avec x dans $UO_{2\pm x}$**

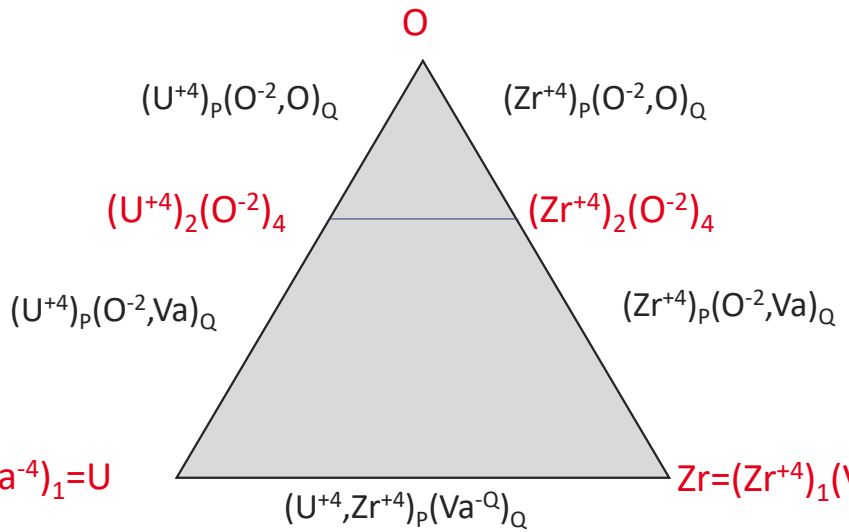
⇨ **Lacune de miscibilité à l'état liquide (L1+L2)**

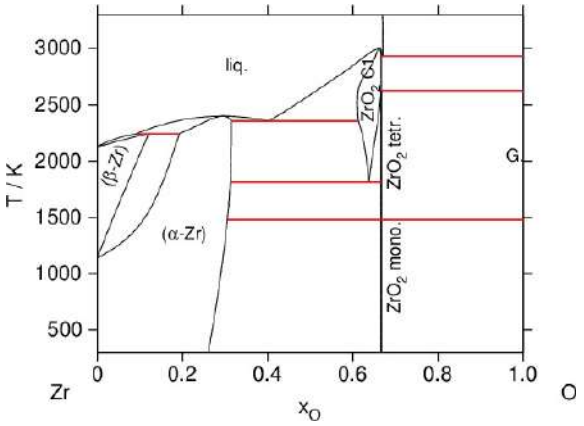
[Guéneau et al, J. Nucl. Mater. 254 (1998) 158
Guéneau et al, J. Nucl. Mater. 419 (2011) 145]

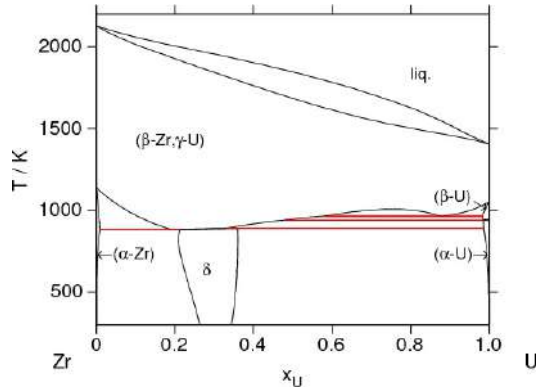
Exemple: Système U-Zr-O

➡ Model $(U^{+4},Zr^{+4})_P(O^{-2},Va^{-Q},O)_Q$







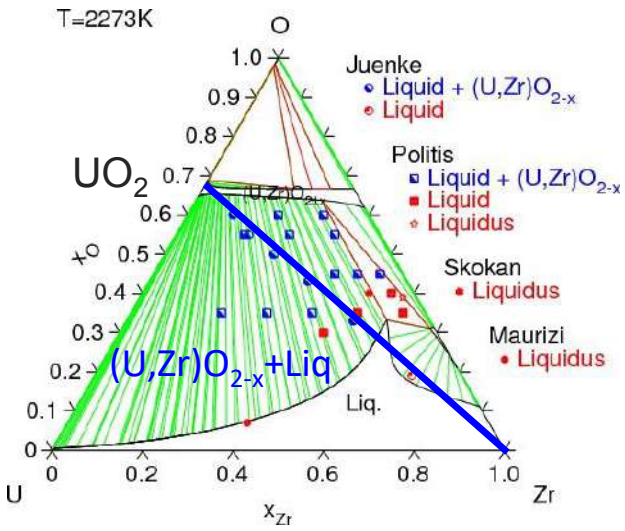


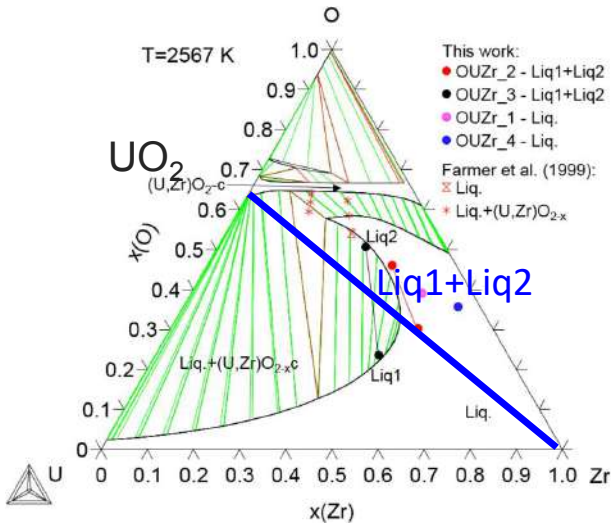
[Guéneau et al, JNM 419 (2011) 145]

