

Thermodynamic modeling of glasses and glass forming liquids

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3rd Summer School on nuclear and industrial glasses for energy transition



Back to SUMGLASS 2013

Informal discussions with Sophie Schuller (CEA), Jacques Rogez (IM2NP-CNRS)

- numerical tools are available to calculate the complete solidification path of multicomponent metal alloys (Al-based, steels...)
- a significant step forward would be to have a similar tool for multicomponent glasses

Launch of a working subgroup focused on glass thermodynamics within the French research group **TherMatHT** (Thermodynamics of materials at high T)

- How to build the thermodynamic brick of a modeling tool adapted to glasses ?
 - 4 annual workshops organized over the period 2016-2019
 - The workshops also covered kinetic aspects of phase transformations such as diffusion, nucleation & growth...
 - <https://www.thermatht.fr/groupe-thermodynamique-des-verres/>



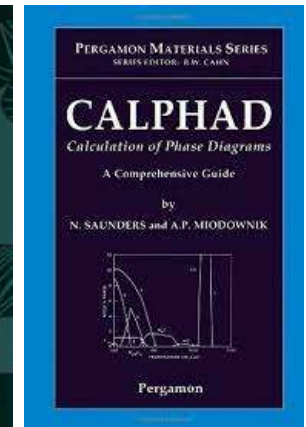
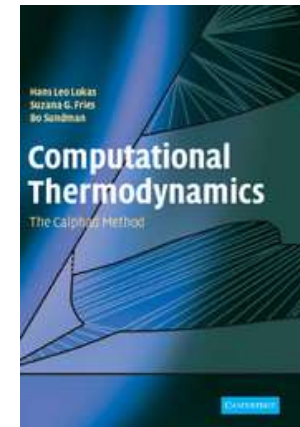
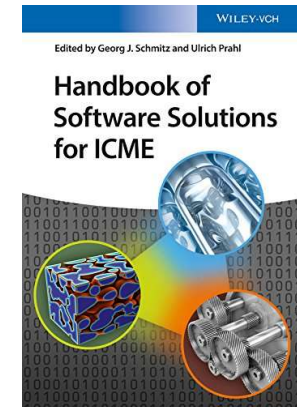
The problem

From the point of view of thermodynamic modelling, nuclear glasses

- Are multicomponent and multiphase materials
 - That have unique characteristics and present many challenges
1. The chemical system is massively multicomponent (> 40)
 2. The liquid phase must be accurately described over a wide temperature range from high T down to T_g
 3. Demixing may take place in both the liquid and glassy phases
 4. Many crystalline phases precipitate because of the limited solubilities of some components in the melt or in the glass
 5. A glass is in a non-equilibrium state requiring a specific modeling approach compared to “usual” thermodynamic phases
 6. ...

General framework = ICME & CALPHAD

- ICME = Integrated Computational Materials Engineering
 - “the combination and the simultaneous or consecutive use of a variety of software and modeling tools”
- Any ICME project must include thermodynamic modeling
 - The reference method in this field is the CALPHAD approach
- CALPHAD
 - = CALculation of PHase Diagram
 - = computer coupling of phase diagram and thermochemistry



Outline of the presentation

- The scope of the presentation is restricted to **unary glass forming liquids**
- In CALPHAD terminology, a unary is
 - a chemical element of the periodic table
 - a pure substance that does not decompose under the conditions of the study
- **Part 1 : Thermodynamic modelling**
 - Drawbacks of 2nd generation CALPHAD descriptions based on 1-state models
 - The ideal 2-state model
 - The regular 2-state model
- **Part 2 : Modeling of the glass transition, coupling thermodynamics and relaxation kinetics**



PART ONE

THERMODYNAMIC DESCRIPTION OF A UNARY GLASS FORMING LIQUID

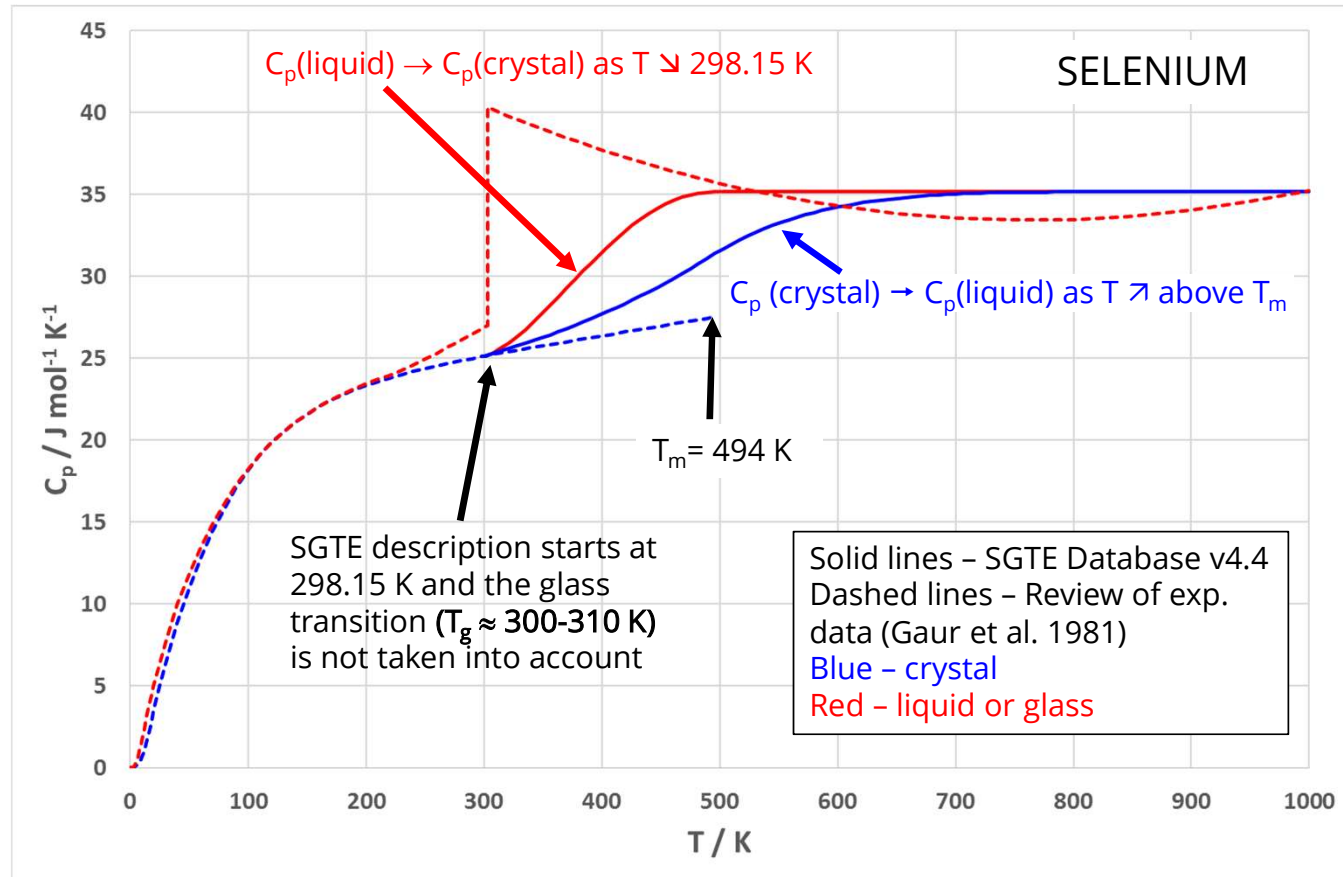


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UMR 7334, CNRS, Universités d'Aix-Marseille (AMU) et de Toulon (UTLN)

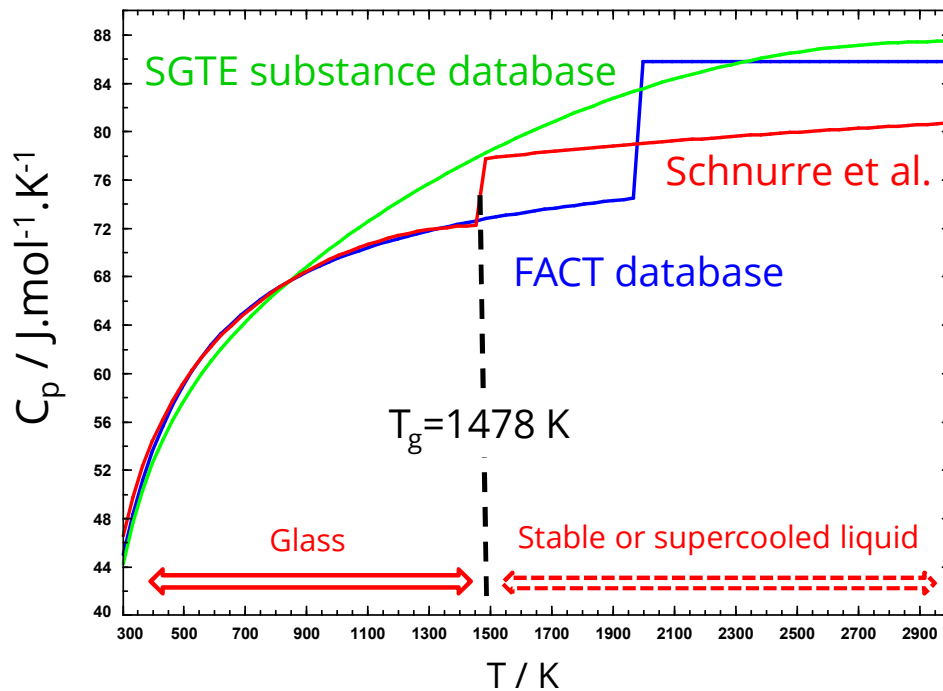


2nd generation CALPHAD descriptions : 1-state model

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



Attempts to include the glass transition in 1-state descriptions – SiO₂



Calculations by A. Pisch CNRS
– SIMAP Grenoble (2017)

