Austen's 2 hours visit to Aalborg for …

June 27, 2012

What occurs during the fragile-to-strong transition?

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Symposium on Fragility, January 5-8, 2014, JNCASR, Bangalore, India

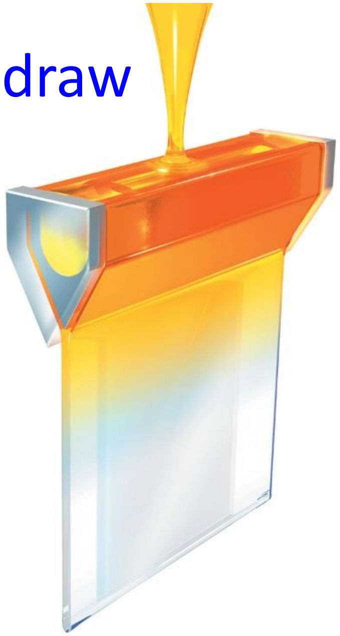
Outline

- Fragile to strong (F-S) transition
- Exploring the F-S transition by
  - Hyperquenching-Annealing-DSC
  - Diving deeply into the supercooled region
  - *In-situ structural characterization (on-going)*
- Perspective

Fragile to strong (F-S) transition

Why Do We Care Fragility?

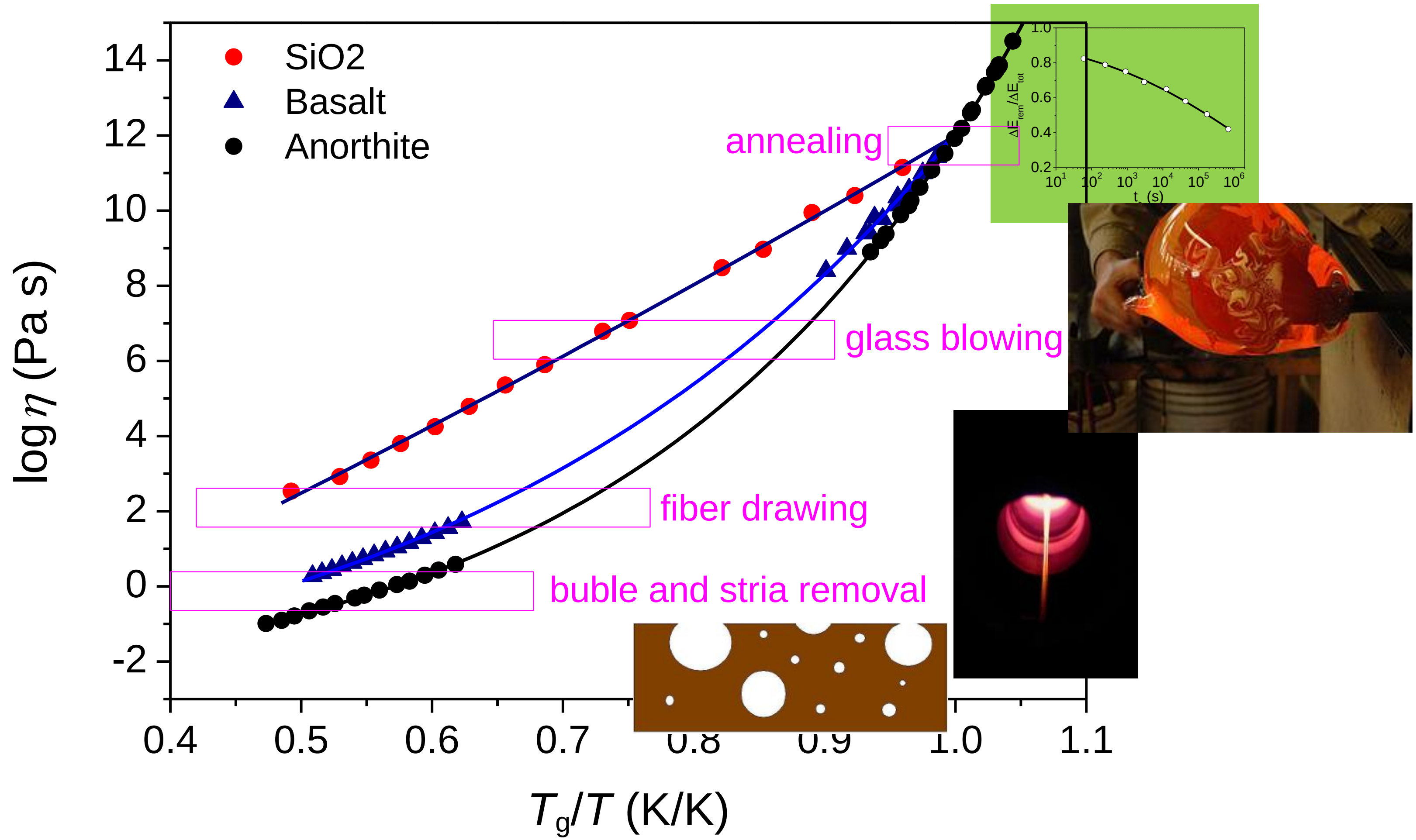
Fusion draw



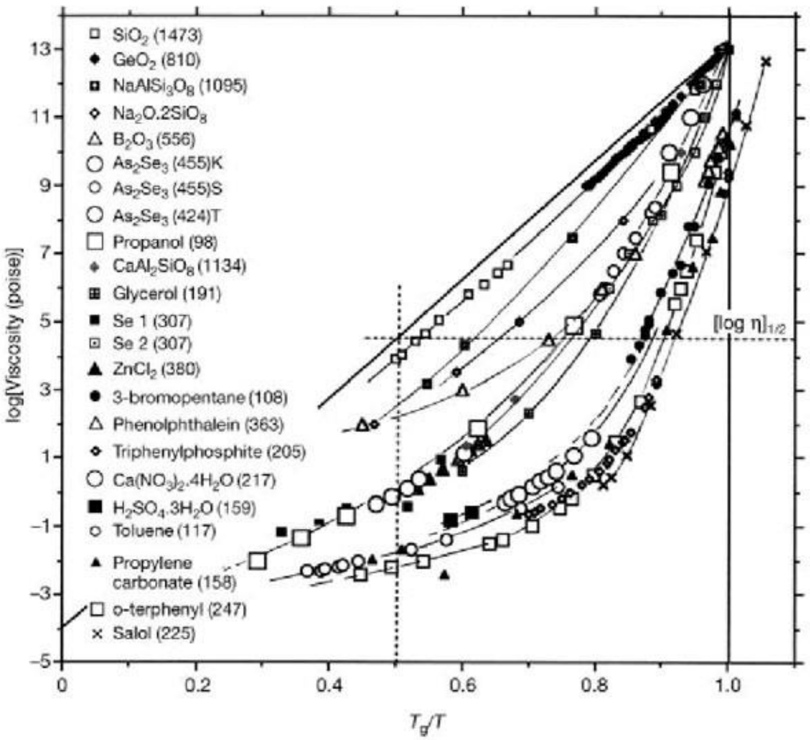
- Every step of industrial glass production depends critically on the viscosity of the glass-forming liquid!
- The fragility concept is linked to fundamental glass problems!

Google: Liquid Fragility: 1.29 mil. results, 0.4 seconds!