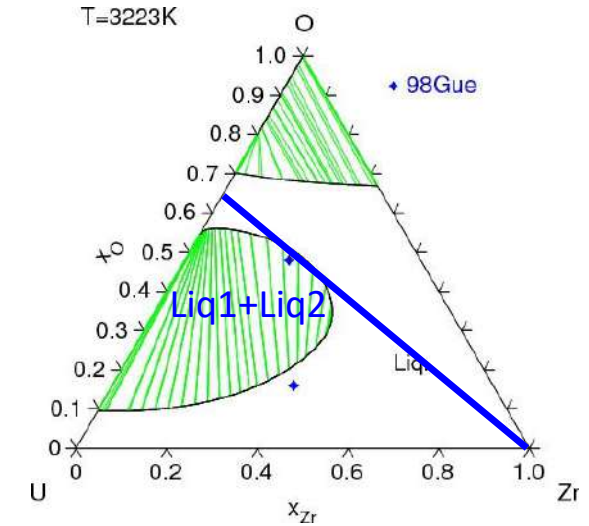
Système U-O-Zr ➡ Interaction UO_2 /Zr

T ↗

Model $(U^{+4},Zr^{+4})_P(O^{-2},Va^{-Q},O)_Q$



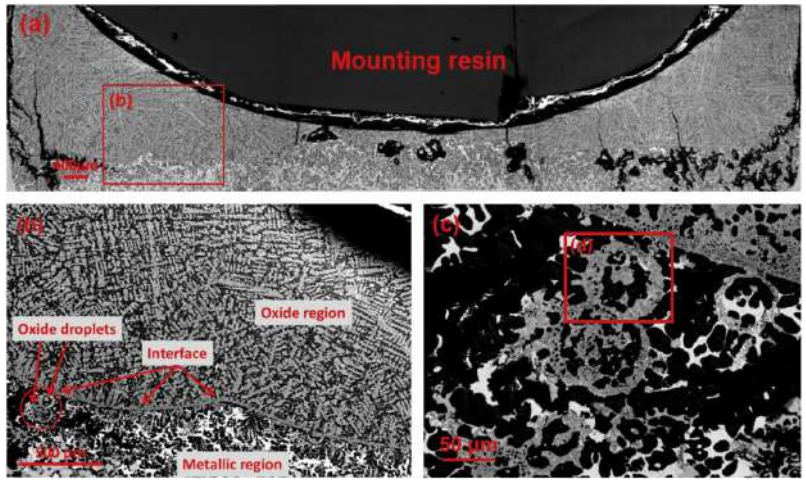


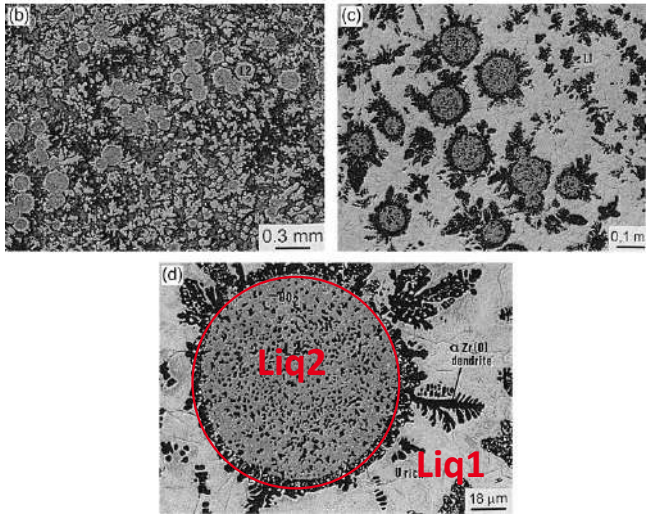


✓ Interaction UO_2/Zr
- T=2273 K: $(U,Zr)O_{2-x}$ + Liq
- T=2567 K: Liq 1 metal + Liq 2 ox

➡ Lacune de miscibilité à l'état liquide

[Thèse Andréa Quaini (2015), Quaini et al, JNM 501 (2018) 104, Guéneau et al, J. Nucl. Mater. 254 (1998) 158]





Journée de prospective sur la physicochimie des liquides à Haute Températures

29 Novembre 2024, Paris

Using machine learning to study liquids

Guillaume Deffrennes

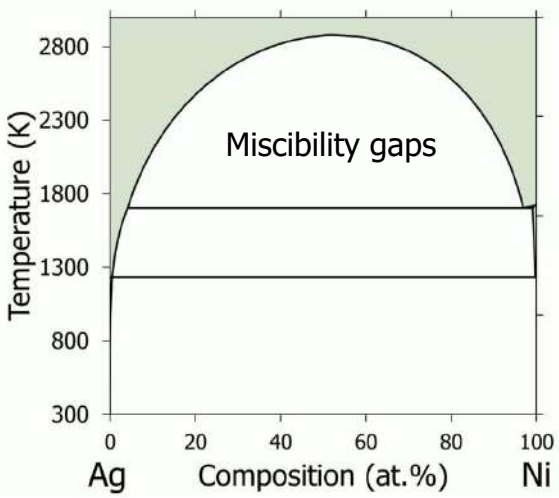
CNRS, Univ. Grenoble Alpes, Grenoble INP, laboratoire SIMaP

Case study of the enthalpy of mixing in the liquid

H_{mix}^{LIQ} is :

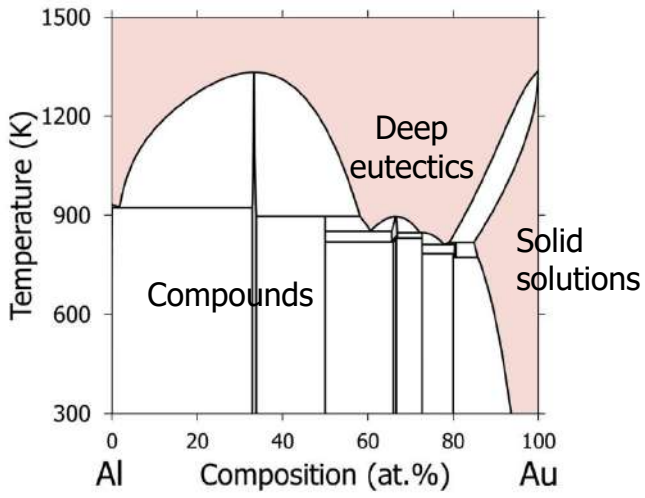
- … essential for modeling the stability of liquids
- … used in empirical rules, e.g., to design metallic glasses Takeuchi *et al.*, Mater. Trans., 46 (2005)
- … correlated to phase diagrams Miedema *et al.*, Physica 100B (1980)

$H_{mix}^{LIQ} >> 0$



Liu *et al.*, J. Electron. Mater. 37 (2008)

$H_{mix}^{LIQ} << 0$



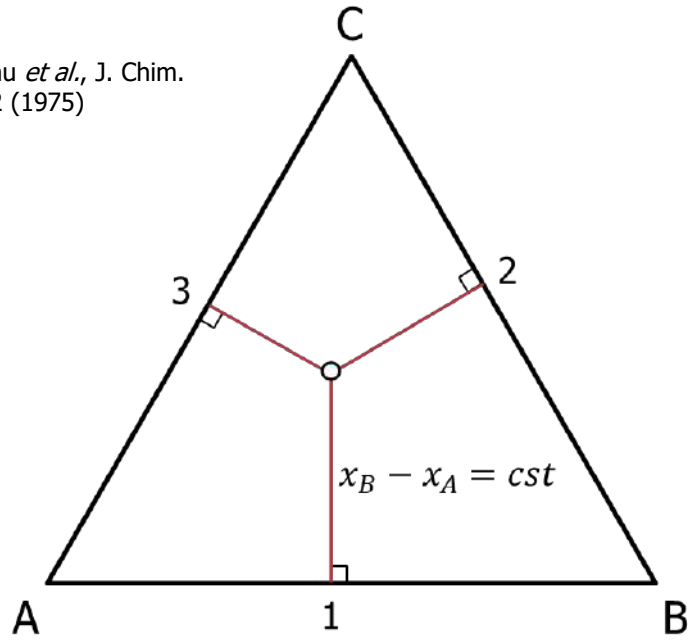
Li *et al.*, J. Alloys Compd. 385 (2004)