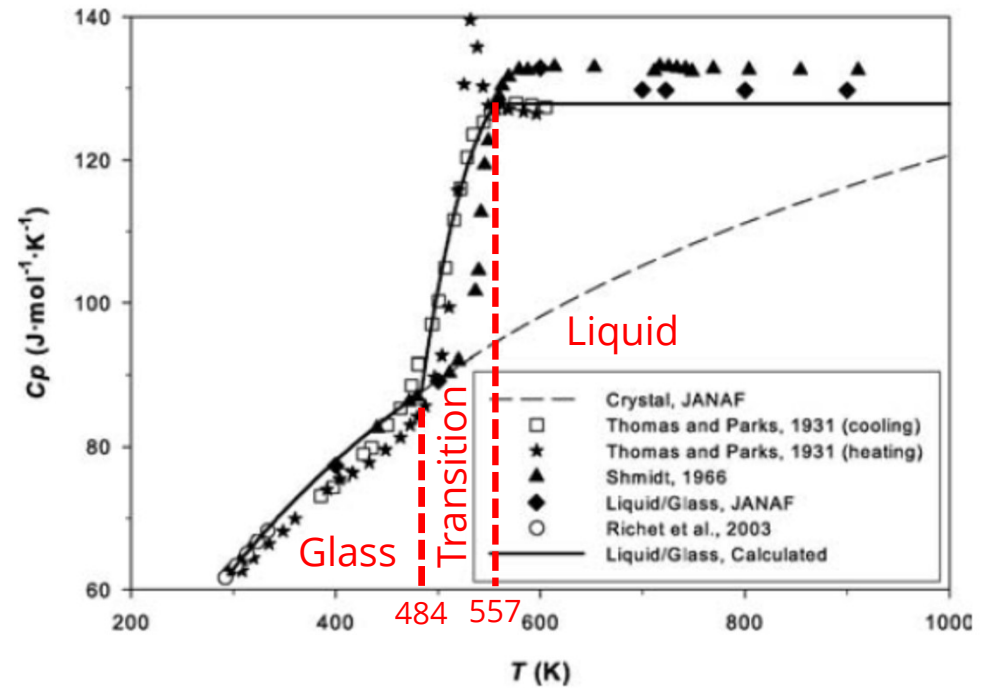
S.M. Schnurre, J. Gröbner, R. Schmid-Fetzer, Thermodynamics and phase stability in the Si-O system, *J. Non. Cryst. Solids.* 336 (2004) 1–25

$$G_{\text{SiO}_2}^{\text{L}} = -9.1911513996 \times 10^5 + 318.651821118 \cdot T - 52.80500652 \cdot T \cdot \ln T - 0.013894085 \cdot T^2 + 1.609929477 \times 10^{-6} \cdot T^3 + 6.17817813 \times 10^5 \cdot T^{-1}$$

$$G_{\text{SiO}_2}^{\text{L}} = -9.35481224 \times 10^5 + 479.632422808 \cdot T - 75.461508414 \cdot T \cdot \ln T - 1.206802642 \times 10^{-3} \cdot T^2 + 3.37604755 \times 10^{-8} \cdot T^3 + 9.26045761 \times 10^5 \cdot T^{-1}$$

Attempts to include the glass transition in 1-state descriptions – B₂O₃

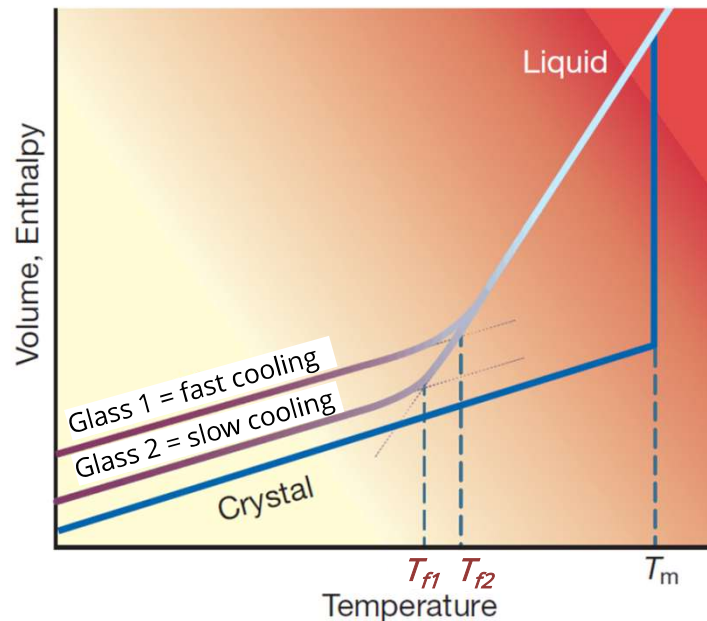
From S.A. Decterov, V. Swamy, I.-H. Jung,
*Thermodynamic modeling of the B₂O₃ – SiO₂ and
 B₂O₃ – Al₂O₃ systems, Int. J. Mater. Res. 98 (2007)
 987–994*



$$C_P \text{ (in } \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = a + b(10^{-3}) T + c(10^5) T^{-2} + d(10^{-9}) T^2 + eT^{-0.5} + f(10^8) T^{-3}$$

Compound	$\Delta H_{298.15}^{\circ}$	$S_{298.15}^{\circ}$	a	b	c	d	e	f
B ₂ O ₃ (liquid)								
298–484 K	–1 253 359	77.9429	187.0657	6.22849	7.10888		–2319.65	
484–557 K	–1 214 072	192.337	1263.646	–1299.53	–1294.49		127.808	
557–2000 K	–1 264 033	50.3148	127.7794					

A glass is not a thermodynamic phase in the usual sense



- The state of a glass
 - not only depends on T and p
 - changes with cooling rate
- **At least one additional thermodynamic variable is required to represent the internal state of the glass**
- One useful additional variable is the **fictive temperature T_f**
 - “the temperature at which the configurational state of the glass would be an equilibrium state of the liquid” (Goldstein)
- A glass heated at $T = T_f$ is at thermodynamic equilibrium
- On cooling, the liquid deviates from its metastable equilibrium state at T_f
- T_f can be measured fairly easily by DSC

Adapted from P. Debenedetti, F. Stillinger, Supercooled liquids and the glass transition, Nature. 410 (2001) 259–26

Thermodynamics of defects: an alternative approach to describe the internal state of a glass

- General principle
 - to introduce defects/excitations of one type or another in an idealized structure
 - Depending on the physical model, the **internal variable** can represent a number of
 - holes or vacancies in the liquid (*Schmelzer, Gutzow and others*)
 - particles or structural entities in a higher energy state (*many authors*)
 - broken bonds (configurons) in a covalent liquid (*Angell, Ojovan*)
 - self-interstitial (dumb-bell) defects in a metallic crystal (*Granato*)
 - ...
- lattice-hole
lattice-gas models
- } 2-state models

and is sometimes called the **structural order parameter ξ**

- In what follows
 - It is assumed that the state of the glass can be described by a single internal variable
 - we will use 2-state models

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 Körpern. (Mit magnetischen, thermischen und chemischen Beziehungen)., Phys. Zeitschrift. 23 (1922) 448–455

The ideal 2-state model

- Key assumptions
 - Liquid = ideal solution of 2 types of structural entities **A** and **B** that exchange through an equilibrium :
 $A(\text{ground state}) \rightleftharpoons B(\text{excited state})$
 - The mole fractions of A and B (denoted ξ_A and ξ_B) vary with the external variable T

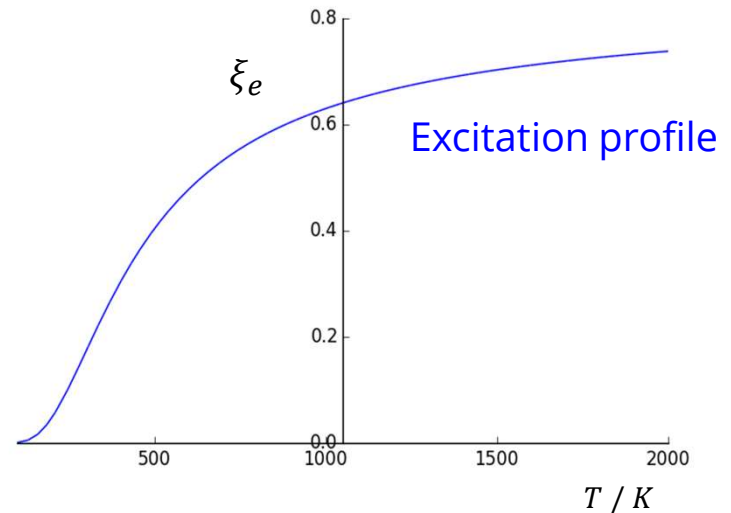
- Liquid Gibbs energy: $G_L = \underbrace{\xi_A G_A^\circ + \xi_B G_B^\circ}_{\text{Mechanical mixture}} + \underbrace{RT(\xi_A \ln \xi_A + \xi_B \ln \xi_B)}_{\text{Ideal entropy of mixing}}$

- $\xi = \xi_B$ chosen as the internal variable = **non-conservative order parameter**
- The molar Gibbs energy of the liquid reads: $G_L = G_A^\circ + \xi \Delta G_d + RT((1 - \xi) \ln(1 - \xi) + \xi \ln \xi)$
- With: $\Delta G_d = G_B^\circ - G_A^\circ$