Importance of viscosity and fragility for glass technology

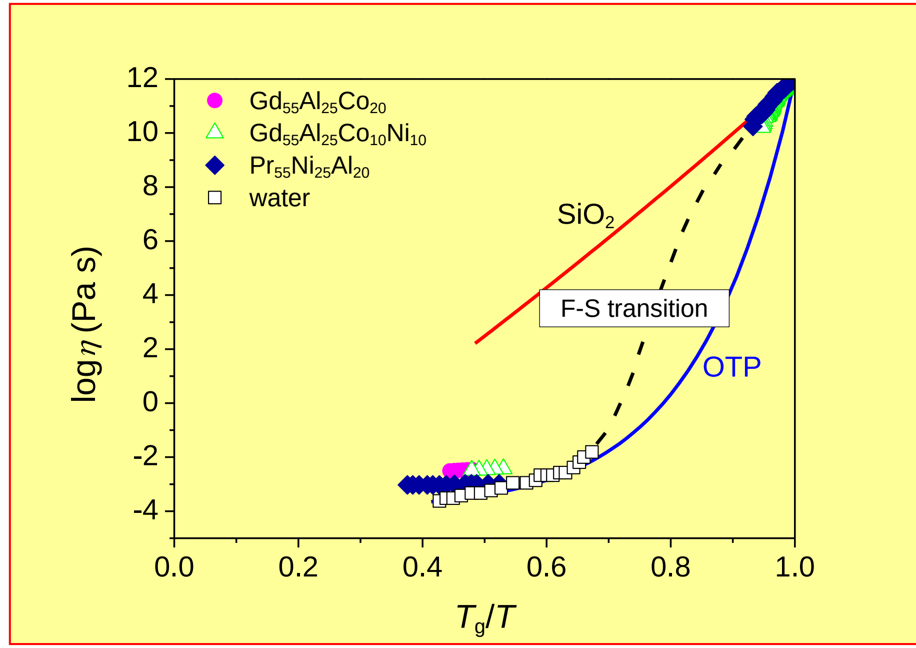


Two types of Angell Plots



Normal cases

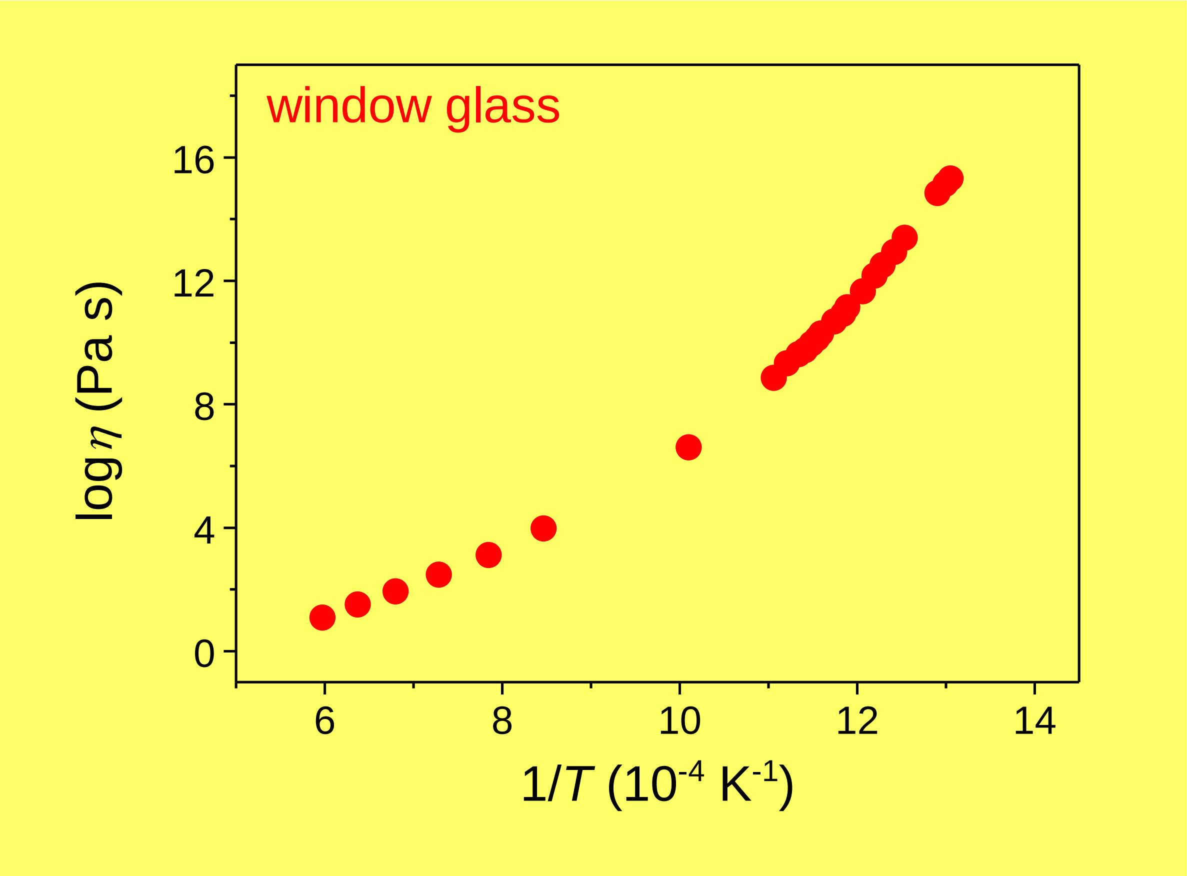
Angell, Science, 1995
Martinez, Angell, Nature 2001



‘Abnormal’ cases (s-type)

Ito, Moynihan, Angell, Nature 1999
Saika-Voivod, Poole, Sciortino, Nature 2001
Way, Wadhwa, Busch, ACTA Mater (2007)
Zhang, Hu, Yue, Mauro, JCP 2010

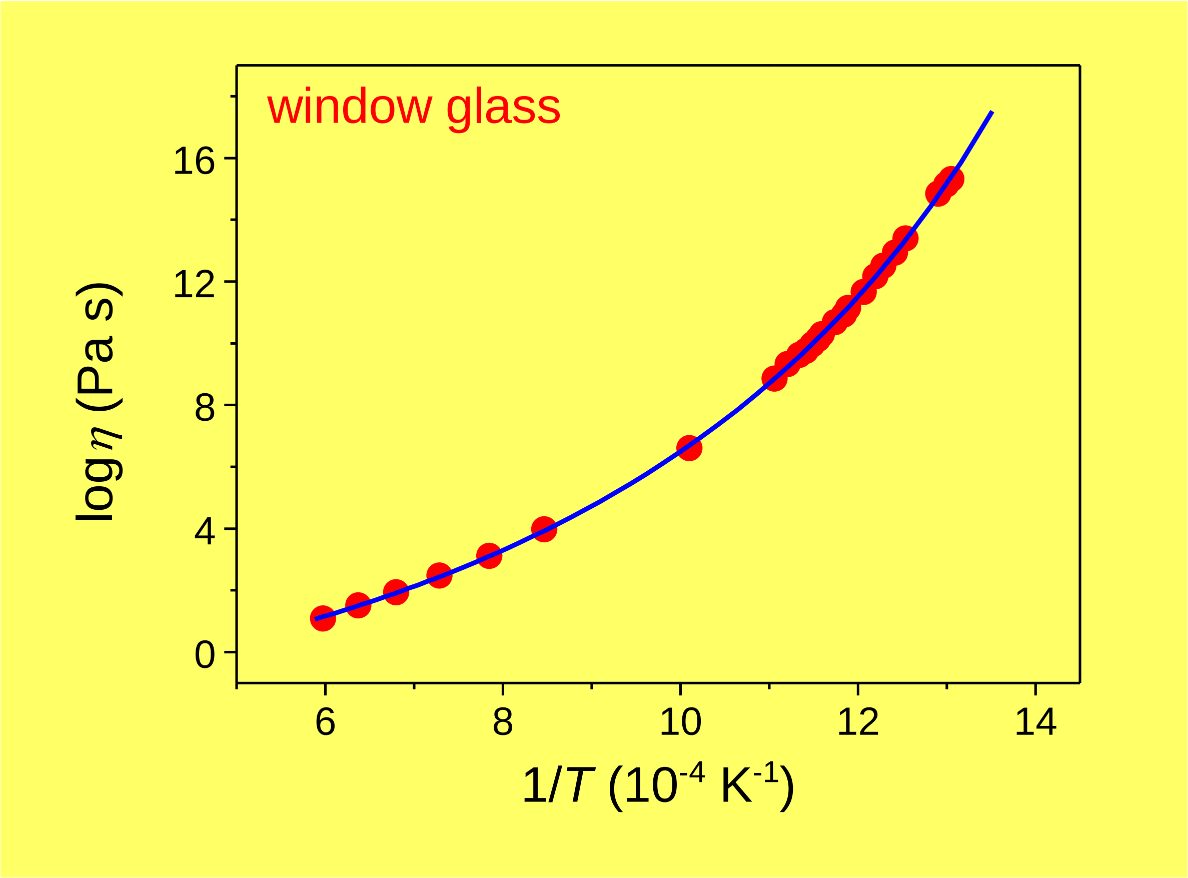
A normal case: window glass!



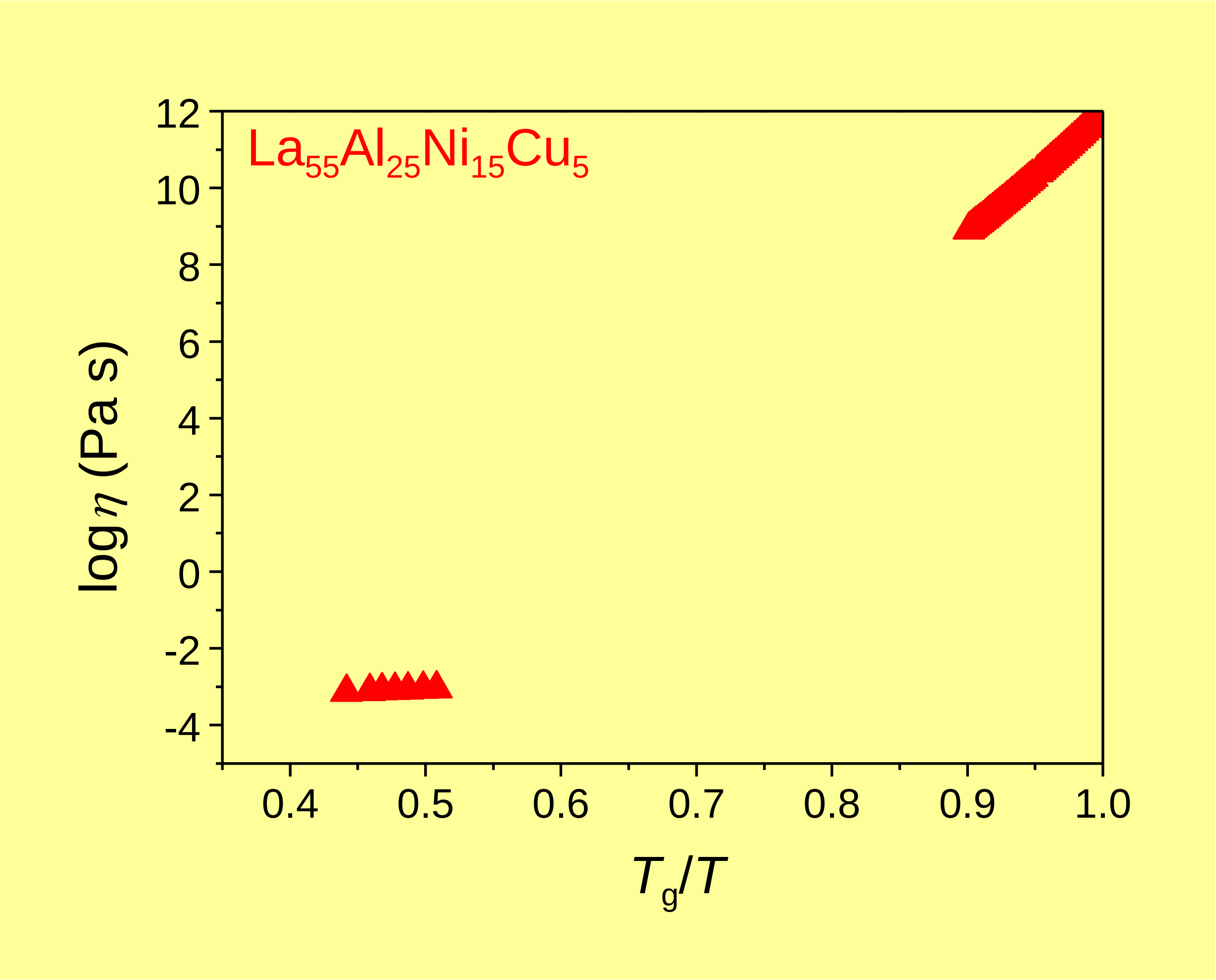
Excellent fitting

$$\log\eta = -3 + 15\frac{T_g}{T}\exp\left[\left(\frac{m}{15}-1\right)\left(\frac{T_g}{T}-1\right)\right]$$

(MYEGA, PNAS 2009)