Extrapolation from binary to multicomponent liquids

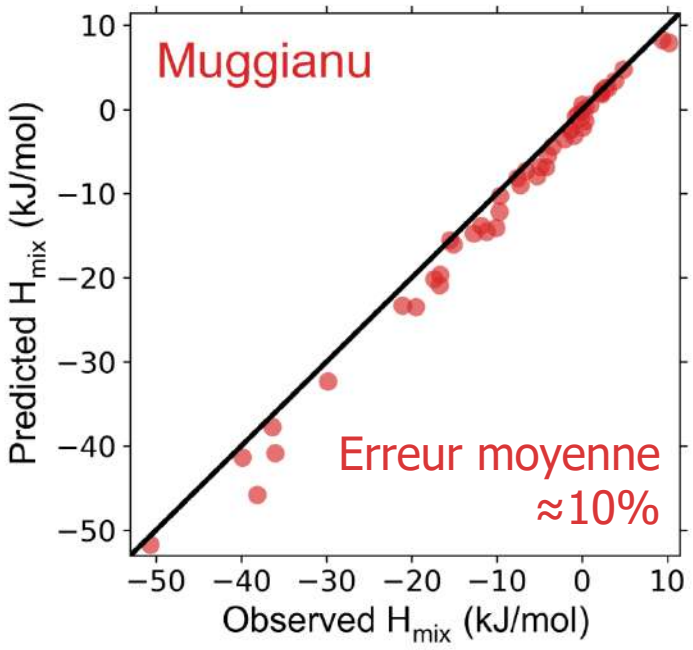
Muggianu's model

$$^{bin}H_{mix} = x_A x_B L_{AB(1)} + x_B x_C L_{BC(2)} + x_C x_A L_{CA(3)}$$

Muggianu *et al.*, J. Chim. Phys. 72 (1975)



Performance on 52 ternary near-equimolar **metallic** liquids



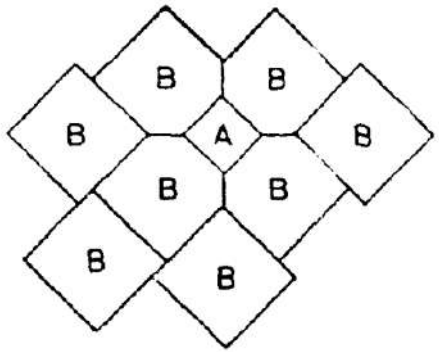
Deffrennes *et al.*, Calphad 87 (2024)

→ Focus on binary liquids

Predictions in binary liquids from Miedema's model

The atomic cell model

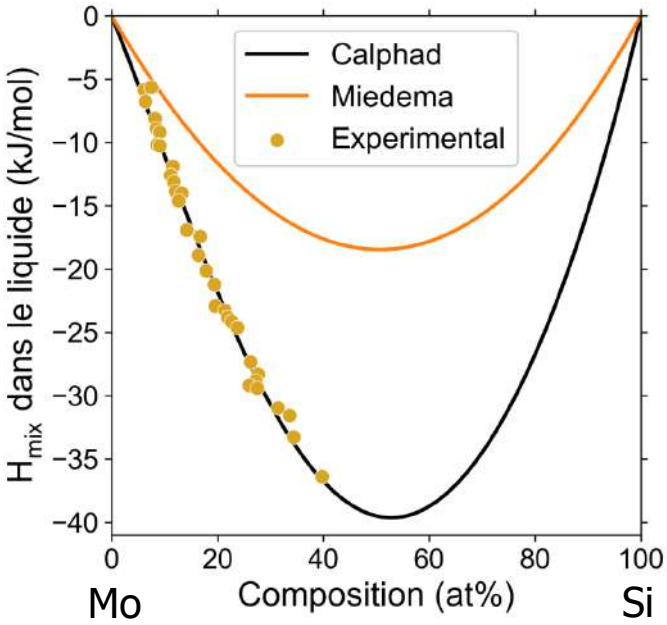
Miedema *et al.*, Physica 103B (1981)



≈ electronegativity

$$H_{mix}^{LIQ} \propto A\,(-P\Delta\varphi^2 + Q(\Delta n_{ws}^{1/3})^2)$$

Area of A-B interface Electronic density at the cell boundary

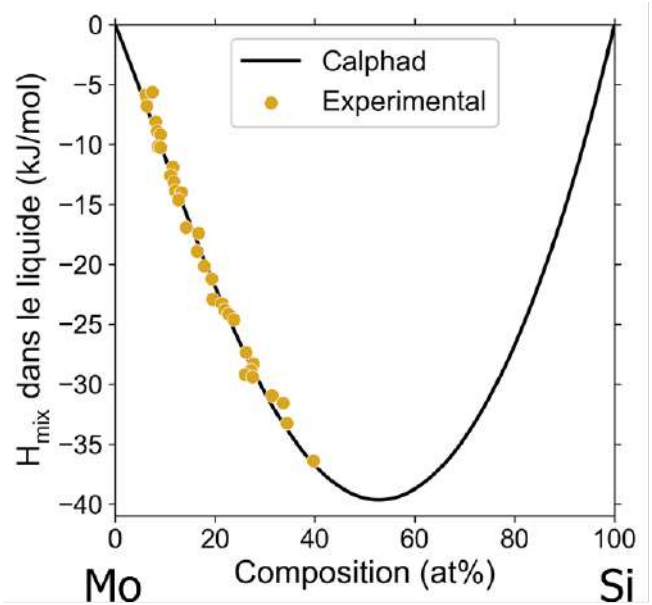


Geng *et al.*, Calphad 34 (2010)

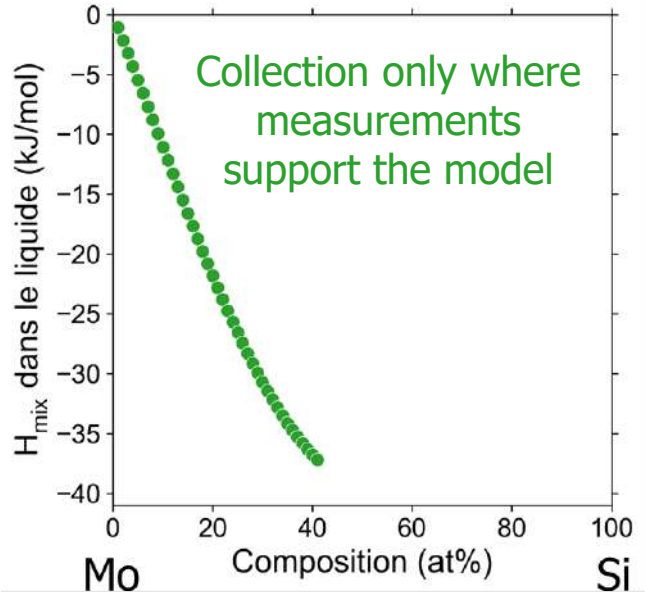
- What accuracy can be expected from Miedema's model?
- Can we correct it using machine learning?