- The internal equilibrium condition: $\left(\frac{\partial G_L}{\partial \xi} \right)_{\xi = \xi_e} = 0$

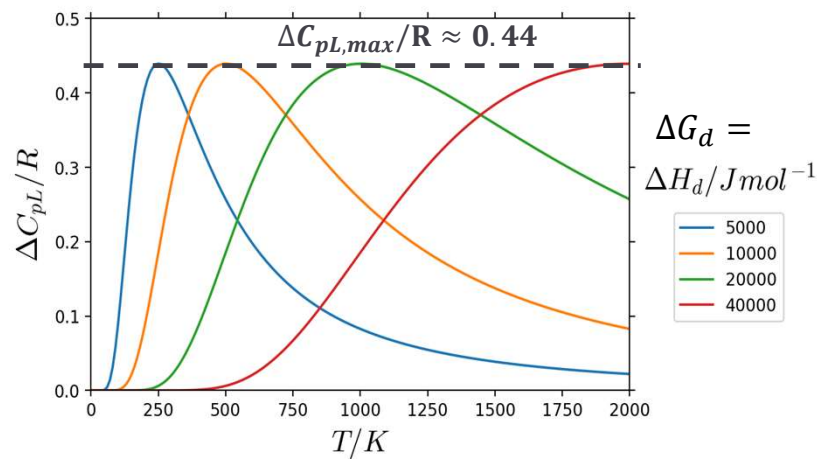
- is expressed as: $\Delta G_d = -RT \ln \frac{\xi_e}{(1 - \xi_e)}$

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

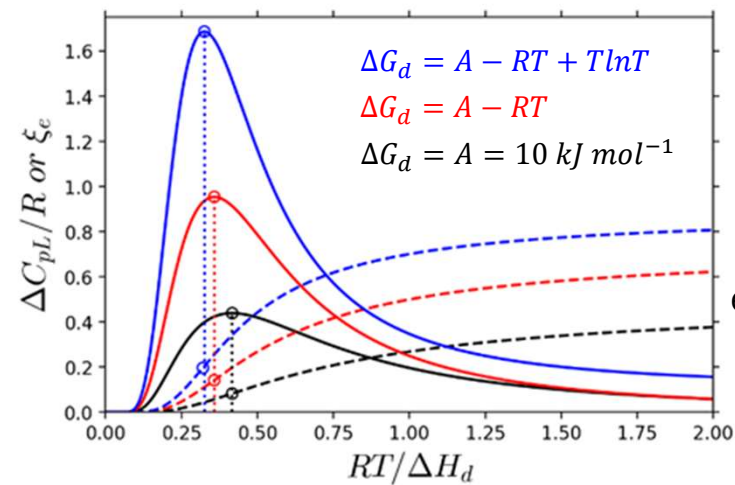


Configurational functions (Δ) of the liquid

- Gibbs energy: $\Delta G_L = G_L - G_A^\circ = -RT \ln(1 + \exp(-\Delta G_d/RT))$
 – with: $\Delta G_d = \Delta H_d - T\Delta S_d = A + BT + CT \ln T$
- Entropy: $\Delta S_L = S_L - S_A^\circ = \xi_e \Delta S_d - R((1 - \xi_e) \ln(1 - \xi_e) + \xi_e \ln \xi_e)$
- Enthalpy: $\Delta H_L = H_L - H_A^\circ = \xi_e \Delta H_d$
- Heat capacity: $\Delta C_{pL} = \left(\frac{\partial \Delta H_d}{\partial T}\right)_p \xi_e + \frac{\Delta H_d^2}{RT^2} \xi_e (1 - \xi_e)$



Schottky heat capacity anomaly (1922)

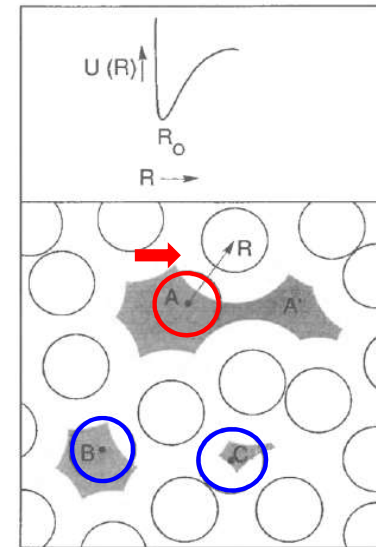


Dashed lines = excitation profiles

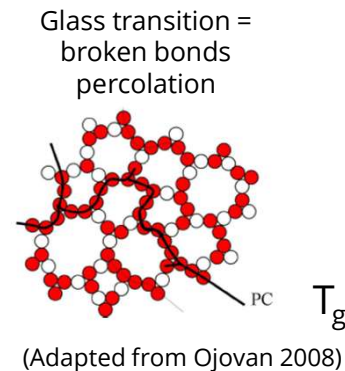
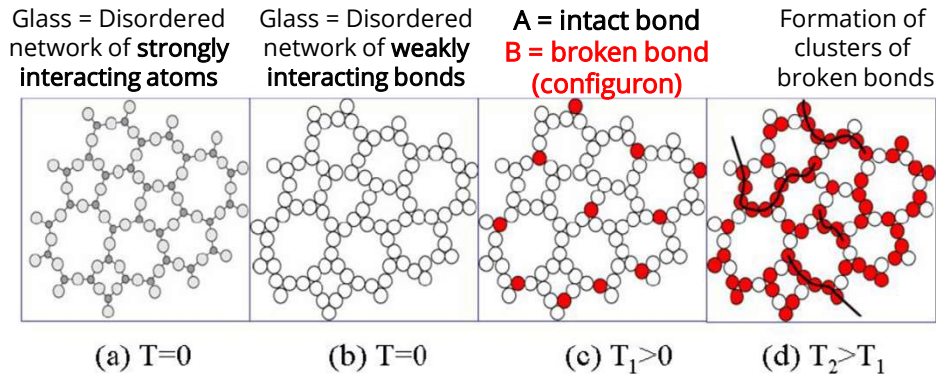
(Dimensionless temperature)

What do these 2 states represent ?

- Agren's interpretation (free volume)
 - **A = solid-like** (vibration)
 - **B = liquid-like or gas-like** (translation + vibration)
 - when $T \searrow$, **liquid-like** entities progressively lose their translational degrees of freedom and become **solid-like**
- Tanaka's picture of liquids: density vs. bond ordering
 - A = **locally favored low-energy structures** with medium-range order (tetrahedral for H_2O -type liquids, icosahedral or compact stacking for metals)
 - B = **normal liquid structures of higher energy**
- Angell & Ojovan description of covalent liquids (network of bonds)



(adapted from Debenedetti 1996 and Zallen 1983)



Application to a real substance

- Liquid Gibbs energy : $G_L = G_A^\circ - RT \ln(1 + \exp(-\Delta G_d/RT))$
- Gibbs energy difference between the two states, CALPHAD type expansion
 - $\Delta G_d = A + BT + CT \ln T$
 - $A, B, C \dots$ coefficients to be fitted to experimental results
- The pure 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

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

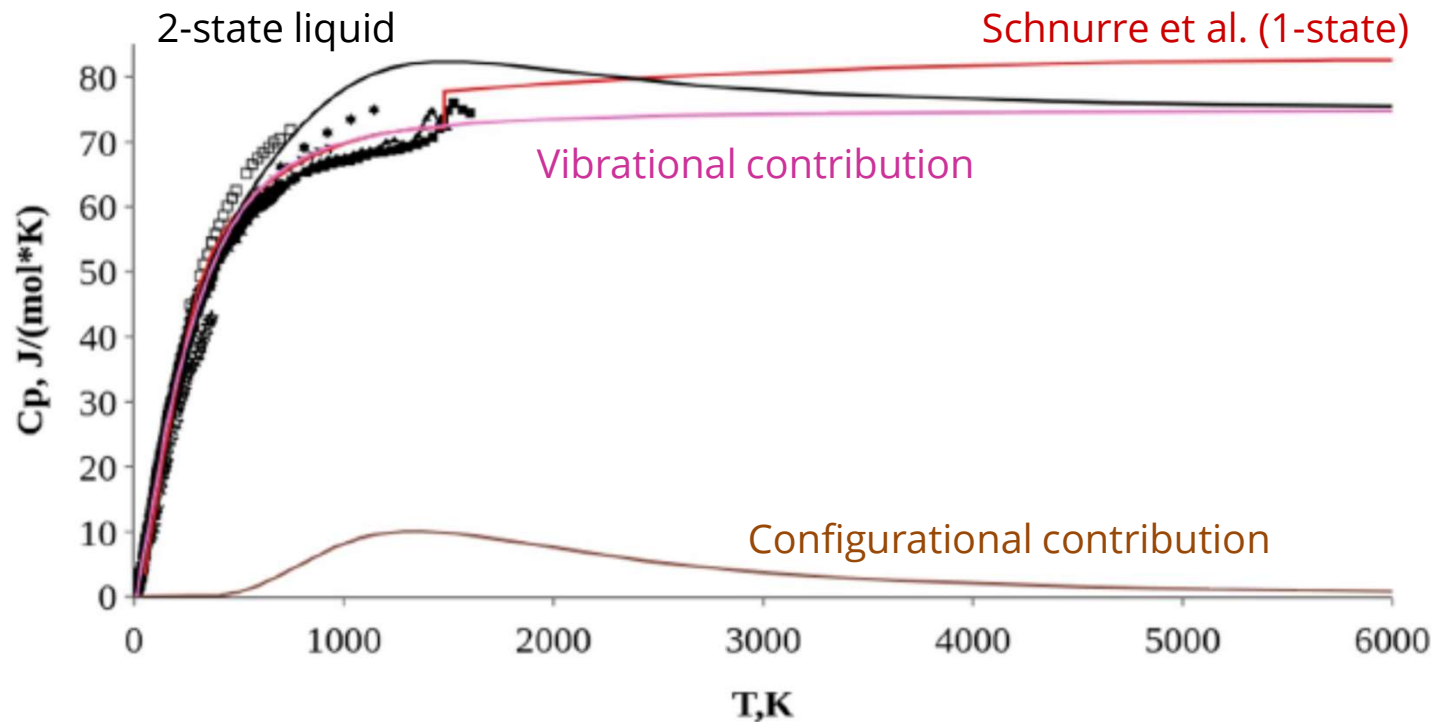
$$S(T) = \sum_i 3R\alpha_i \left(\frac{\Theta_i}{T} \frac{e^{\Theta_i/T}}{e^{\Theta_i/T} - 1} - \ln(e^{\Theta_i/T} - 1)\right)$$