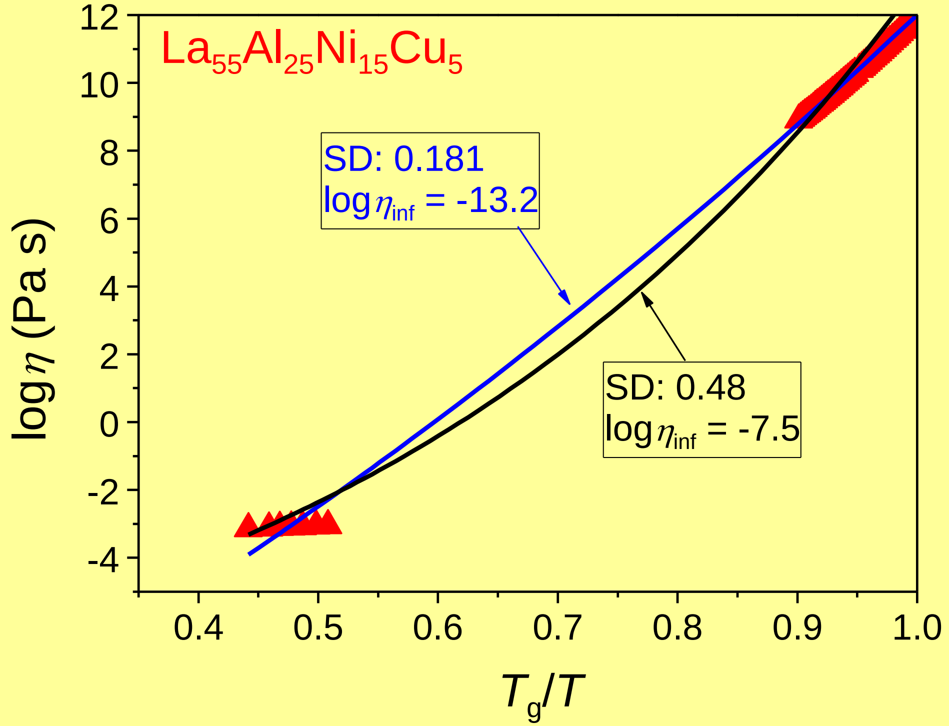


An abnormal case: a glass-forming metallic liquid!



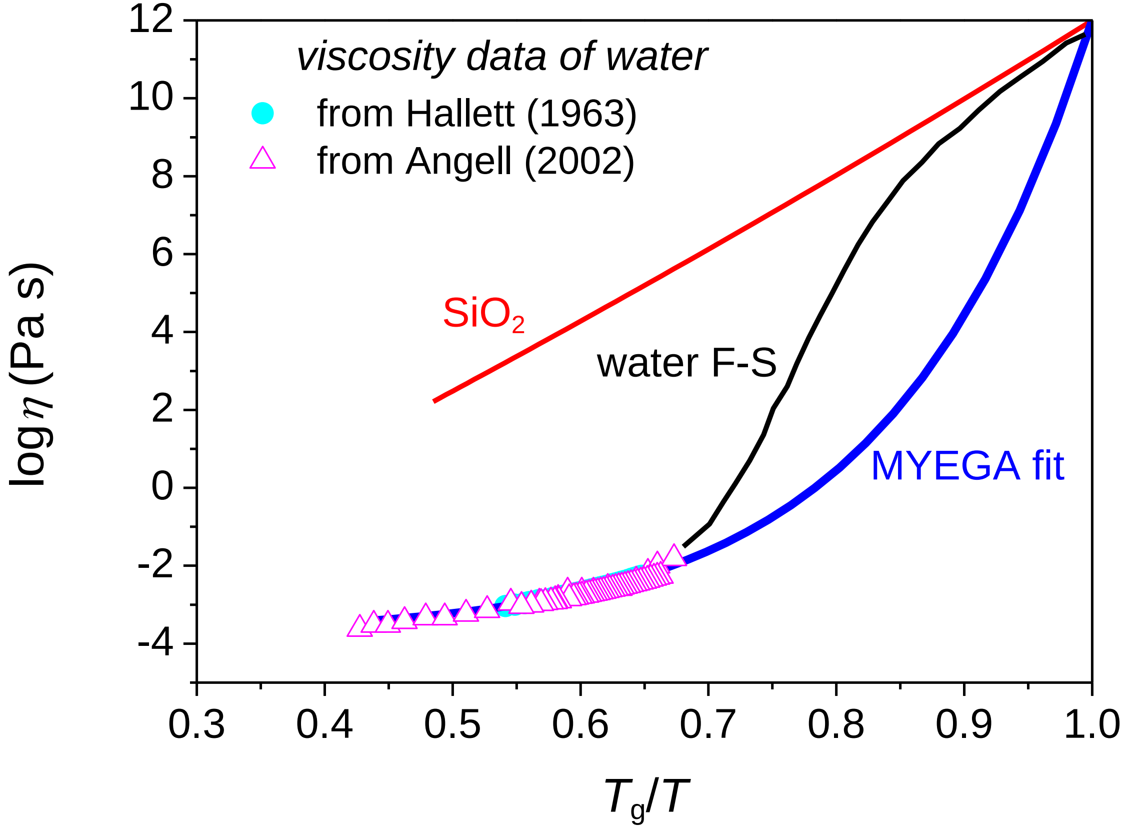
The existing viscosity models cannot describe its dynamics.

$$\log \eta = -3 + 15\frac{T_g}{T}\exp\left[\left(\frac{m}{15}-1\right)\left(\frac{T_g}{T}-1\right)\right]$$



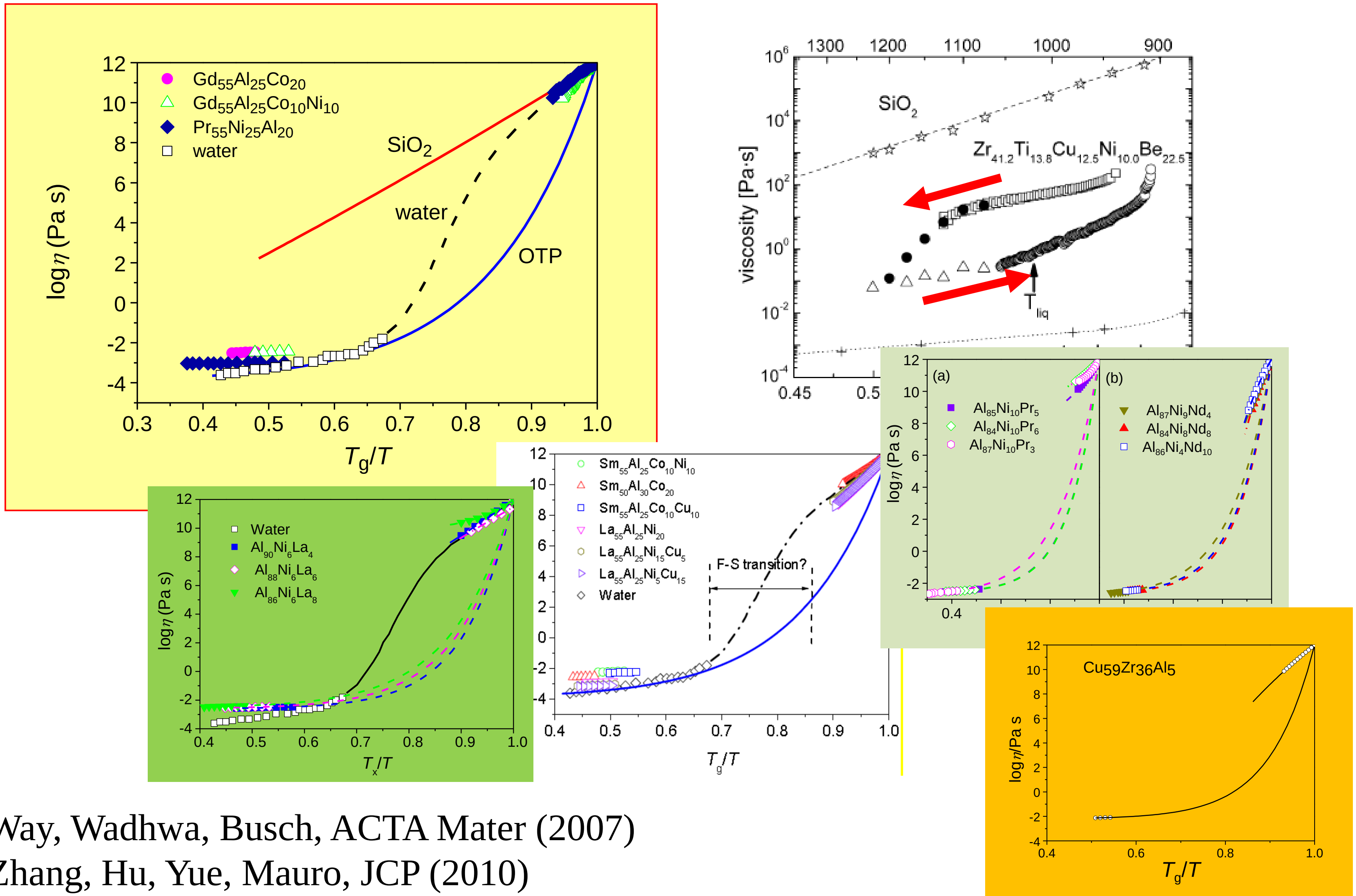
The failed data fitting leads to our initial perception about the abnormal dynamics of metallic liquids and then recalled the case of water.

We recall a striking case – water!