Data collection

CALPHAD assessments



Dataset

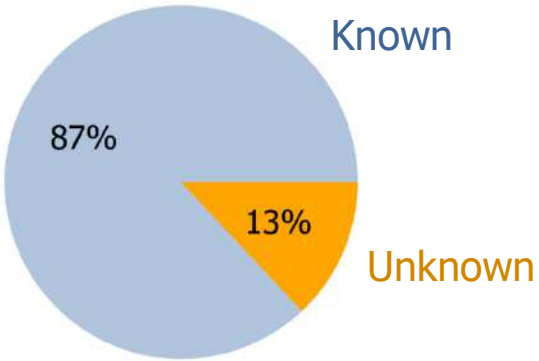


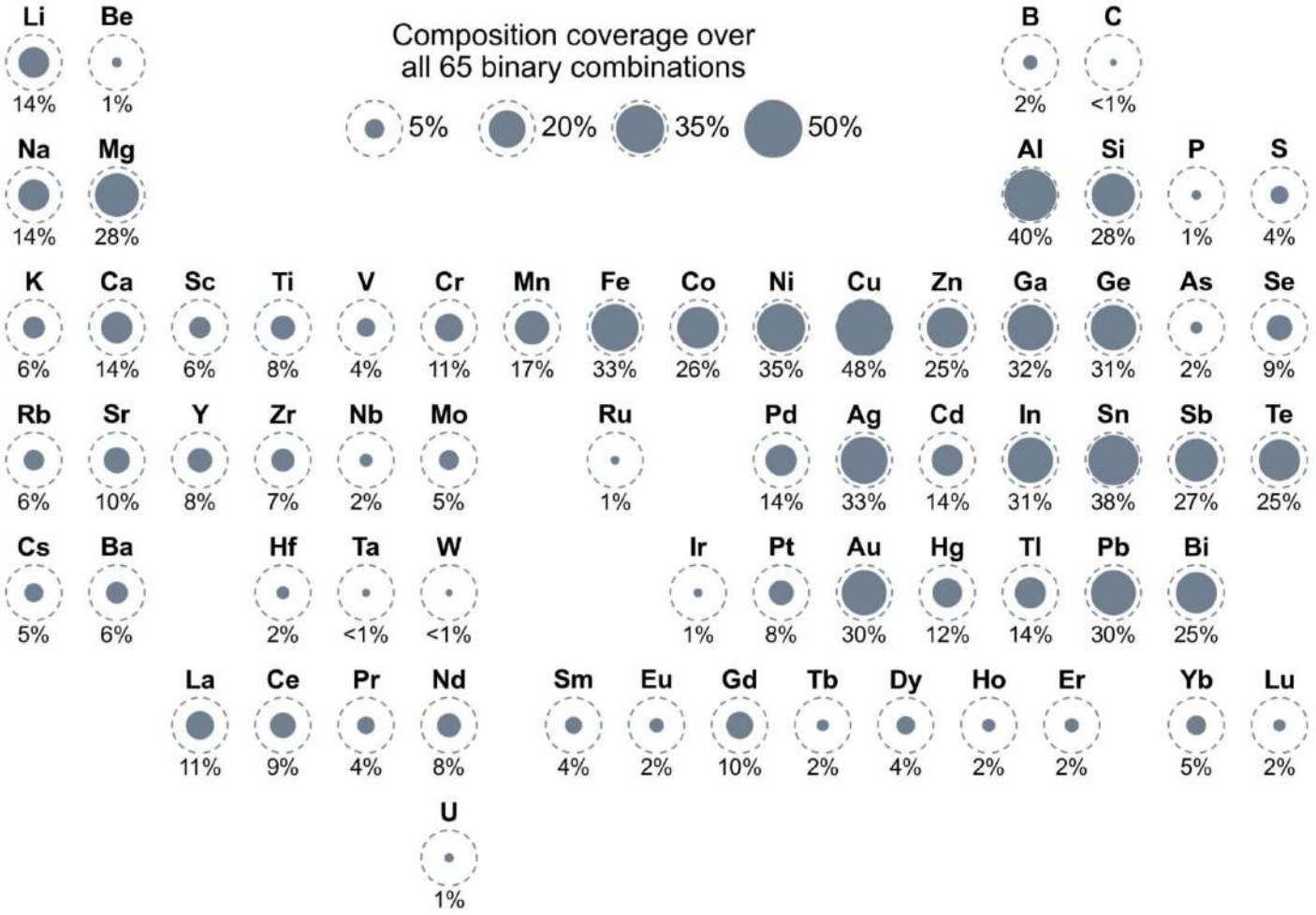
- Review of ~1000 Calphad assessments
- Reliable data found in 375 binary systems

Dataset

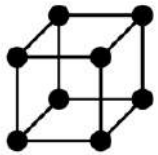
Deffrennes *et al.*, Calphad 87 (2024)

Amount of data per element



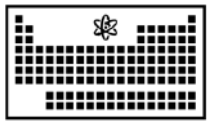


$H_{mix}^{Réel} - H_{mix}^{Miedema} = f_{ML}$ (features)



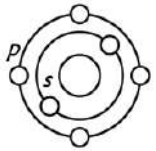
Physico/chemical properties

Molar volume (at 300K)
Thermal conductivity (at 300K)
Density (at 300K)



Periodic table

Atomic number
Mendeleev number
Row
Column

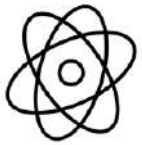


Electronic properties

Valence electron
Unfilled valence orbitals
First ionization energy
Polarizability
Electronegativity

Thermodynamic properties

Boiling point
Melting point
Heat of vaporization
Enthalpy and entropy of fusion (at Tm)
Enthalpy and entropy of liquid (at Tm)
Enthalpy and entropy of solid (at Tm)
Heat capacity of solid, liquid and fusion (at Tm)
Heat capacity and entropy (at 300K)