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

- The Einstein temperatures Θ_i and corresponding weights α_i are adjustable parameters to be fitted to experimental results

2-state modeling of liquid/glassy SiO₂

I. Bajenova, A. Khvan, A. Dinsdale, A. Kondratiev, Implementation of the extended Einstein and two-state liquid models for thermodynamic description of pure SiO₂ at 1 atm, Calphad Comput. Coupling Phase Diagrams Thermochem. 68 (2020) 101716



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

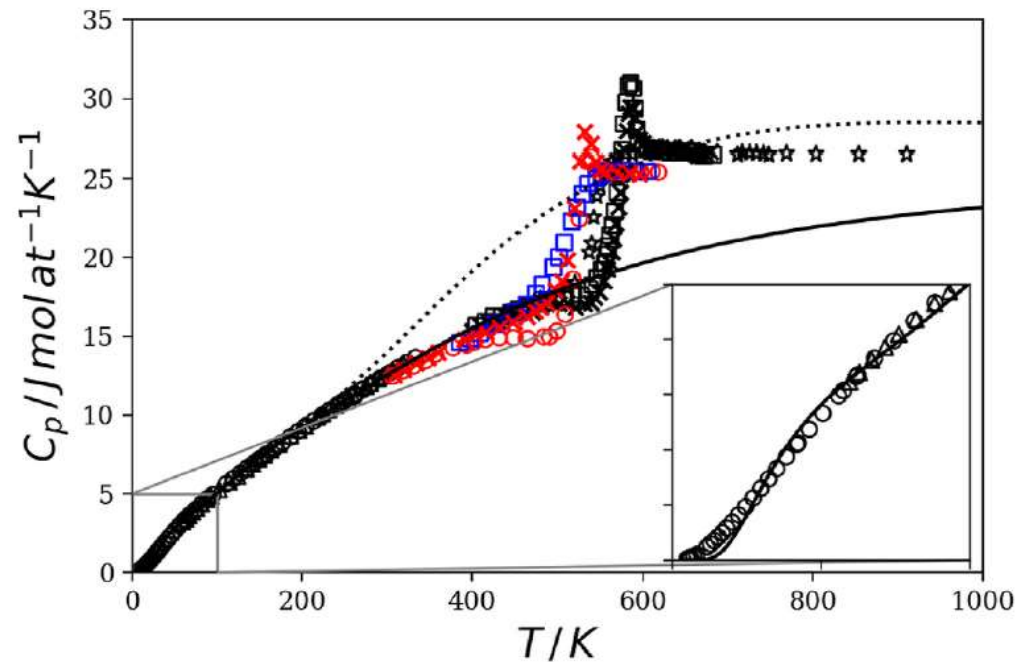
2-state modeling of liquid/glassy B₂O₃

- Parameters of the vibrational model adjusted using the **CpFit free software** on 132 data points

i	α_i	$\Delta\alpha_i$	θ_i/K	$\Delta\theta_i/K$
1	0.528162913	0.0135499	1600.727224	55.0723
2	0.180141253	0.00822347	121.9903056	5.50505
3	0.328836748	0.0157812	546.1879661	26.548

- Parameters of the Gibbs energy difference adjusted using a homemade Python program

$A/J\ mol\ at^{-1}$	15248.47522169
$B/J\ mol\ at^{-1}K^{-1}$	$-\frac{3}{4}R$



P. Benigni, CALPHAD modeling of the glass transition for a pure substance, coupling thermodynamics and relaxation kinetics, Calphad. 72 (2021) 102238.

Some arguments to enrich the ideal model

- The Schottky function has a **limited fitting ability**
 - *“the Schottky function is a beast that is a little hard to fudge”* (Westrum 1985)
 - *“the Schottky function does not render the shape of the ΔC_p experimental curves over a wide temperature range correctly”* (Nemilov 1995)
- The physical model of the liquid should have a **cooperative character**
 - easier to break bonds in the vicinity of bonds that have already been broken
 - tendency to cluster defects
- By its very construction, the ideal 2-state model is **unable to describe any phase separation** phenomenon such as
 - **liquid polymorphism**
 - Occurs in the domain of liquid stability for elements such as Bi and S
 - Suspected to occur in the domain of liquid metastability (supercooled range) for some substances (e.g. H₂O or Si)
 - amorphous polymorphism = **poly-amorphism**
 - = existence of 2 distinct glasses of the same chemical composition with very different atomic structures and volume properties (e.g. density)
 - observed in several pure substances in which the tetrahedral structure predominates at room temperature: H₂O, Si, Ge, SiO₂, GeO₂, A_{III}B_V (GaSb, GaAs, InSb)
 - suspected in at least one binary case: Al₂O₃-Y₂O₃
 - may result from the prior existence of a liquid/liquid transition
 - if there are 2 different liquids, quenching one or other of these 2 liquids should result in the formation of 2 distinct glasses

The regular 2-state model

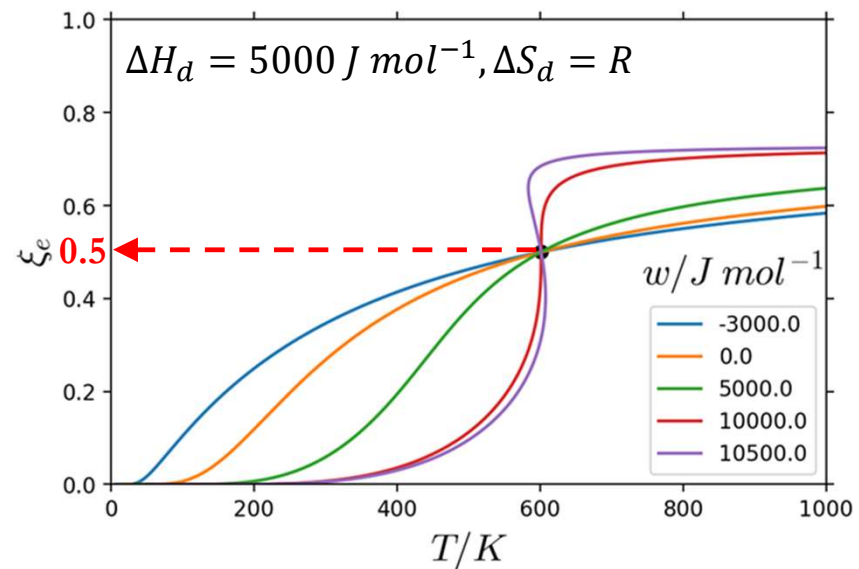
- Gibbs energy: $G_L = \xi_A G_A^\circ + \xi_B G_B^\circ + RT(\xi_A \ln \xi_A + \xi_B \ln \xi_B) + \underbrace{w \xi_A \xi_B}$
- Internal equilibrium: $\Delta G_d + RT \ln \frac{\xi_e}{1-\xi_e} + w(1 - 2\xi_e) = 0$
 - With: $\Delta G_d = G_B^\circ - G_A^\circ = \underline{\Delta H_d} - \underline{T \Delta S_d}$ 3 parameters
- The shape of the excitation profile $\xi_e(T)$ changes with the value of the interaction parameter w