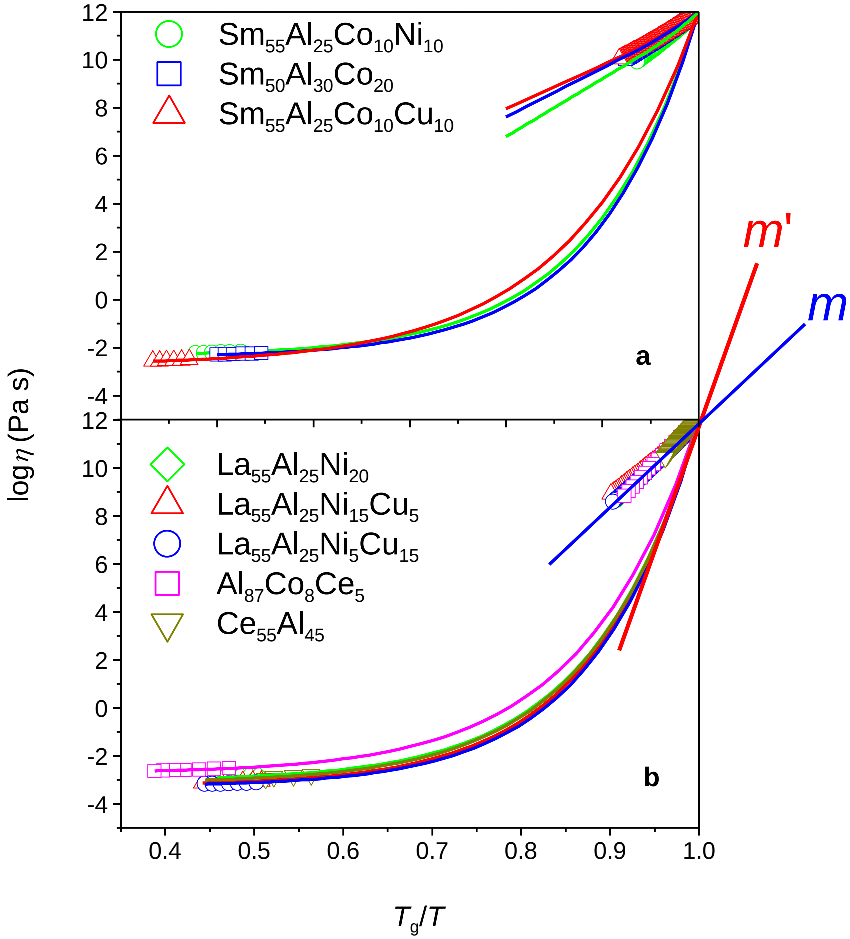
Ito, Moynihan, Angell, *Nature* 1999

Many metallic liquids are similar to water regarding
Fragile-to-Strong (F-S) Transition



Way, Wadhwa, Busch, ACTA Mater (2007)
Zhang, Hu, Yue, Mauro, JCP (2010)

The strength of the F-S transition is determined by:



$$f = m'/m$$

f > 1: F-S transition

f = 1: no F-S transition

f < 1: never seen

$1 \leq f \leq 12$?

Zhang, Hu, Yue and Mauro, JCP (2010)

The calculated *f* values for different MGFLs

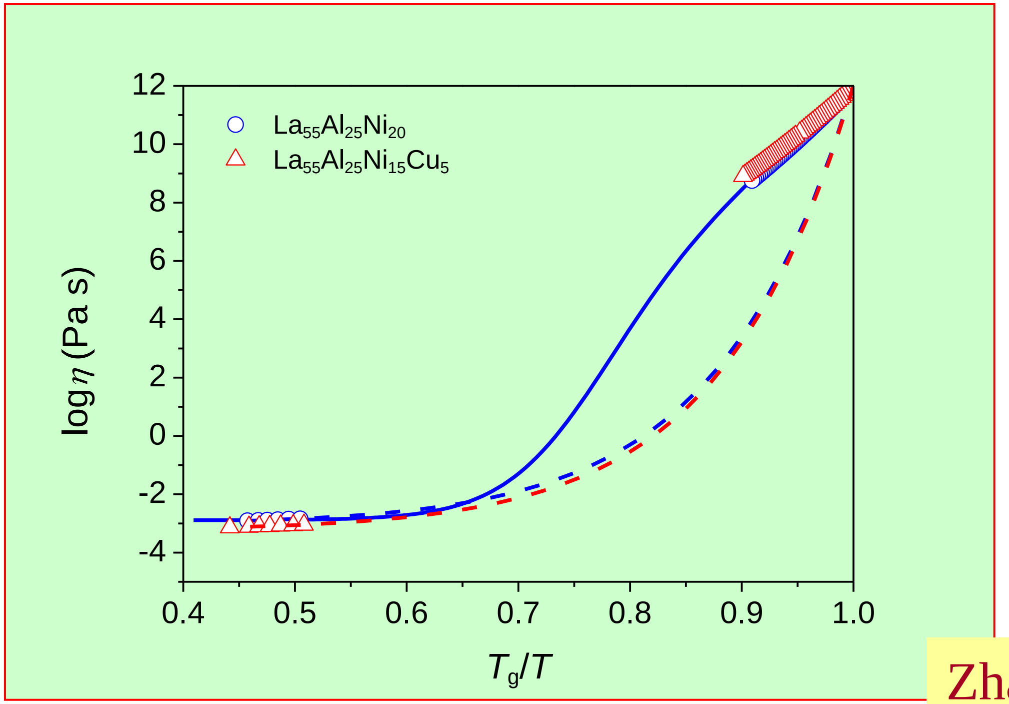
Composition	m'	m	f
$Gd_{55}Al_{25}Co_{20}$	113	25	4.5
$Gd_{55}Al_{25}Ni_{10}Co_{10}$	133	25	5.3
$Pr_{55}Ni_{25}Al_{20}$	156	19	8.2
$Sm_{55}Al_{25}Co_{10}Ni_{10}$	130	37	3.5
$Sm_{50}Al_{30}Co_{20}$	136	29	4.7
$Sm_{55}Al_{25}Co_{10}Cu_{10}$	114	27	4.2
$La_{55}Al_{25}Ni_{20}$	127	40	3.2
$La_{55}Al_{25}Ni_{15}Cu_{5}$	130	34	3.8
$La_{55}Al_{25}Ni_{5}Cu_{15}$	134	40	3.4
$Al_{87}Co_{8}Ce_{5}$	114	34	3.3
$Ce_{55}Al_{45}$	127	32	4.0
Water	98	22	4.5

The factor *f* confirms the existence of the F-S transition in the investigated MGFLs.

The extended MYEGA model describes the F-S transition:

$$\log \eta = \log \eta_\infty + \frac{1}{T\left[W_1 \exp\left(-\frac{C_1}{T}\right) + W_2 \exp\left(-\frac{C_2}{T}\right)\right]}$$

Fragile term Strong term

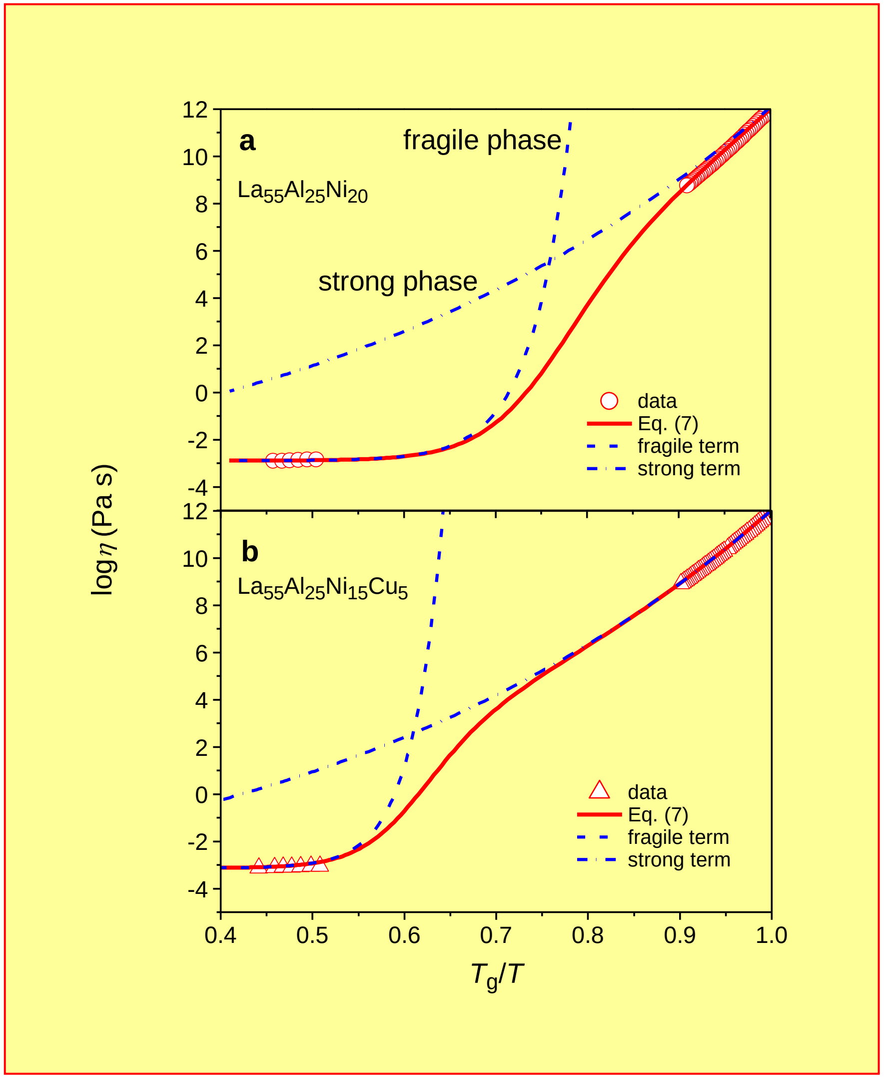


C_1 and C_2: two constraint onsets .
W_1 and W_2: normalized weighting factors.
If $C_1 = C_2$, the equation reduces to the one for normal liquids.

Zhang, Hu, Yue, Mauro, JCP (2010)

Two "phases" co-exists during the F-S transition: Fragile and strong phases

The former one is being transformed into the latter one.



Fragile phase:

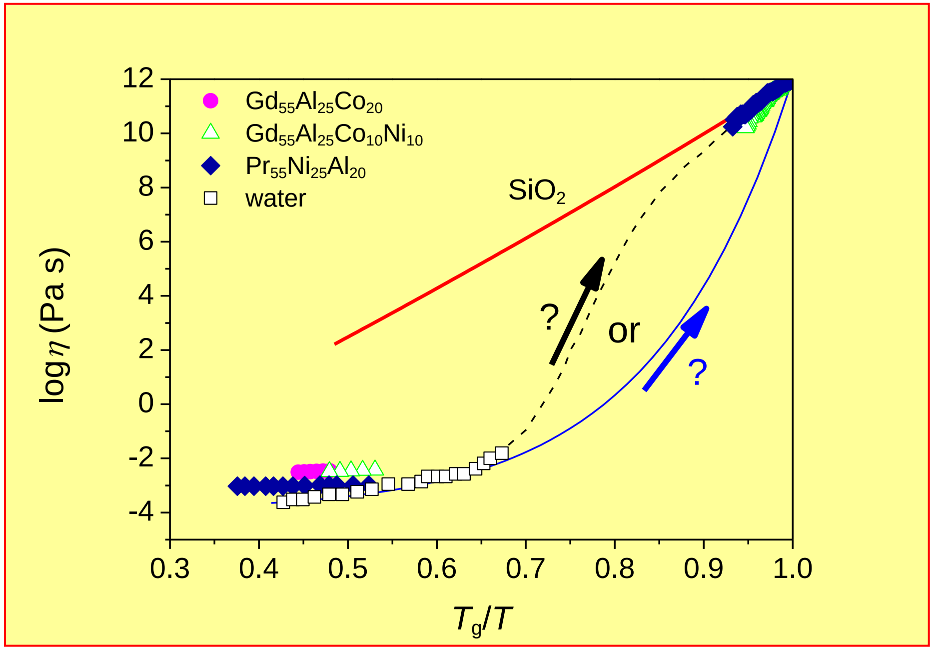
- higher T_g
- higher activation enthalpy
- higher entropy

Strong phase:

- lower T_g, i.e. actual T_g
- lower activation enthalpy
- lower entropy

The fragile phase is cooled, the F-S transition intervenes, mitigating the increase in viscosity with decreasing T.