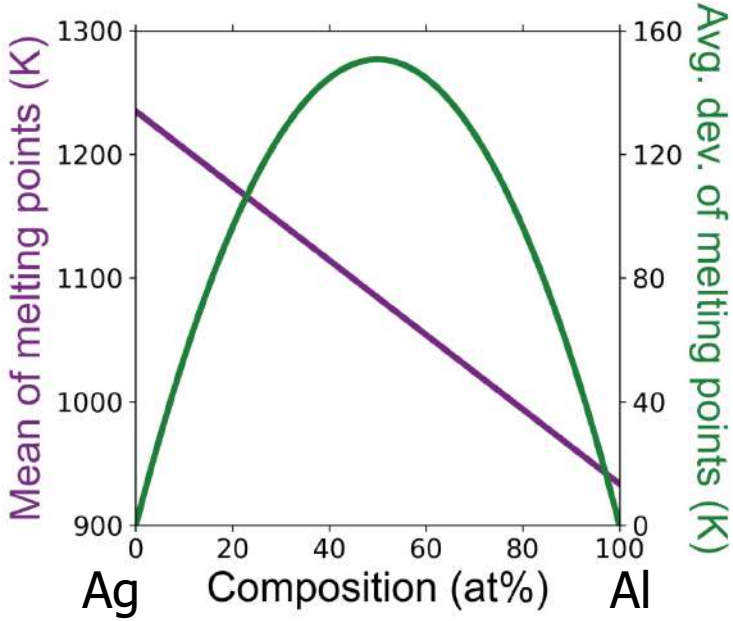


Atomic properties

Atomic weight
Atomic radius
Covalent radius

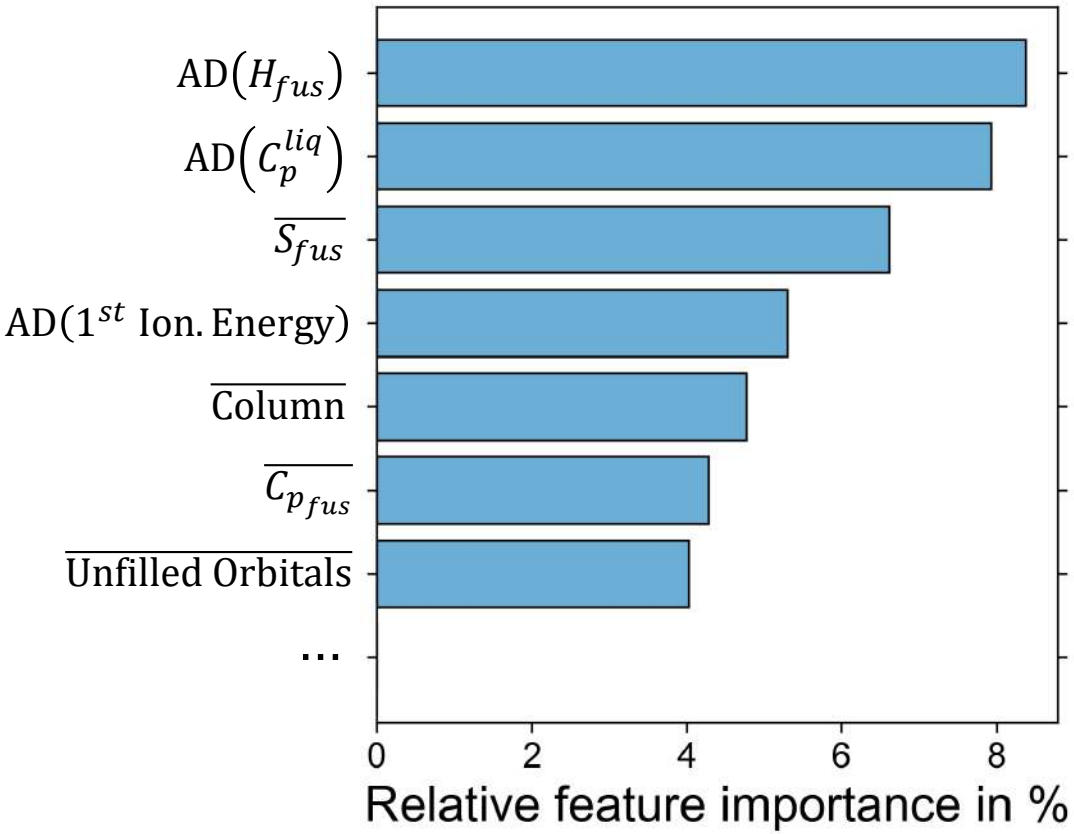
Features obtained from the composition weighted properties of the pure elements

(mean and average deviation)



$$x_A|T_A - \bar{T}| + x_B|T_B - \bar{T}|$$

Feature importance

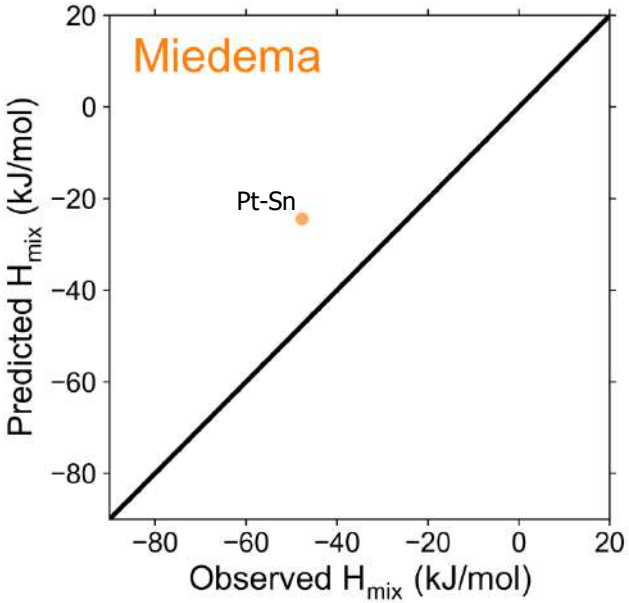


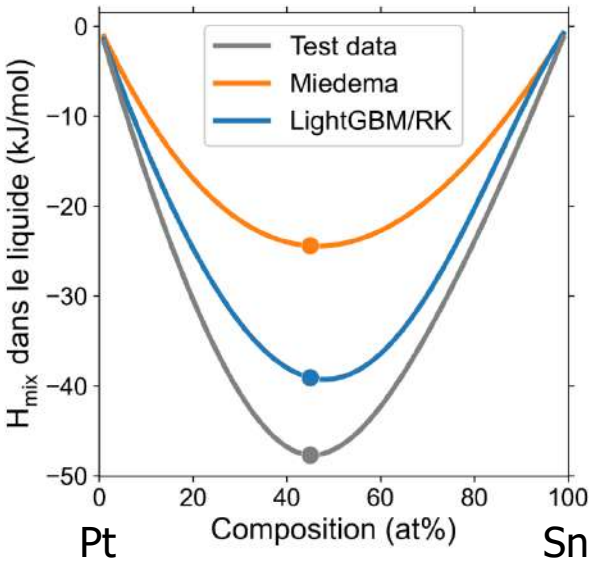
Can be useful to establish empirical laws

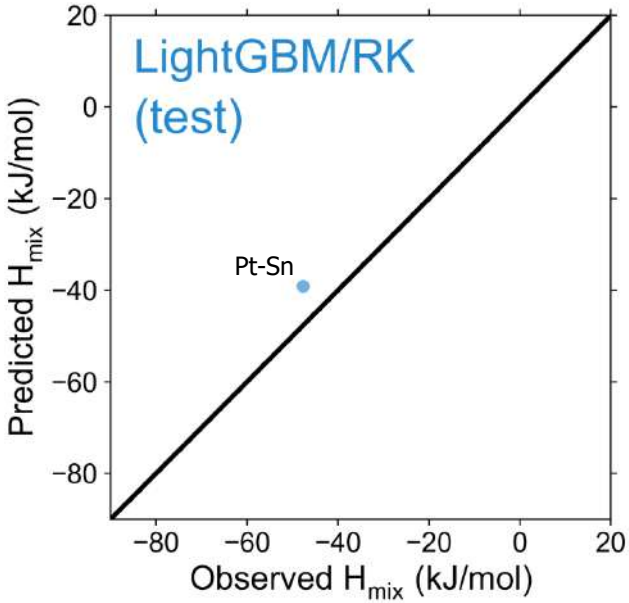
e.g.: Vazquez *et al.*, npj comput. mater. 68 (2023)