$$\xi_e(T_c) = 1/2$$

$$T_c = \frac{\Delta H_d}{\Delta S_d} \approx 601.4K$$

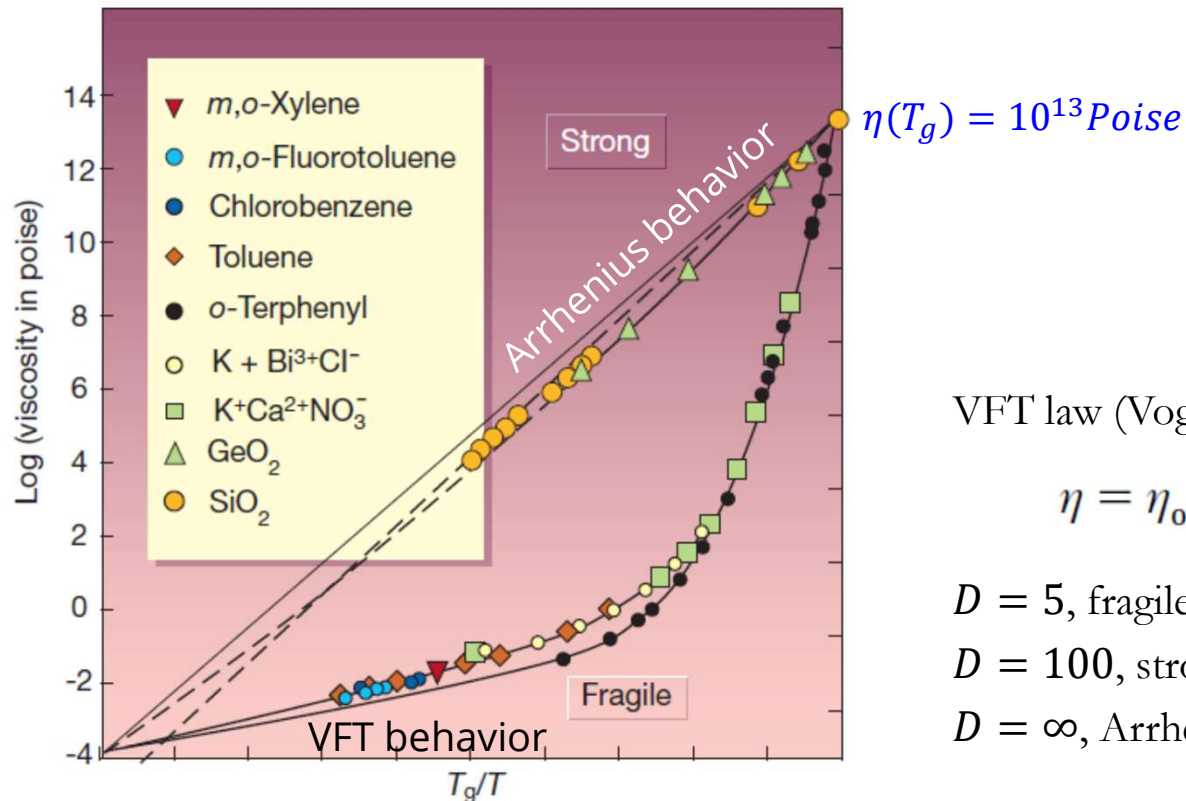
$$w_c = 2RT_c = 10000 J mol^{-1}$$

Demixing if $w > w_c = 2RT_c$

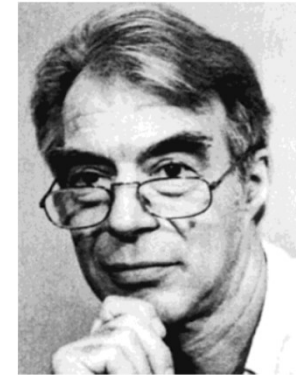


2 archetypes of glass forming liquids

Angell - Oldekop's plot



C.A. Angell (1933-2021)



VFT law (Vogel-Fulcher-Tammann)

$$\eta = \eta_0 \exp(DT_0/[T - T_0])$$

$D = 5$, fragile liquid

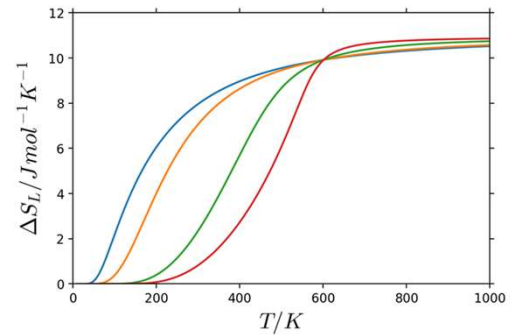
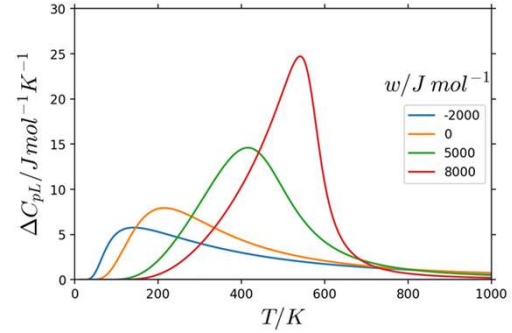
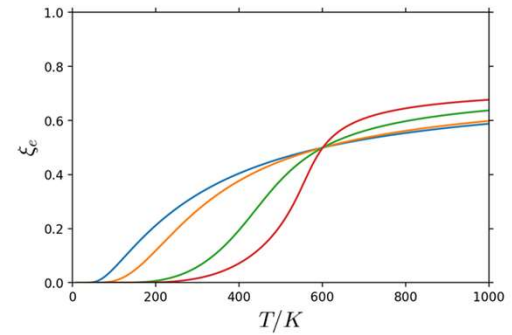
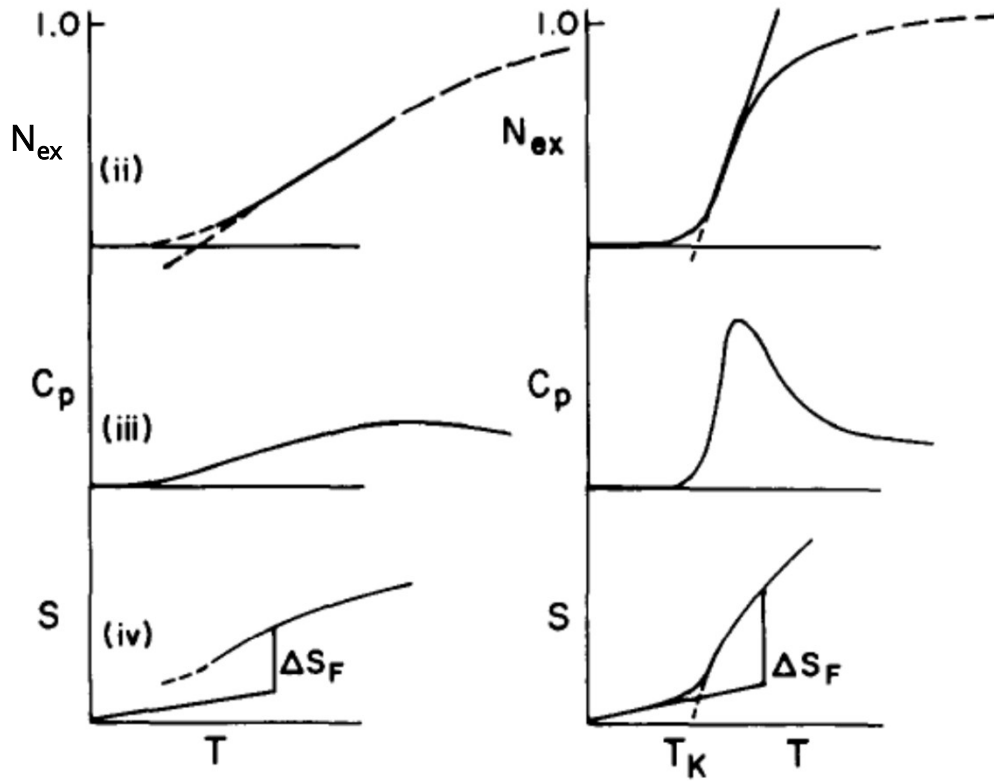
$D = 100$, strong liquid

$D = \infty$, Arrhenius

Adapted from Angell, C. A. 1995. "Formation of Glasses from Liquids and Biopolymers." *Science* 267 (5206): 1924–35 and P. Debenedetti, F. Stillinger, *Supercooled liquids and the glass transition*, *Nature*. 410 (2001) 259–26

Strong liquid

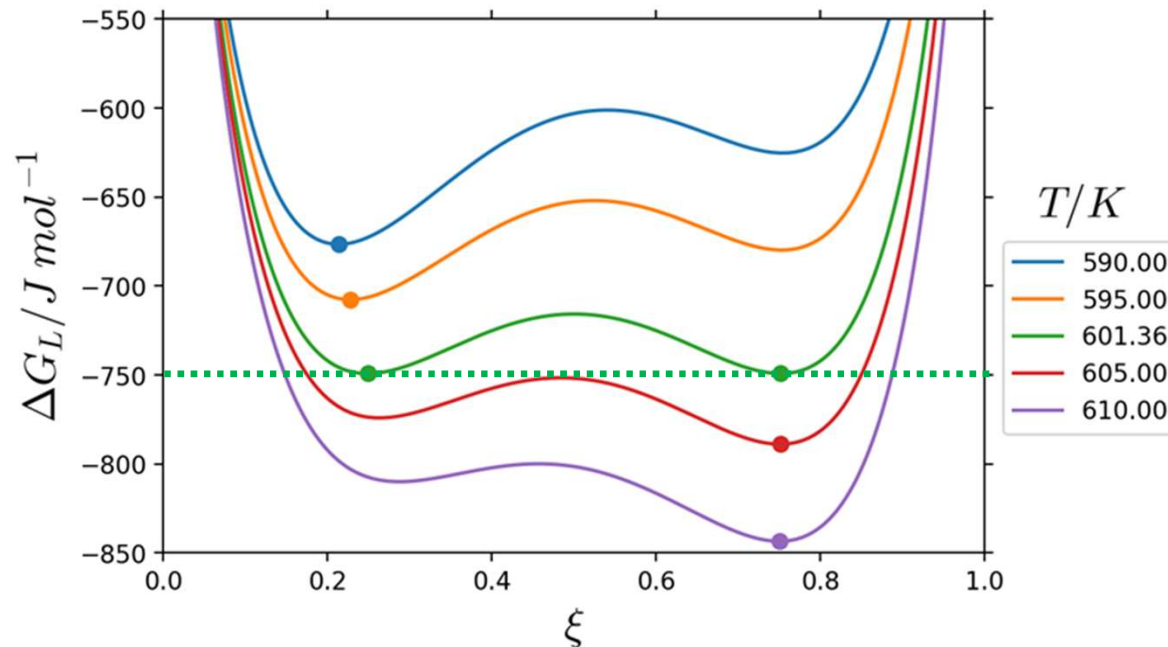
Fragile liquid



Angell, C.A. 1988. "Perspectives on the Glass Transition."
J. Phys. Chem. Solids 49 (8): 863–71