A crucial question: what is the cooling parth during the F-S transition?



It is likely that

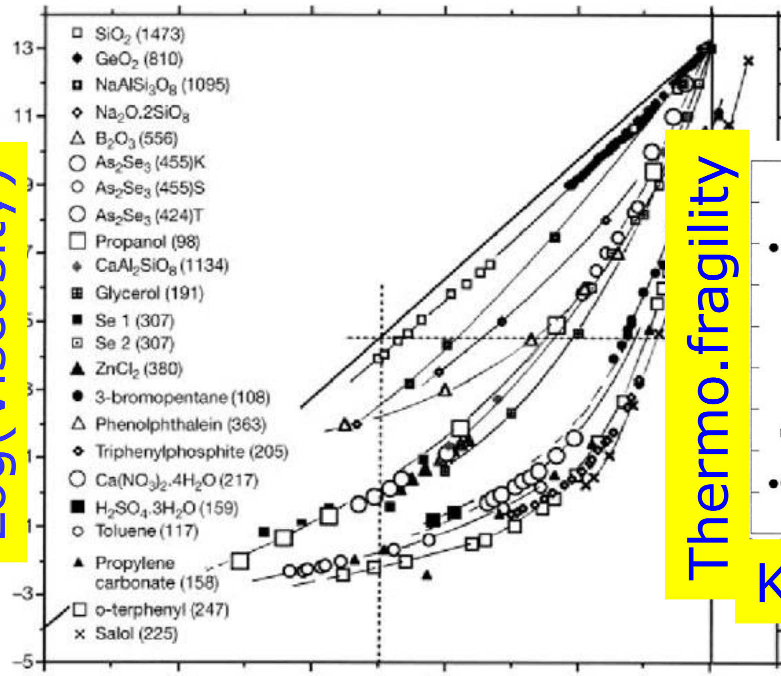
- A direct F-S transition occurs upon cooling,
- It occurs in the low *T* range, e.g., around $1.2T_g$, and
- Structural and thermodynamic values varies rapidly.

Link between kinetic and thermodynamic fragility

Kinetic fragility

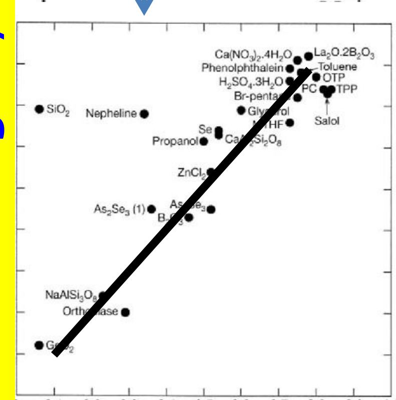
Thermodynamc fragility

Log(Viscosity)



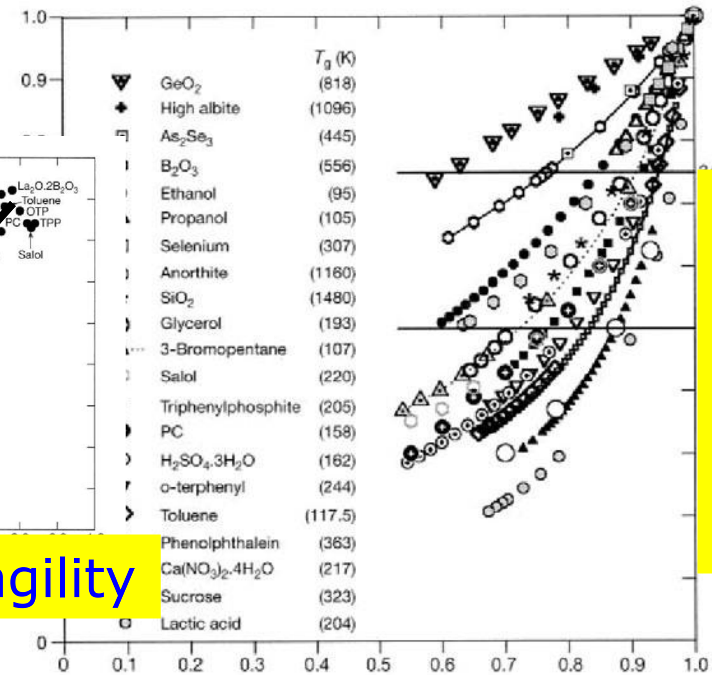
T_g/T

Thermo.fragility



Kinetic Fragility

$S_{ex}(T_g)/S_{ex}(T)$



T_g/T

Martinez and Angell, Nature 2001

Viscous slowing-down upon cooling

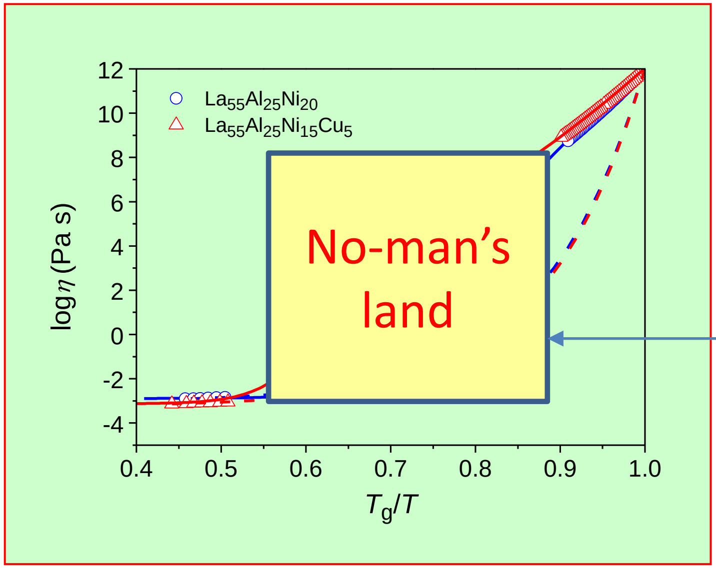
Entropy loss upon cooling

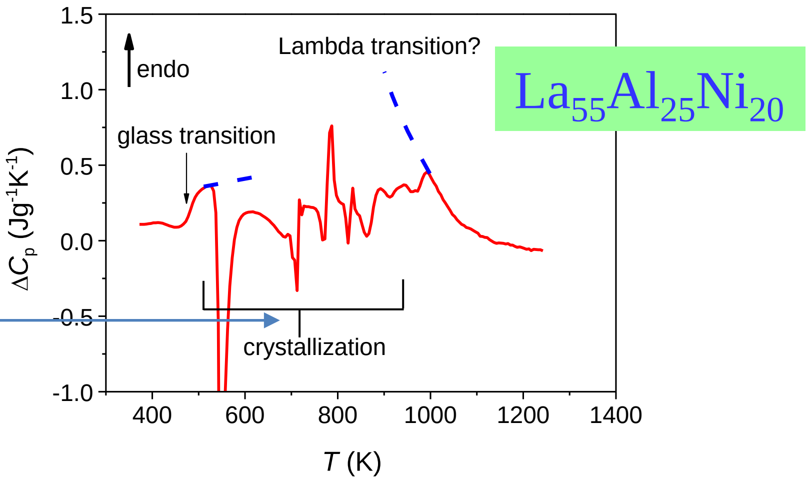
But this link is missing for F-S transition liquids!

Why?

Because

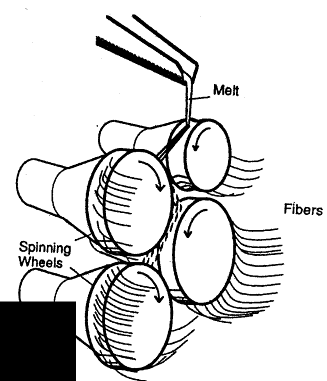
- The F-S transition mostly occurs in the no-man's land, i.e., in the crystallization region.
- The crystallization hinders detection of the thermodynamic responses of the F-S transition.
- Experimental approaches for detecting rapid changes in dynamical properties are not available yet.