AD: average deviation

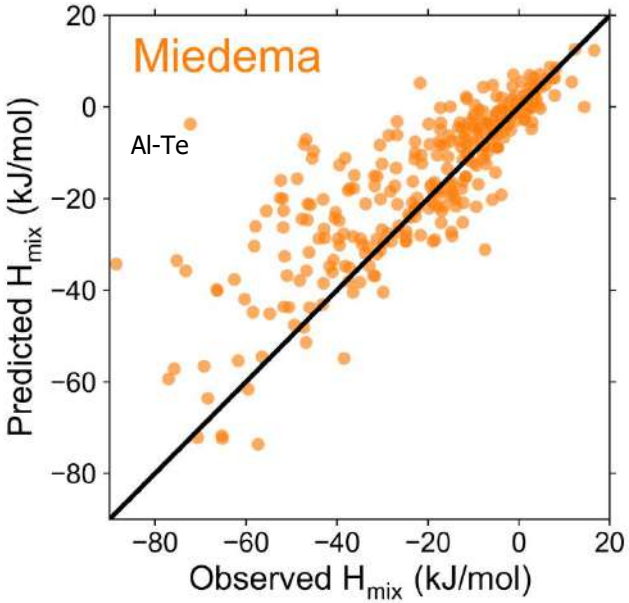
Performances







Performances



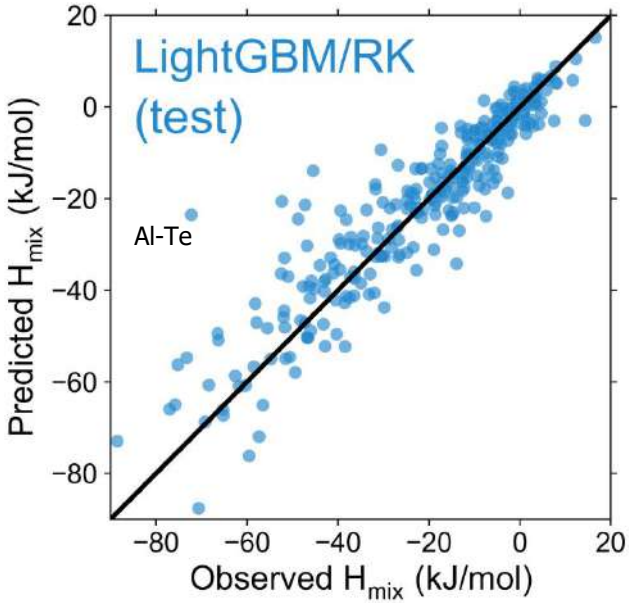
31%

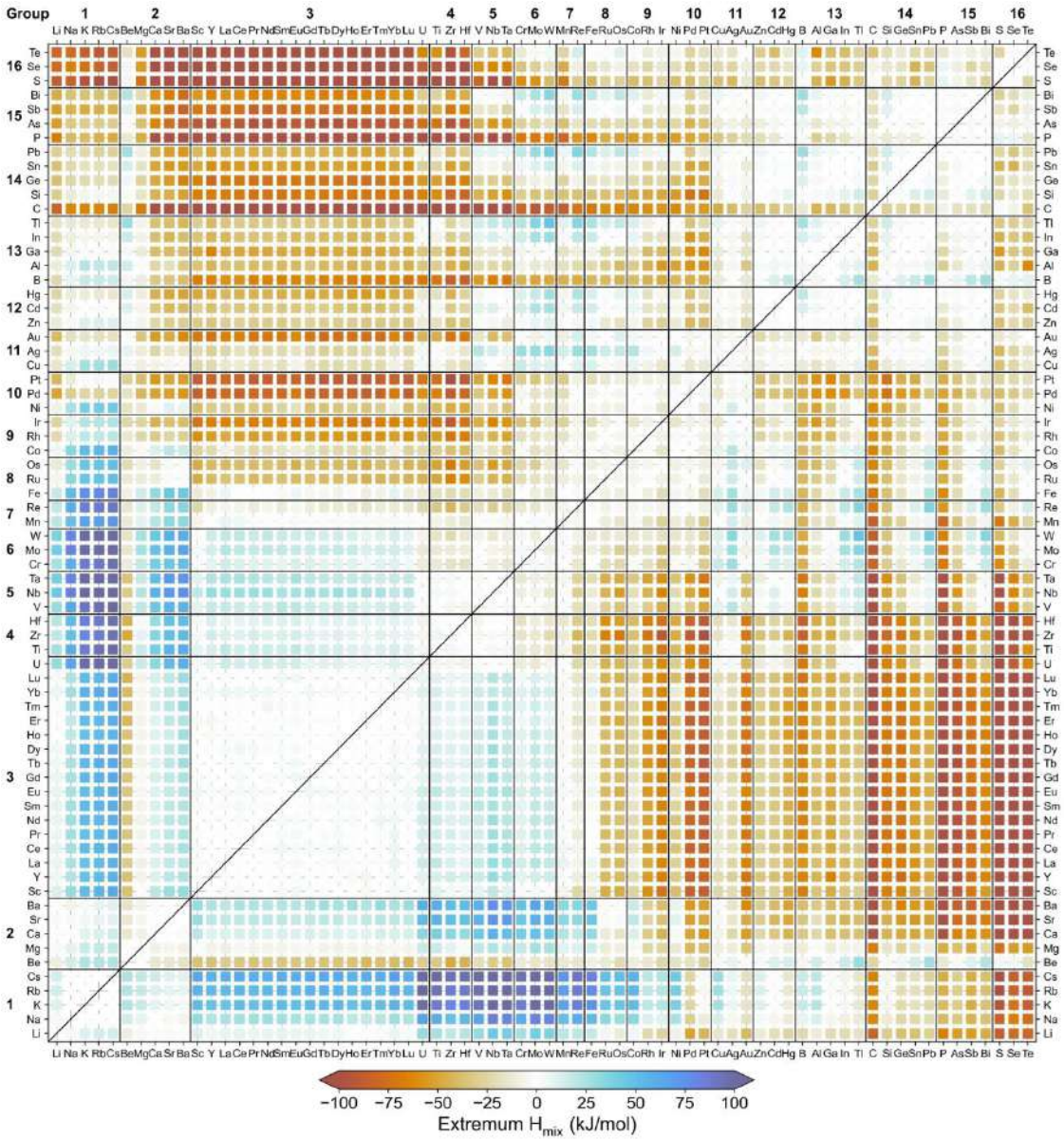
Mean Absolute % error

(on data > 15 kJ/mol in abs. value)

$$= \frac{100}{n} \sum_n \frac{\left| H_{mix}^{True} - H_{mix}^{Pred} \right|}{H_{mix}^{True}}$$