Liquid-liquid transition

- $\Delta H_d = 5000 \text{ J mol}^{-1}$, $\Delta S_d = R$
- Repulsive interaction $w = 11000 \text{ J mol}^{-1} > w_c = 10000 \text{ J mol}^{-1}$



2 liquids coexists only when ΔG_L has 2 minima of equal depth i.e.
 when $\Delta G_d(T_{LL}) = 0$ at $T_{LL} = \Delta H_d / \Delta S_d \approx 601.36 \text{ K}$

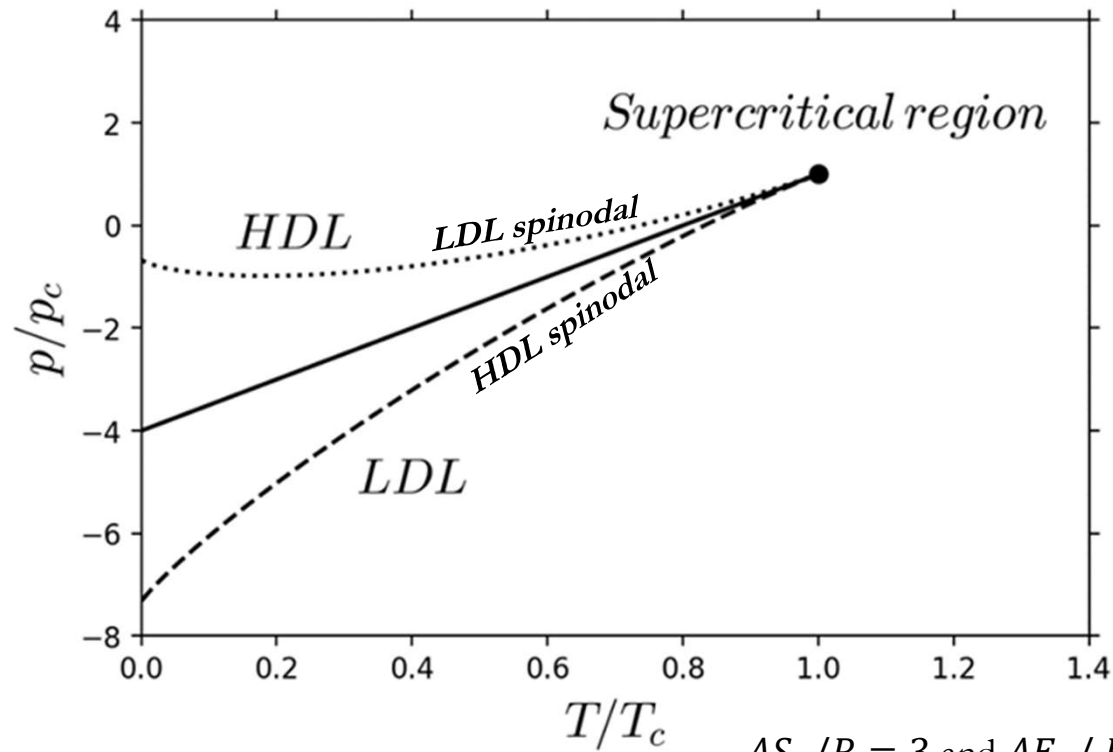
Pressure-induced phase changes

- Despite the disappearance of long-range order, the short-range order characteristic of a solid phase may persist in a liquid of the same composition
- If a substance has a stable **High-Pressure (HP)** polymorph distinct from the stable **Low-Pressure (LP)** polymorph, **the short-range order of the HP crystal may persist in the lower-pressure liquid**
- The liquid would then contain 2 species
 - each characterized by a coordination, a 1st neighbor distance, a type of bonding (metallic, ionic, covalent)
- As an example, for Ge, Si, $A_{III}B_V$ liquids, Ponyatovsky assumes that
 - Entity A = tetrahedral short-range order, characteristic of the semiconductor phase stable at atmospheric pressure
 - Entity B = compact stacking-type short-range order, characteristic of the metal phase stable at higher pressures
- The $(-p, V)$ pair of conjugate variables must be taken into account in the model

p - T phase diagram of the regular 2-state model

pressure work due to the molar volume difference between the 2 states

- $\Delta G_d = \Delta E_d + p\Delta V_d - T\Delta S_d$
- Condition of coexistence: $p = \frac{T\Delta S_d - \Delta E_d}{\Delta V_d}$



Application to supercooled water and amorphous ice

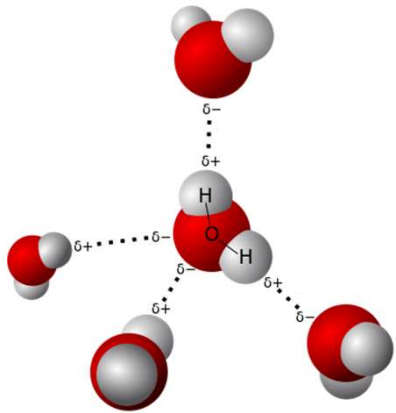
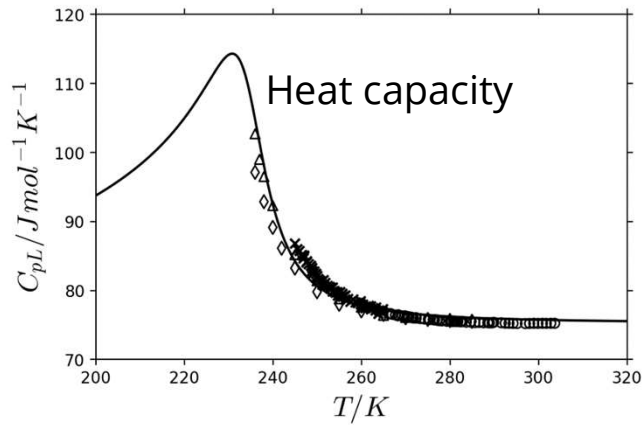
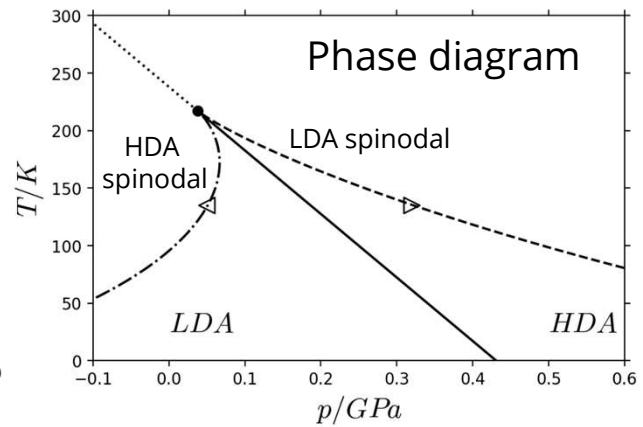
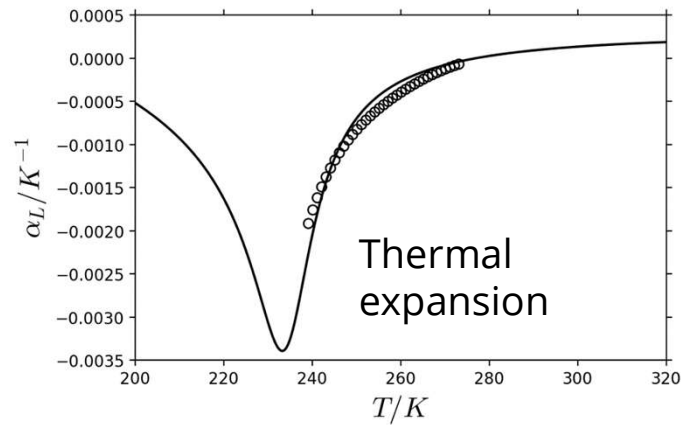
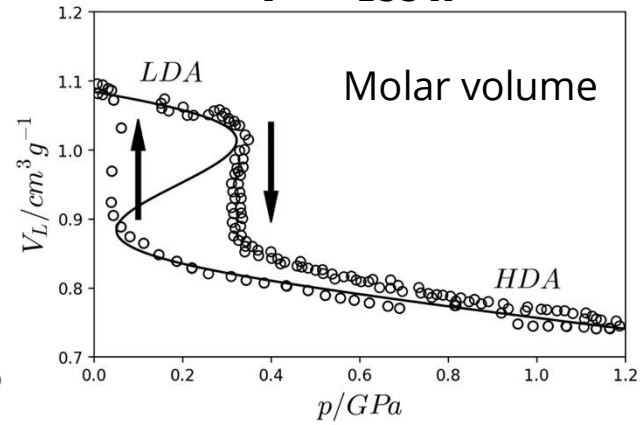


Image from Wikipedia

$p = 1 \text{ atm}$



Mishima's experiment
 $T = 135 \text{ K}$



Main conclusions about thermodynamic models

- The so-called 2nd generation 1-state liquid models have made it possible to build the large multicomponent thermodynamic databases currently available
- Despite their great usefulness, however, they have a number of drawbacks
 - They do not allow optimal modeling of glass-forming liquids at high supercooling
 - They are unsuitable for simulating the glass transition, as they have no internal variables
- The use of an ideal 2-state model improves descriptions, but fails to reproduce the full diversity of behavior observed between different unary glass-forming liquids
- The regular/cooperative form considerably enriches the 2-state model, making it potentially suitable for modelling
 - Fragile and strong behaviors
 - Liquid-Liquid (LL) separations in pure substances (liquid polymorphism, polyamorphism, Fragile to Strong (FTS) transitions on cooling...)