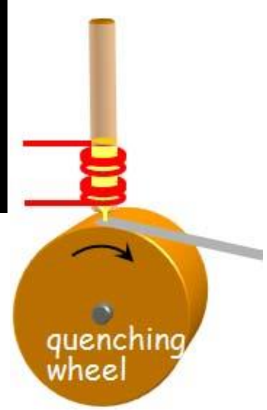


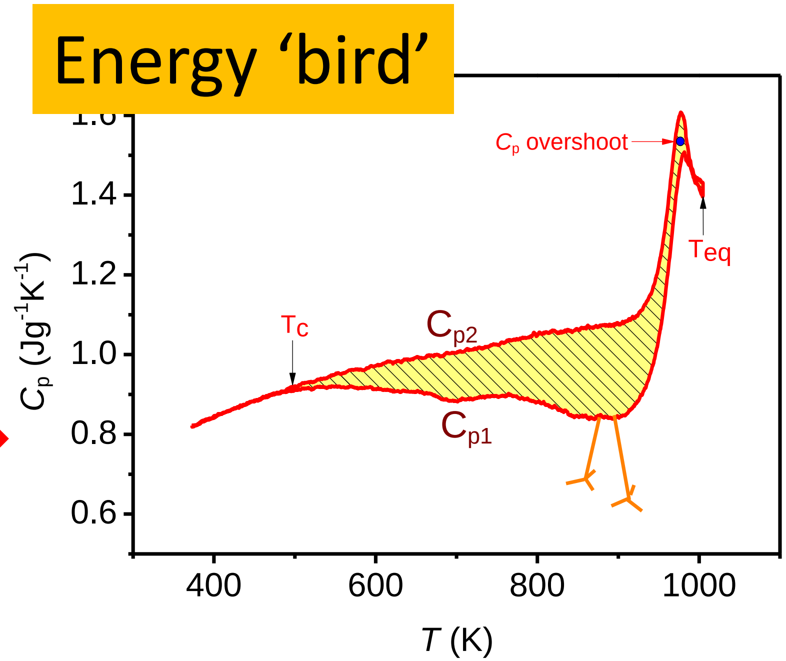


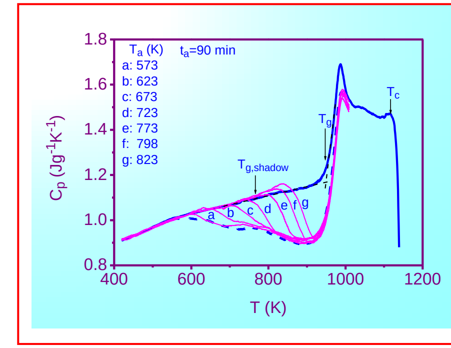
Exploring the F-S transition by

–Hyperquenching-Annealing-DSC





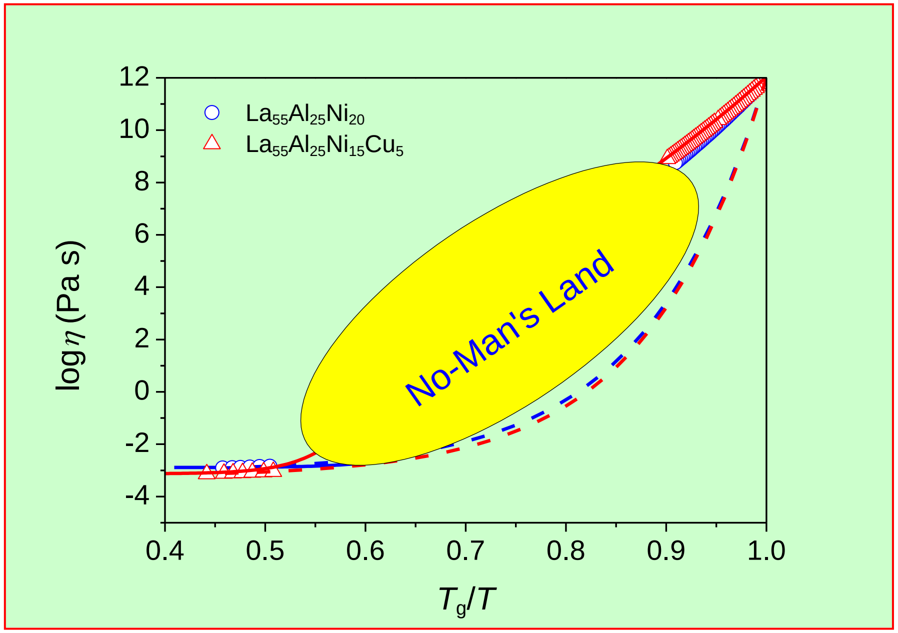


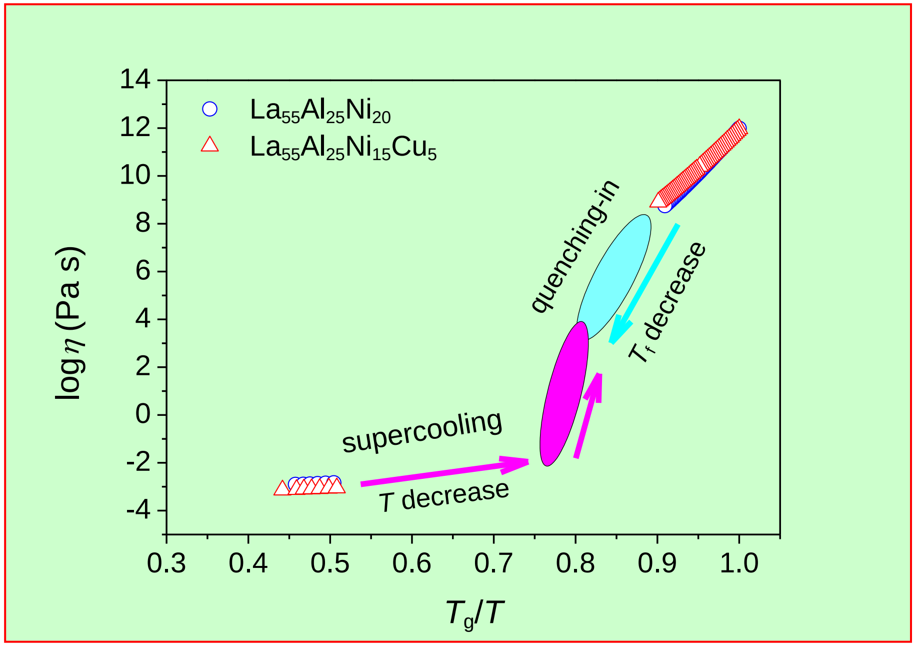


Yue, et al, APL, 2002

Yue and Angell, Nature 2004

Access No-Man's land...

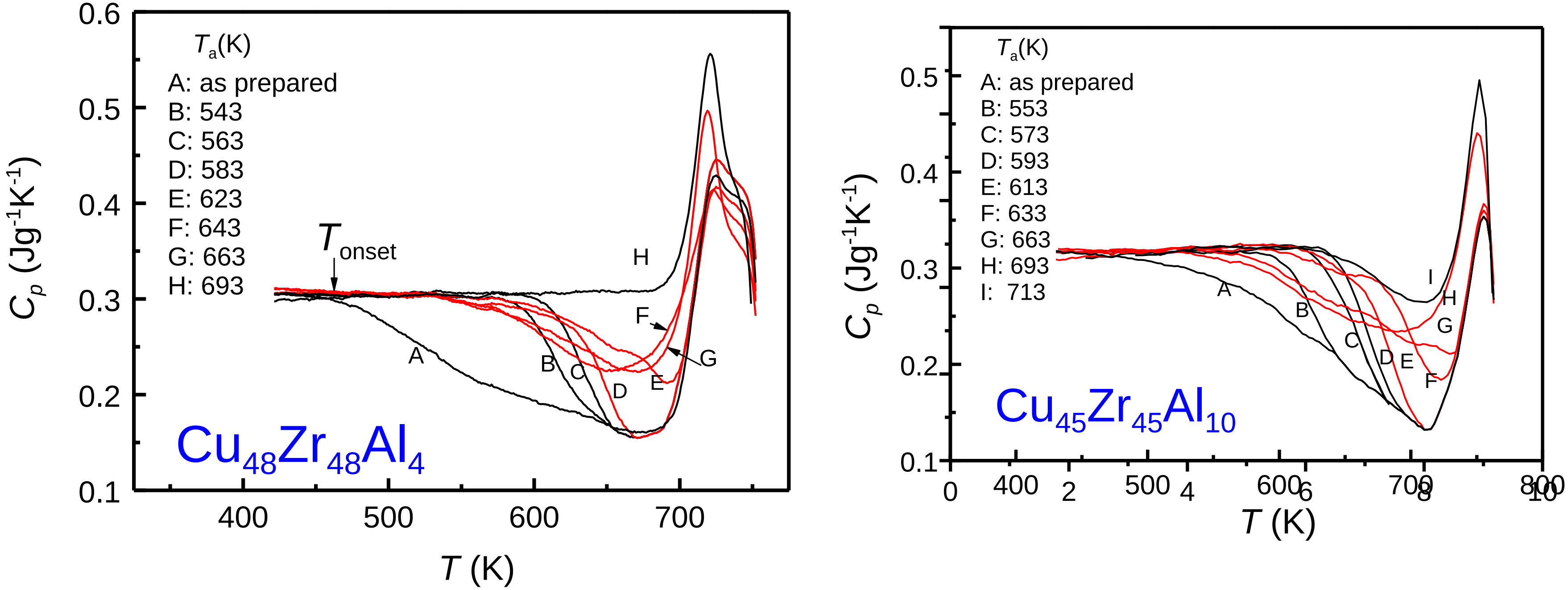




Possibilities:

- Trap the structure at high T_f and then relax it via annealing and calorimetric scan
- Dive deeply into the supercooled region

Using the "Bird", we try to find out the structural and thermodynamic elvolution during the F-S transition.



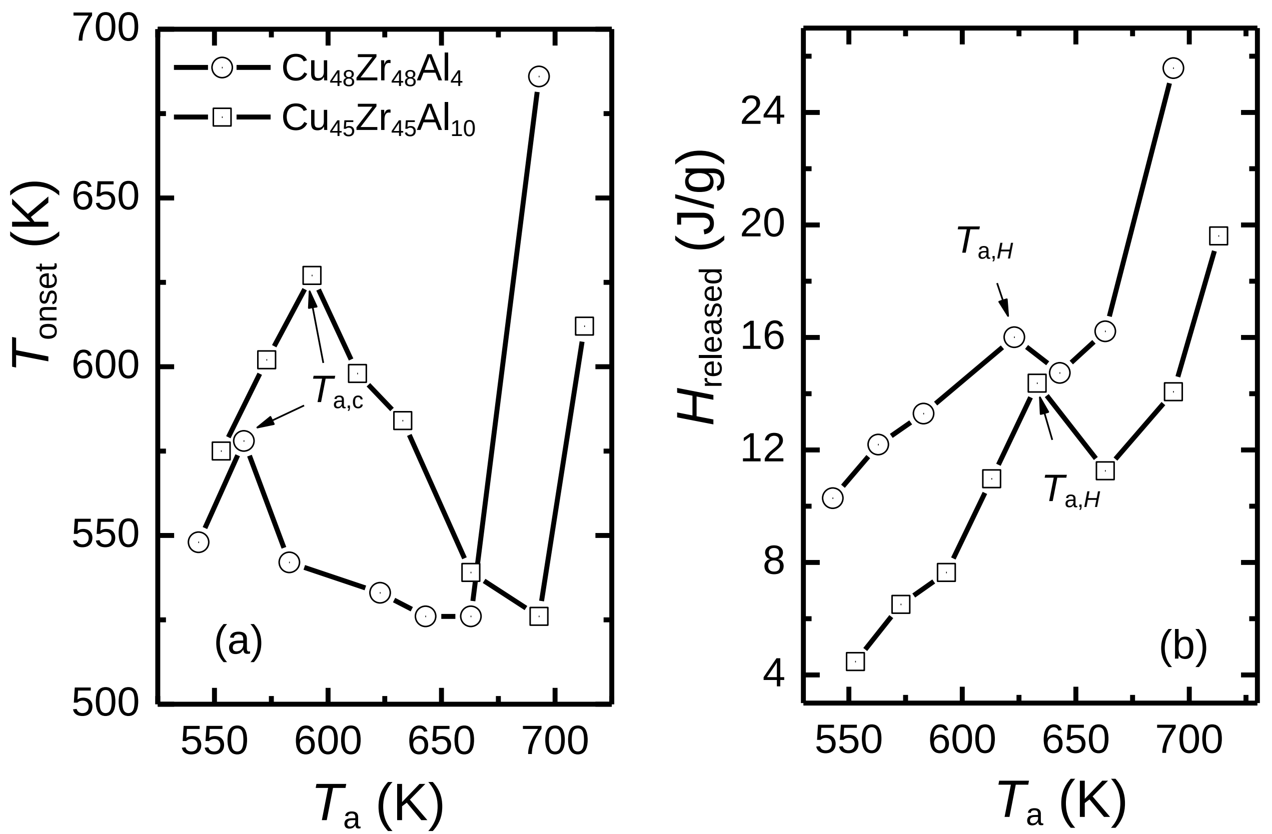
Enthalpy relaxation of the hyperquenched (HQ) metallic ribbons annealed at various temperatures for 1 hour.