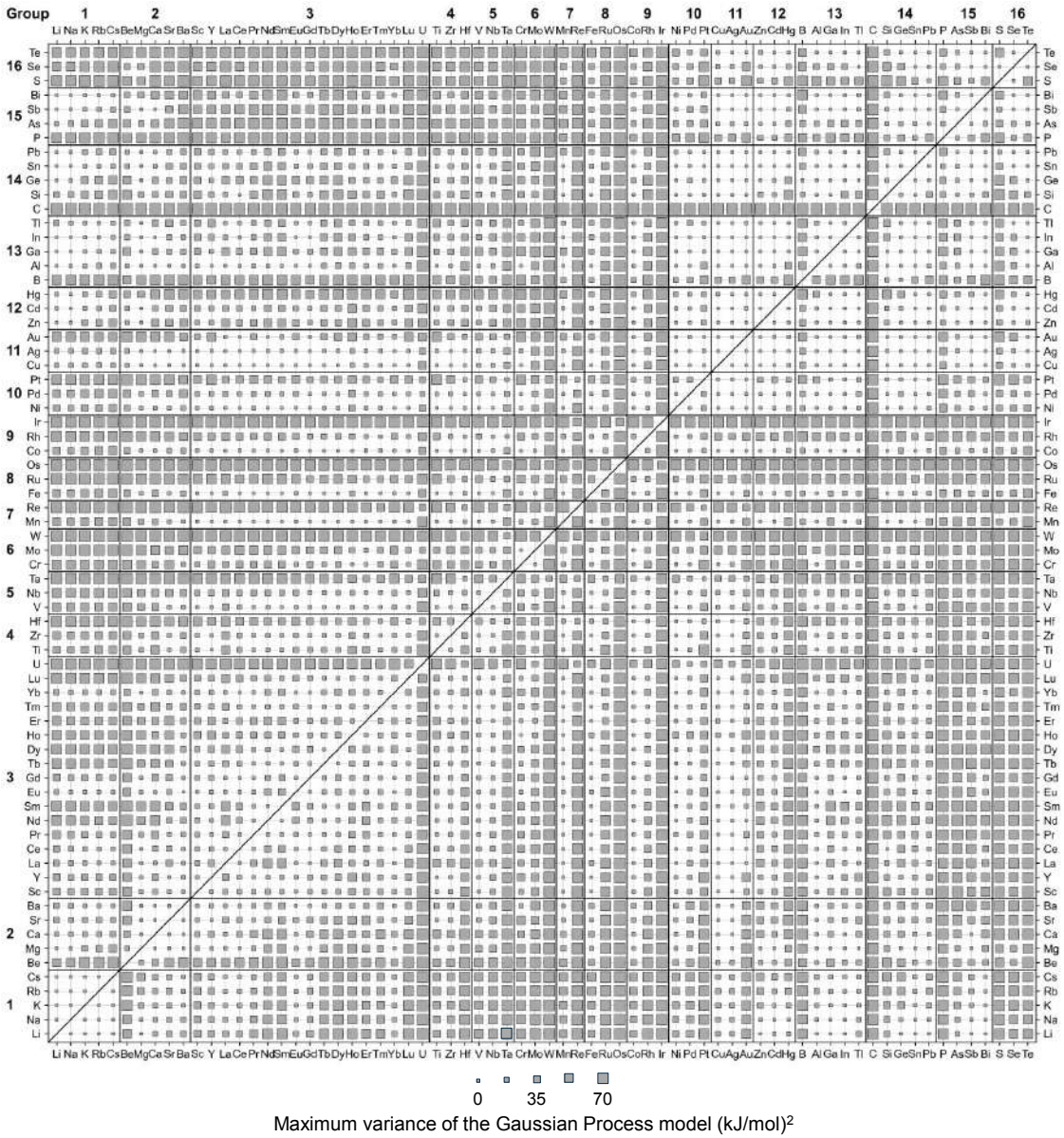
18%





Predictions in 2415 binary liquids between 70 elements

Deffrennes *et al.*, Calphad 87 (2024)



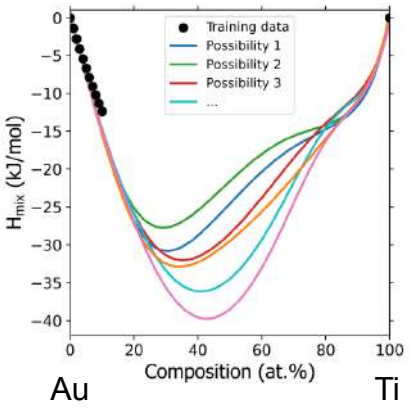
Where is new data needed the most?

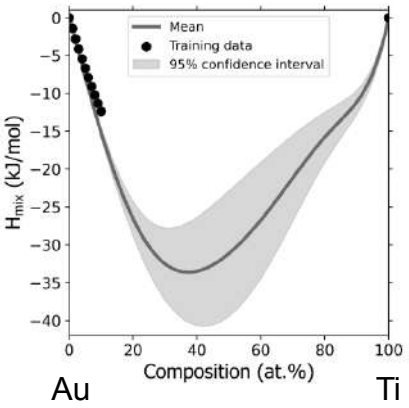
→ Active learning

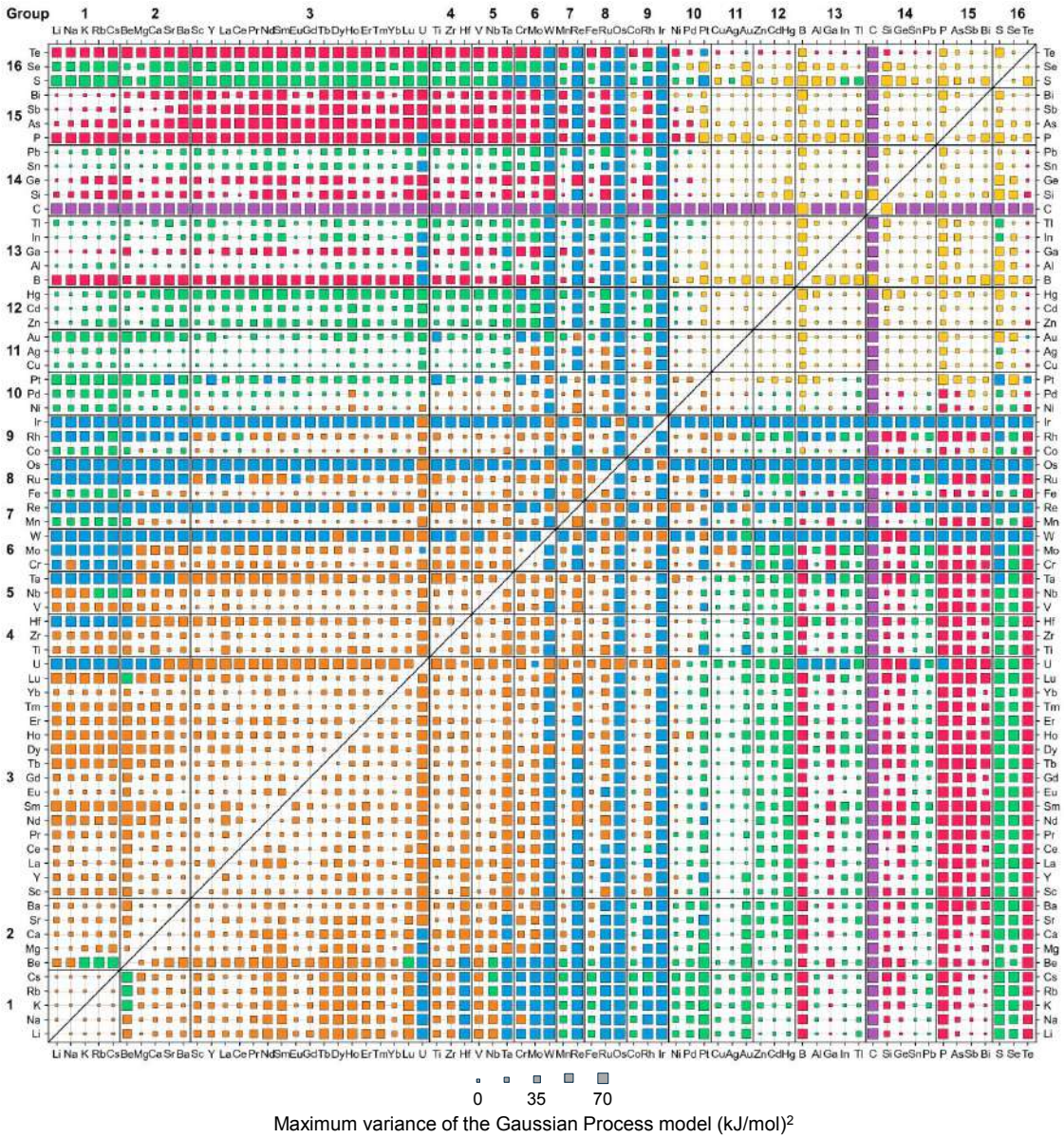
Work of Quentin Bizot
(post-doc)