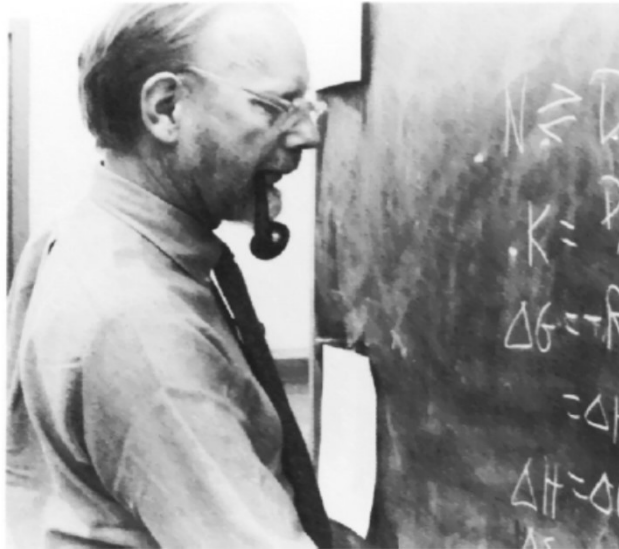


PART TWO

MODELING OF THE GLASS TRANSITION, COUPLING THERMODYNAMICS AND RELAXATION KINETICS

Kauzmann's view

- "... a glass is a liquid in which certain degrees of freedom characteristic of liquids are "frozen-in" and can no longer contribute to the specific heat and thermal expansion. The problem presented to us by the glassy state is **simply** to determine what these degrees of freedom are and to explain how they are frozen in at the glass-transformation point"



W. Kauzmann (1916-2009)

Kauzmann, Walter. 1948. "*The Nature of the Glassy State and the Behavior of Liquids at Low Temperatures.*" *Chemical Reviews* 43 (2): 219–56

Principle of the modeling

- Adopting Kauzmann's view, a phenomenological model of the glass transition should combine **three elementary building blocks**

- A **thermodynamic model** of the liquid involving at least **one internal variable** (= degree of freedom)

$$G_L = G_L(T, \xi)$$

- In our modeling, the single order parameter ξ is the fraction of excited units in a 2-state model

- An equation giving the **rate of the relaxation process**

- Using the thermodynamics of irreversible processes, we can show that this equation has the form

$$v = \frac{d\xi}{dt} = -\frac{1}{\tau}(\xi - \xi_e)$$

- For a given temperature program $T(t)$, integration of this ODE versus time t requires to chose a **relaxation law** i.e. an analytical expression of the relaxation time τ

$$\tau = \tau(T, \xi)$$

- In this approach, the **glass transition** is equated with the **freezing of the ξ value**

Relaxations laws found for B₂O₃ in the glass literature

- Vogel-Fulcher-Tammann (VFT):
 - $\langle \tau \rangle$ depends on T but not on the internal state of the glass
- Tool-Narayanaswamy-Moynihan (TNM) also called modified Arrhenius:
- Adam-Gibbs-Logarithmic (AGL):
 - Scherer-Hodge formulation

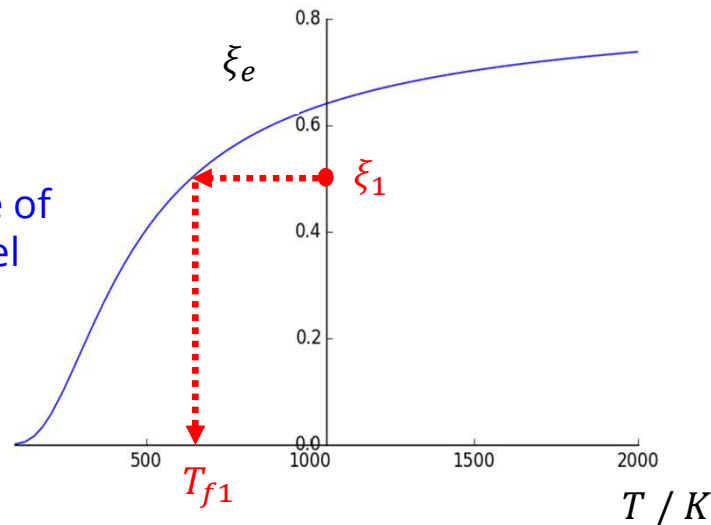
$$\langle \tau \rangle = A_{VFT} \exp\left(\frac{B_{VFT} T_{VFT}}{T - T_{VFT}}\right)$$

$$\langle \tau \rangle = A_{TNM} \exp\left(\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right)$$

$$\langle \tau \rangle = A_{AGL} \exp\left(\frac{Q_{AGL}}{RT \ln(T_f/T_{AGL})}\right)$$

T_f = fictive temperature

Excitation profile of the 2-state model



Comparison of relaxation laws for B₂O₃

- Arrhenius plots of the average relaxation time $\langle\tau\rangle$
 - comparison to experimental data obtained by US, LSCS and PJVR techniques

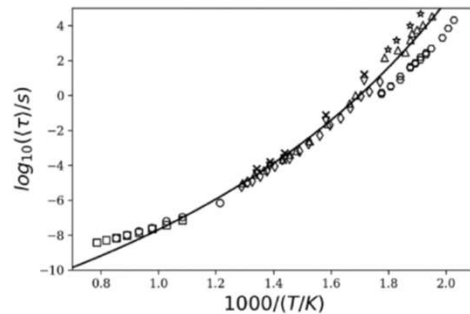
VFT

Hassan et al.

$$A_{VFT} = 10^{-13.5} \text{ s}$$

$$B_{VFT} = 35$$

$$T_{VFT} = 277 \text{ K}$$



TNM

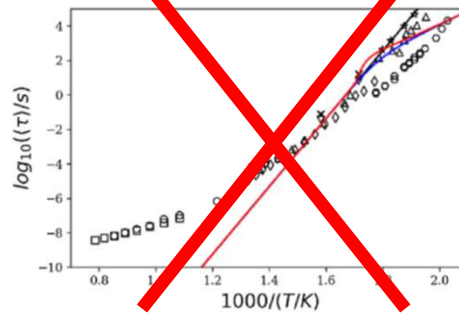
Debolt et al.

$$A_{TNM} = 1.51 \cdot 10^{-33} \text{ s}$$

$$x = 0.4$$

$$\Delta h^* = 90 \times 4.184 \text{ kJ mol}^{-1}$$

Unphysical!



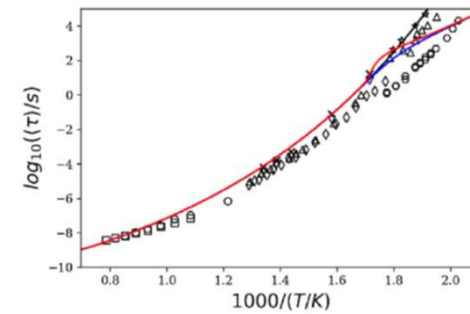
AGL

Moynihan et al.

$$A_{AGL} = 7 \cdot 10^{-12} \text{ s}$$

$$Q_{AGL} = 11.6 \times R \text{ kJ mol}^{-1}$$

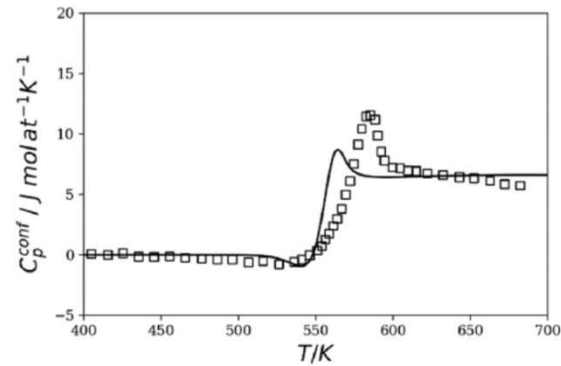
$$T_{AGL} = 286 \text{ K}$$



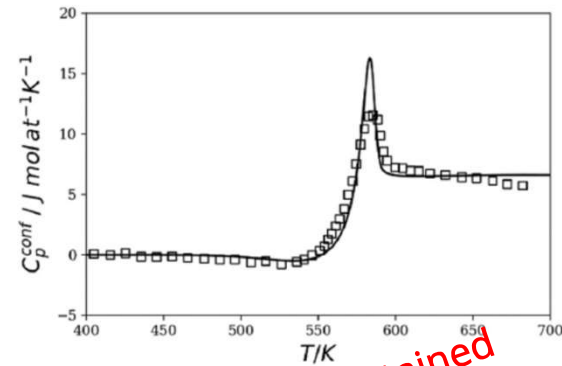
Heat capacity of B_2O_3 modeling of DSC curves on heating at 10 K/min