Very different from enthalpy relaxation of HQ oxide glasses. See the following slides!

Hu, Yue, Zhang, APL (2011)
Hu, et al. JCP 2013

Onset temperature T_{onset} versus T_a

Released enthalpy H_{anneal} vs. T_a

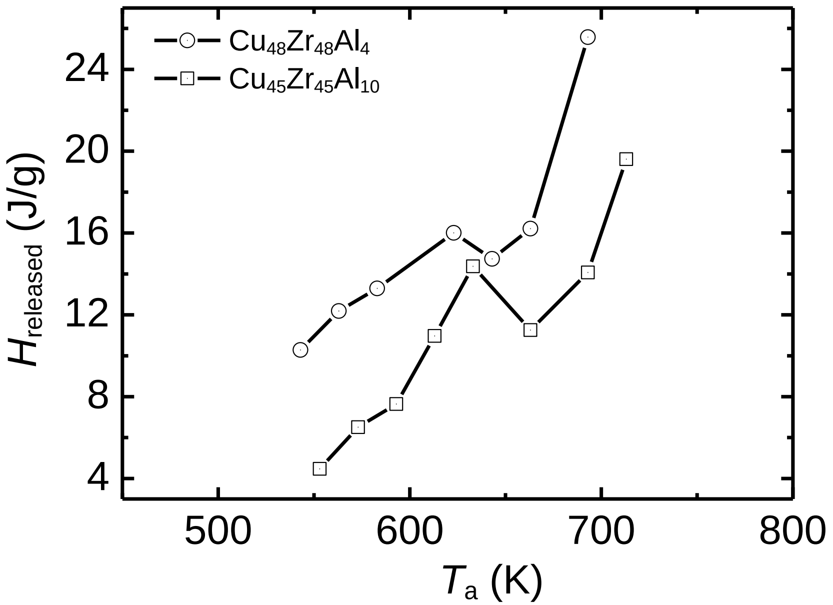


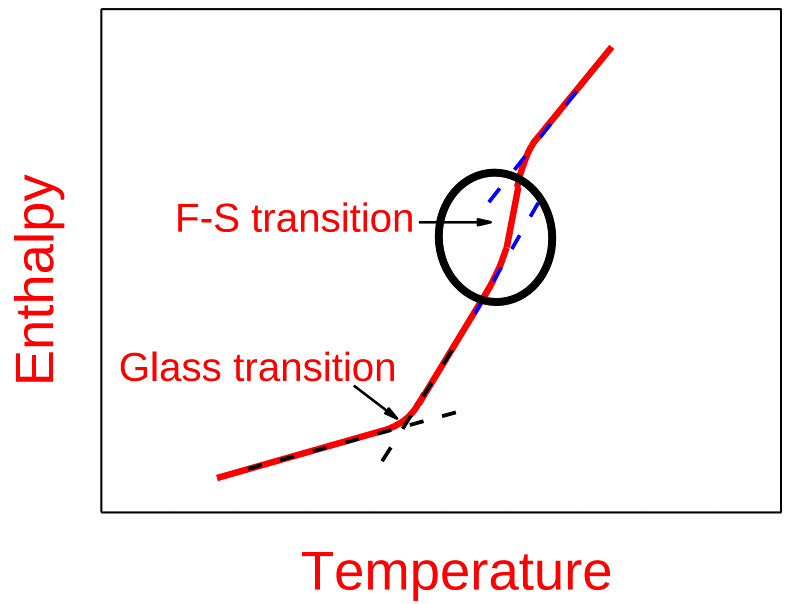
Non-monotonic changes!

Implication: high degree of structural heterogeneity

Hu, et al. APL (2011)

Thermodynamic implications?



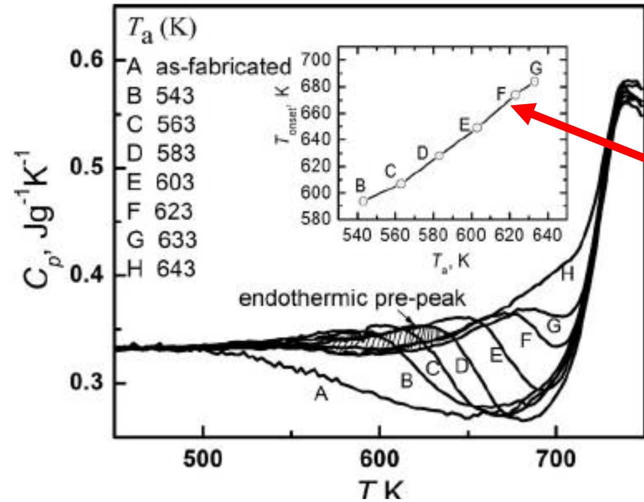


- Is this non-monotonic tendency is related to the thermodynamic F-S transition?
- Is it due to a sudden transformation from high to low *T* clusters?

THE JOURNAL OF CHEMICAL PHYSICS 138, 174508 (2013)

Thermodynamic anomaly of the sub-T_g relaxation in hyperquenched metallic glasses

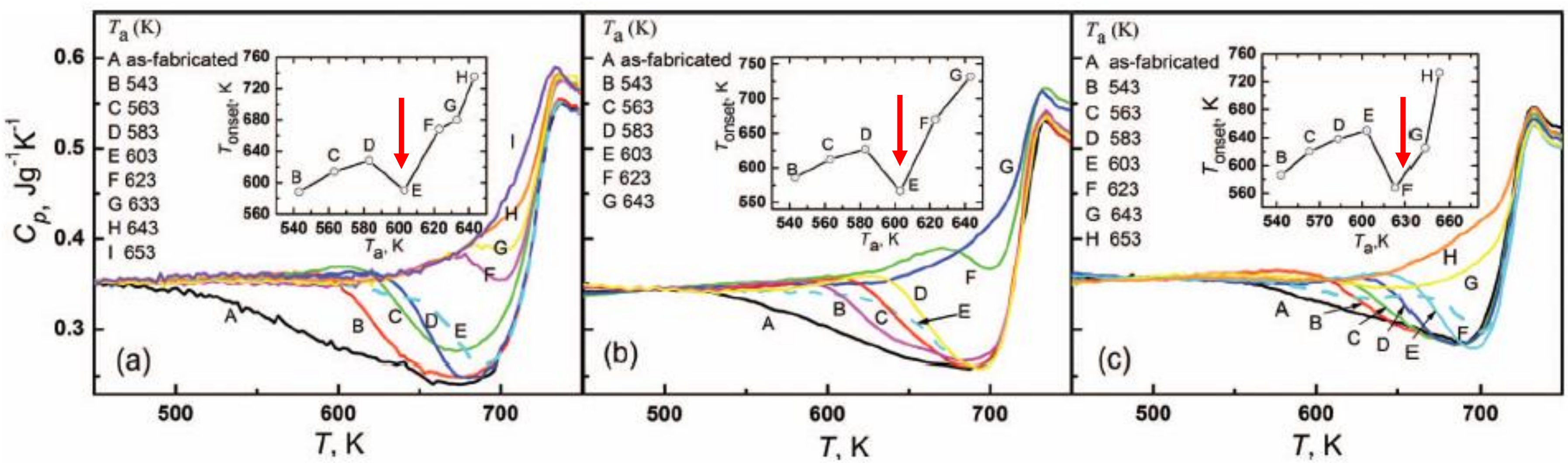
Lina Hu,[1,a)] Chao Zhou,[1] Chunzhi Zhang,[2] and Yuanzheng Yue[1,3]



monotonic

(49m/s)