MIAI Grenoble Alpes

Gaussian Process







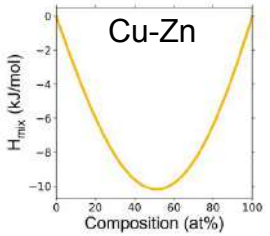
Clustering for a better understanding

K-means on 10 Features

- Column (mean & avg. deviation)
- $C_{p,liq}$ (mean & avg. deviation)
- $C_{p,fus}$ (avg. deviation)
- H_{fus} fus (avg. deviation)
- S_{fus} fus (mean & avg. deviation)
- 1st ion. energy (avg. deviation)
- Density (avg. deviation)

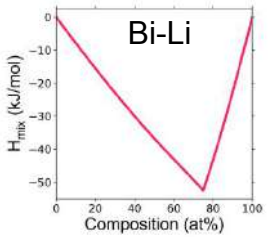
Orange & Yellow (Similar groups)

- Some data
- High accuracy



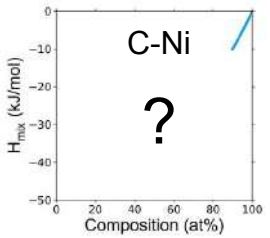
Green & Red (Different groups)

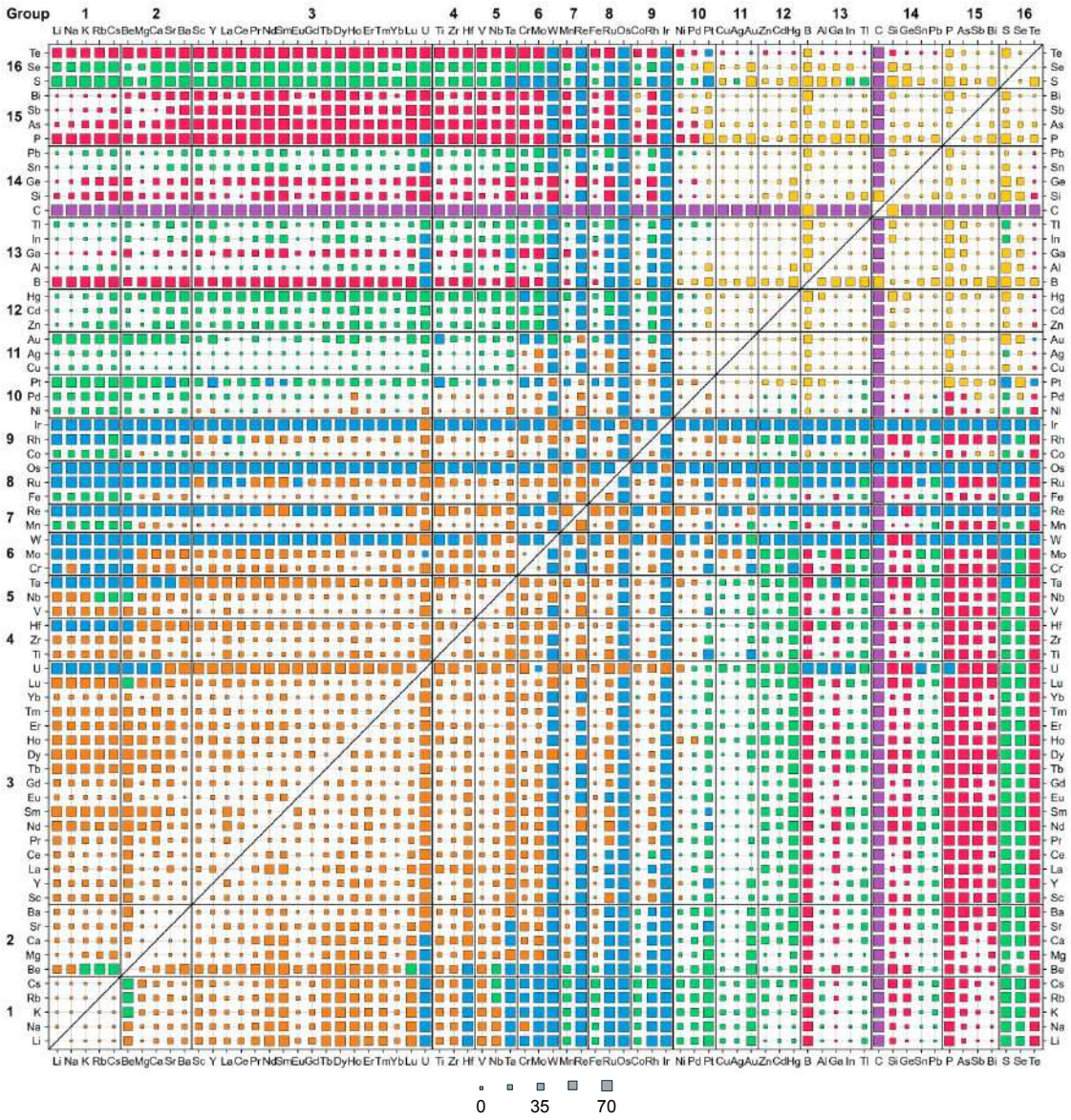
- Some data
- Low accuracy due to SRO



Purple & Blue (Refractory elements)

- Little data
- Low accuracy



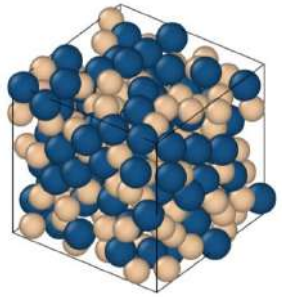


Maximum variance of the Gaussian Process model $(kJ/mol)^2$

Data acquisition for refractory alloys

(work in progress)

Ab initio Molecular Dynamics



Ir-Si
(equimolar)

Conclusion

Machine learning can help with:

- Estimations
- Data acquisition
- Reasoning and establishing empirical laws
- … and more !

Thank you for your attention !

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Conclusion & Outlook

Calphad is a success story since 1970

- Large multicomponent databases available (commercial / public)
- Large variety of applications
- Base of ICME

The future

- Third generation description & two-state model
- Integration of DFT / AIMD generated data
- New insights by ML / AI
- Still (desperately) needed : high temperature phase equilibria data & experimental thermodynamic properties
- Challenges
  - Modeling Metal - Oxide / Salt / … equilibria & phase diagrams
  - Extrapolation to high temperatures & pressure dependence of condensed phases

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