After prior cooling at 10 K/min

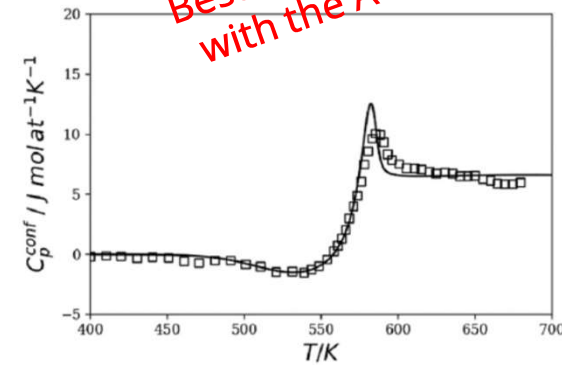
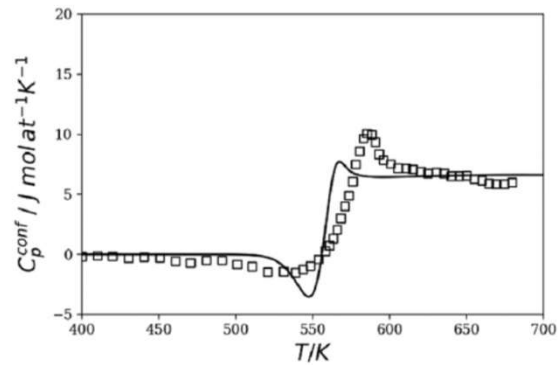
VFT



AGL

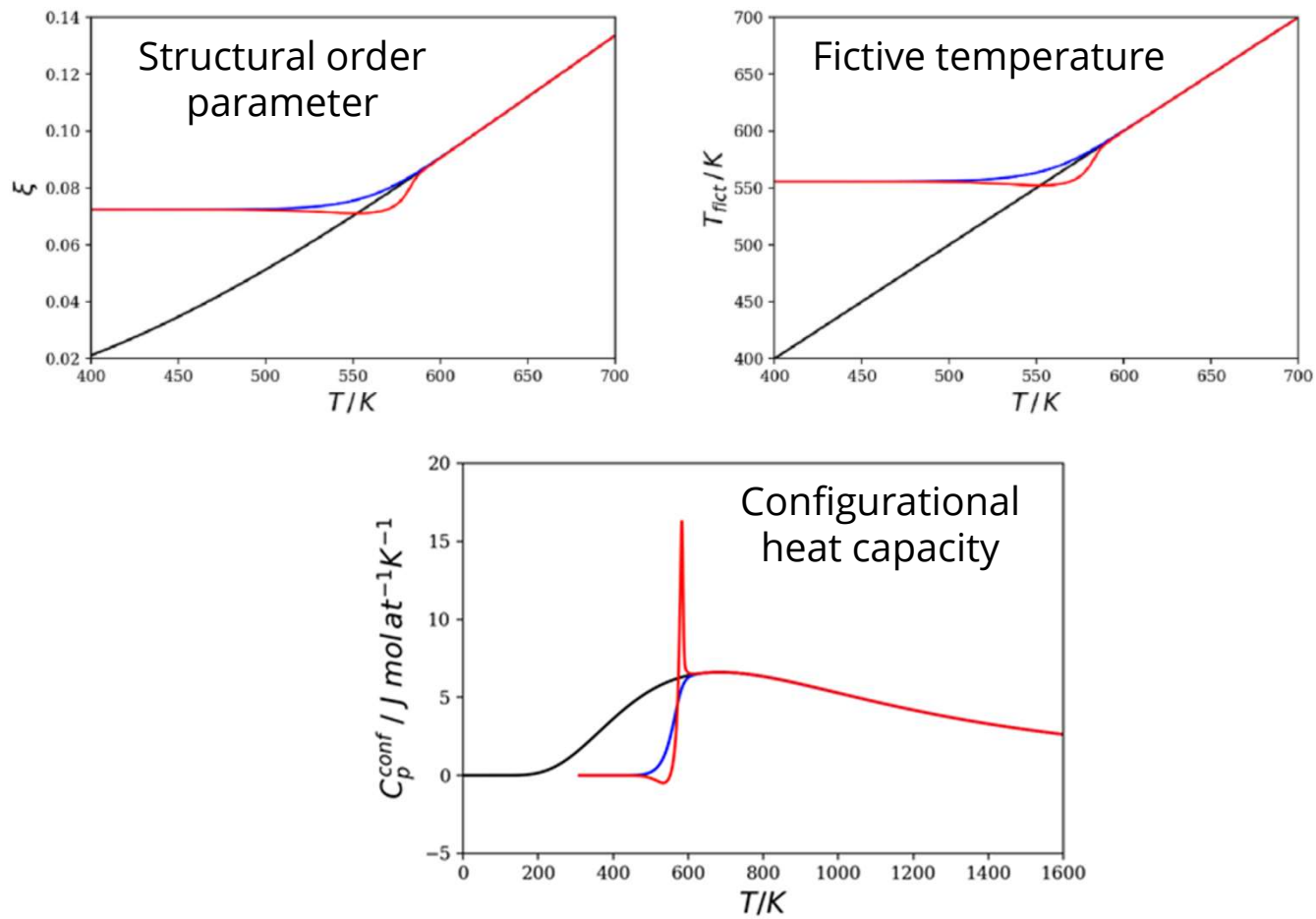


After prior cooling at 80 K/min



Best fit is obtained with the AGL law

Hysteresis effects for B₂O₃ during a cooling/heating cycle at 10 K/min



Residual entropy $S^\circ(0\text{ K})$ of B_2O_3 glasses having a fictive temperature T_f

Reference	T_f / K	$S^{\circ\text{glass}}(0\text{ K}) / \text{J mol}^{-1}\text{K}^{-1}$
Nemilov	540	11.09 – 11.38
Richet et al.	543	11.2 ± 0.8
This work, cooling at 1 K/min	540.77	12.2
Johari	521	9.9
This work, cooling at 0.025 K/min	520.06	11.1



Conclusions

- Within the frame of the **CALPHAD** approach
- A methodology has been proposed to model the glass transition in a unary glass forming substance
- The configurational part of the thermodynamic functions is described with a **2-state model**
- It is possible to calculate
 - The evolution of the thermodynamic functions in the glass transition range where they depart from their equilibrium values
 - Their residual values at 0 K
 - For B_2O_3 , with reasonable agreement with the numerous, but sometimes conflicting, experimental data
- No difficulty (in principle) in extending the approach to multi-component liquids... although this remains to be done!

More details in

CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 72 (2021) 102238

Contents lists available at [ScienceDirect](#)

 **Calphad** 

journal homepage: <http://www.elsevier.com/locate/calphad>

CALPHAD modeling of the glass transition for a pure substance, coupling thermodynamics and relaxation kinetics

P. Benigni^{a,b,*}



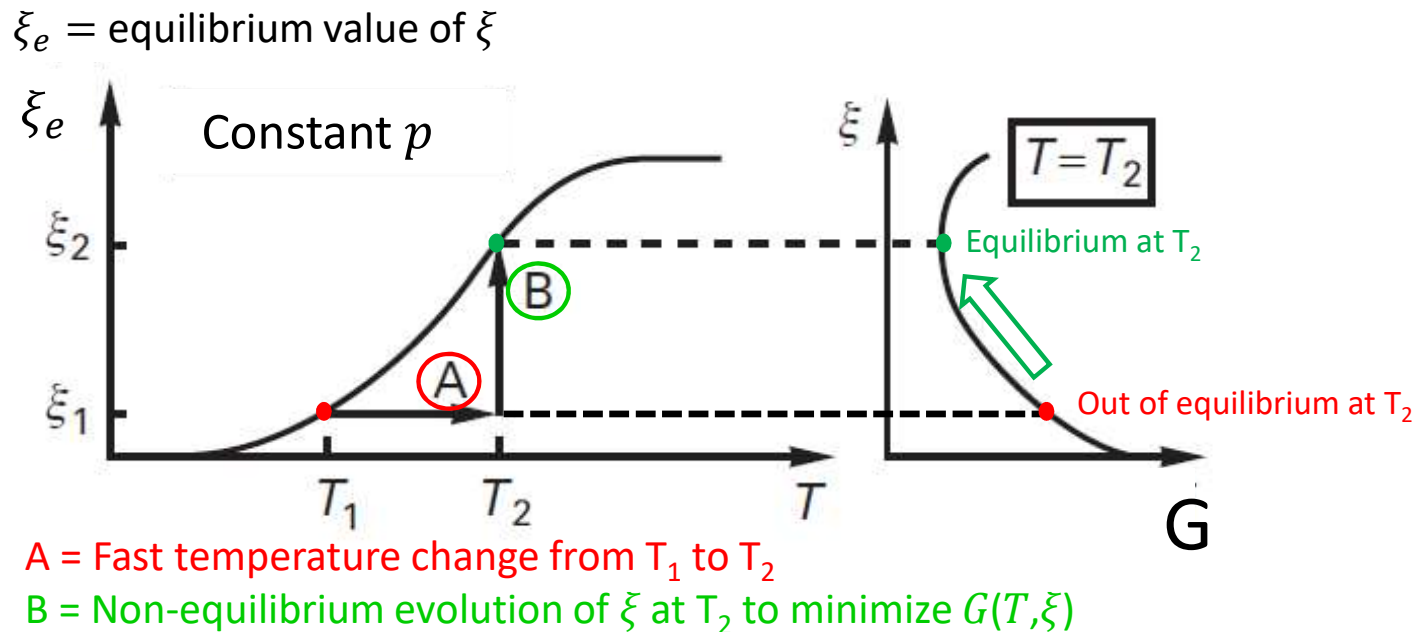
Thanks to the organizers for inviting me to this conference

and

Thank you for your attention!

Evolution of the order parameter ξ during a rapid change in T

- The experimentalist can arbitrarily control the temperature program $T(t)$ but not $v = \frac{d\xi}{dt}$ which depends on T and the state of the system



Adapted from M. Hillert, Phase equilibria, phase diagrams and phase transformations: their thermodynamic basis, 2nd ed., Cambridge University Press, 2007.