$Cu_{46}Zr_{46}Al_8$

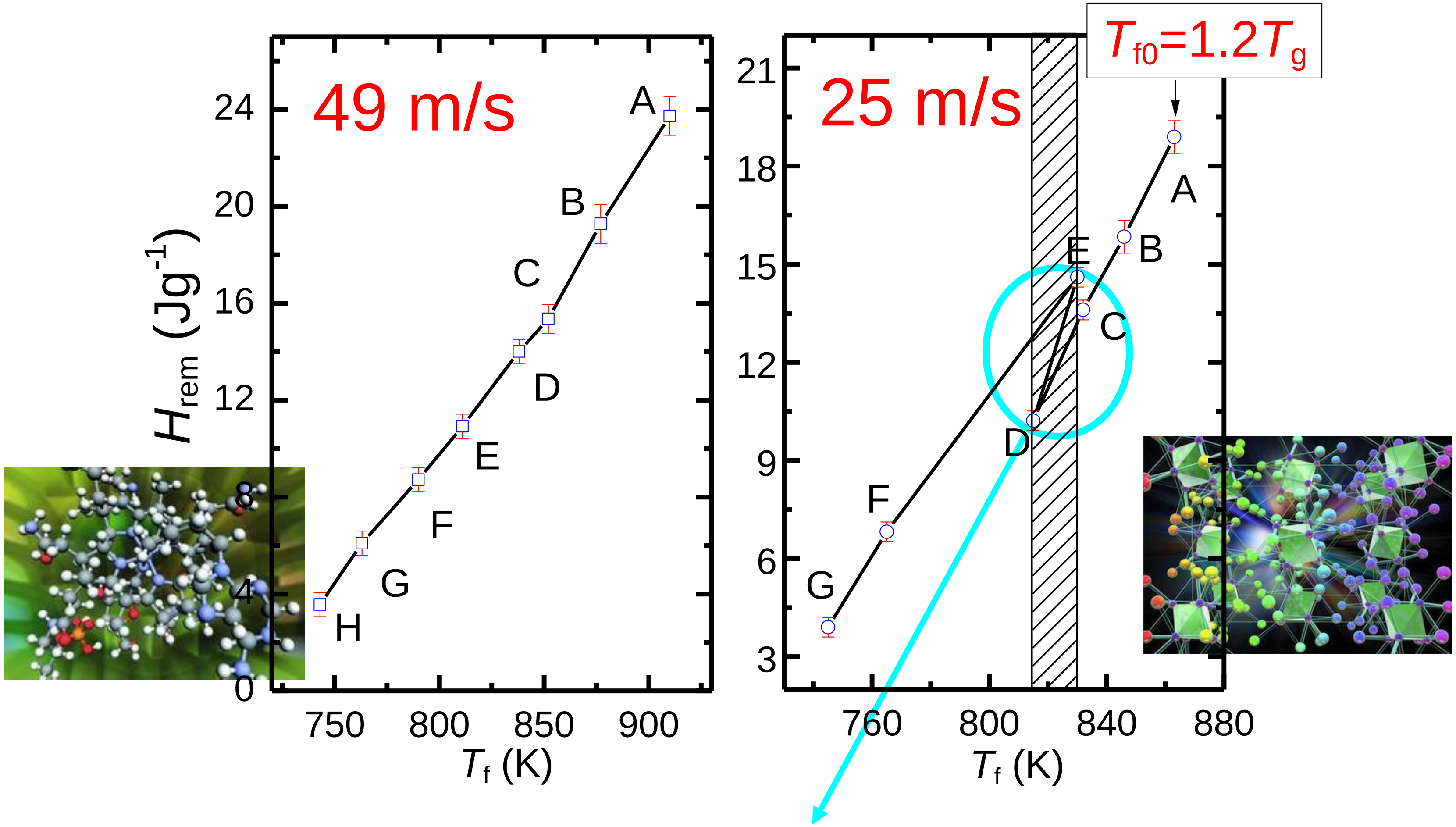


(35m/s)

(25m/s)

(17m/s)

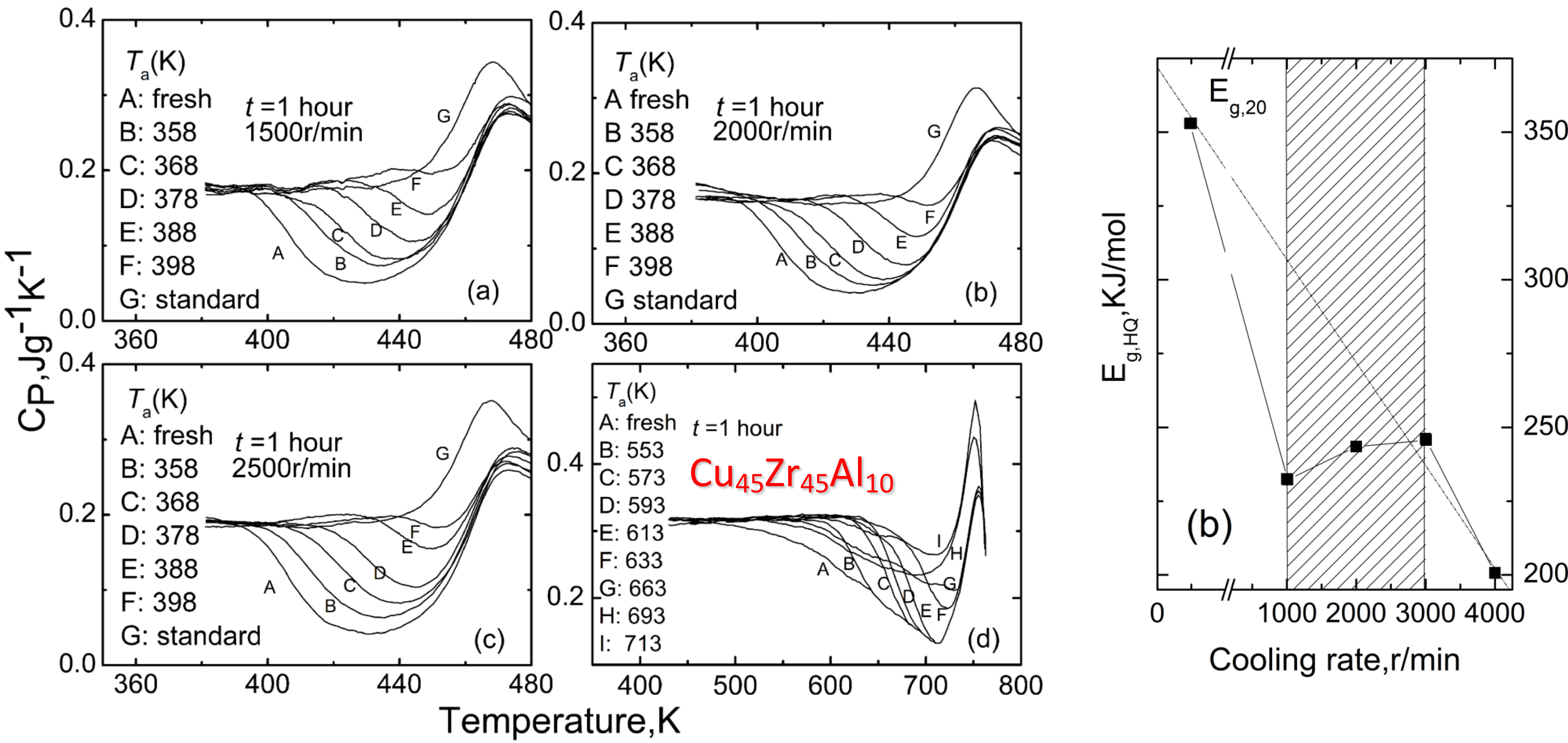
T_f dependence of the remaining enthalpy during annealing



Implications of the abrupt increase in H_{rem}:

- High T micro-domains are unstable during cooling.
- A rapid transition occurs between the high T and low T clusters.
- The F-S transition range is rather narrow, possibly around 1.2-1.3T_g?

$La_{55}Al_{25}Ni_5Cu_{15}$ glass ribbons



Similar to the behaviors observed in $La_{55}Al_{25}Ni_{20}$ glass ribbons

Hu, et al., to be submitted

Relation between the F-S transition and structural relaxation

F-S transition strength

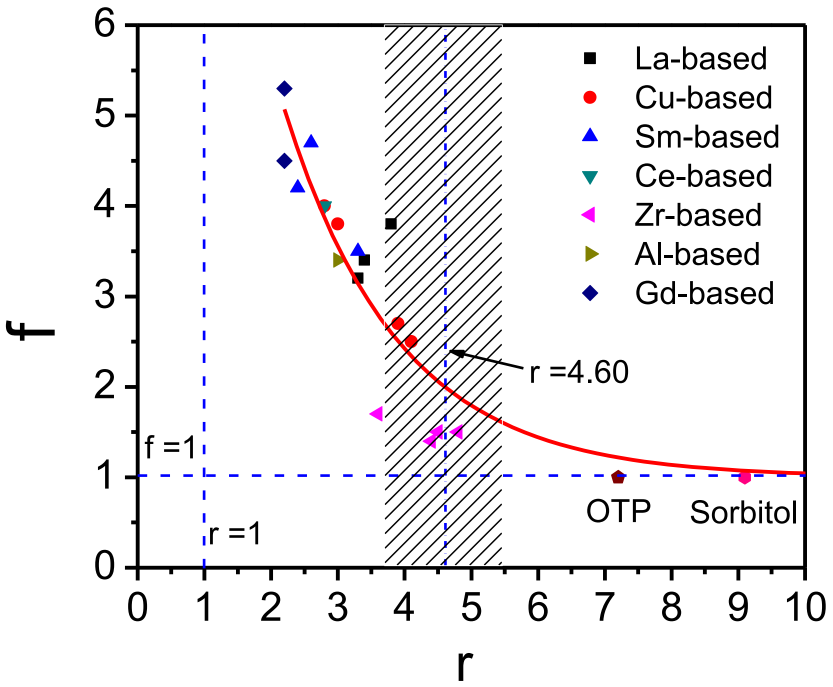
$f = m'/m$

Ratio of activation energy for the α to the β relaxation

$r = E_\beta/E_\alpha$

Hu, Yue, JPC-B 2009

$$f = 11\exp(-0.58r)+1$$



- *f* is exponentially associated with the competition between α and β relaxation.
- Whether a liquid exhibits the F-S transition could be predicted from relaxation behaviour.

Sun et al., in progress

Origin of the F-S transition of some liquids?

Water:

- Jagla (1999): competition between two different local structures
- Tanaka (2003): crossover from a non- to glass-forming branch
- Liu (2005): a high to a low-density liquid

Silica:

- Saika-Voivod et al (2004) : polyamorphic behaviour of silica glass

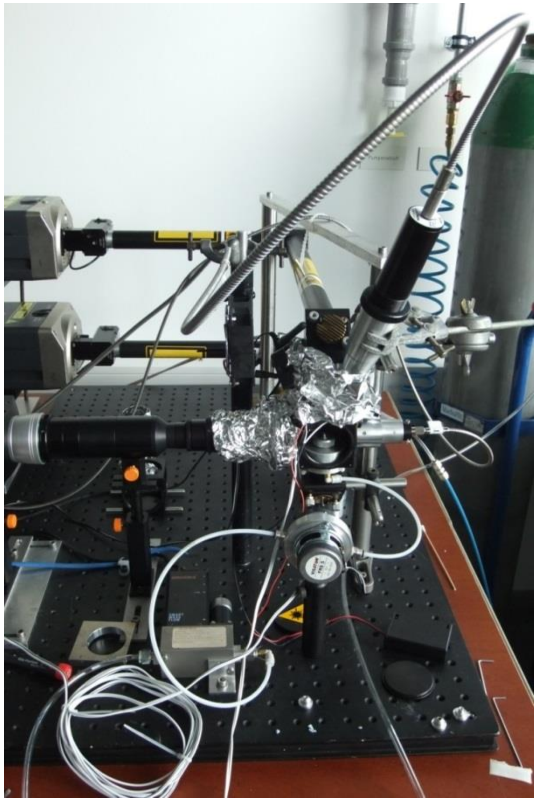
BeF_2:

- Angell et al (2001): Order-disorder transition and Lambda peak

MGFLs:

- Way, et al (2007): Order-disorder hysteritic anomaly
- Sheng et al (Nature Mat. 2007): Polyamorphic transition
- Hu and Yue (APL 2011, on-going): two kinds of clusters?

Exploring the F-S transition by
–Diving deeply into the supercooled region

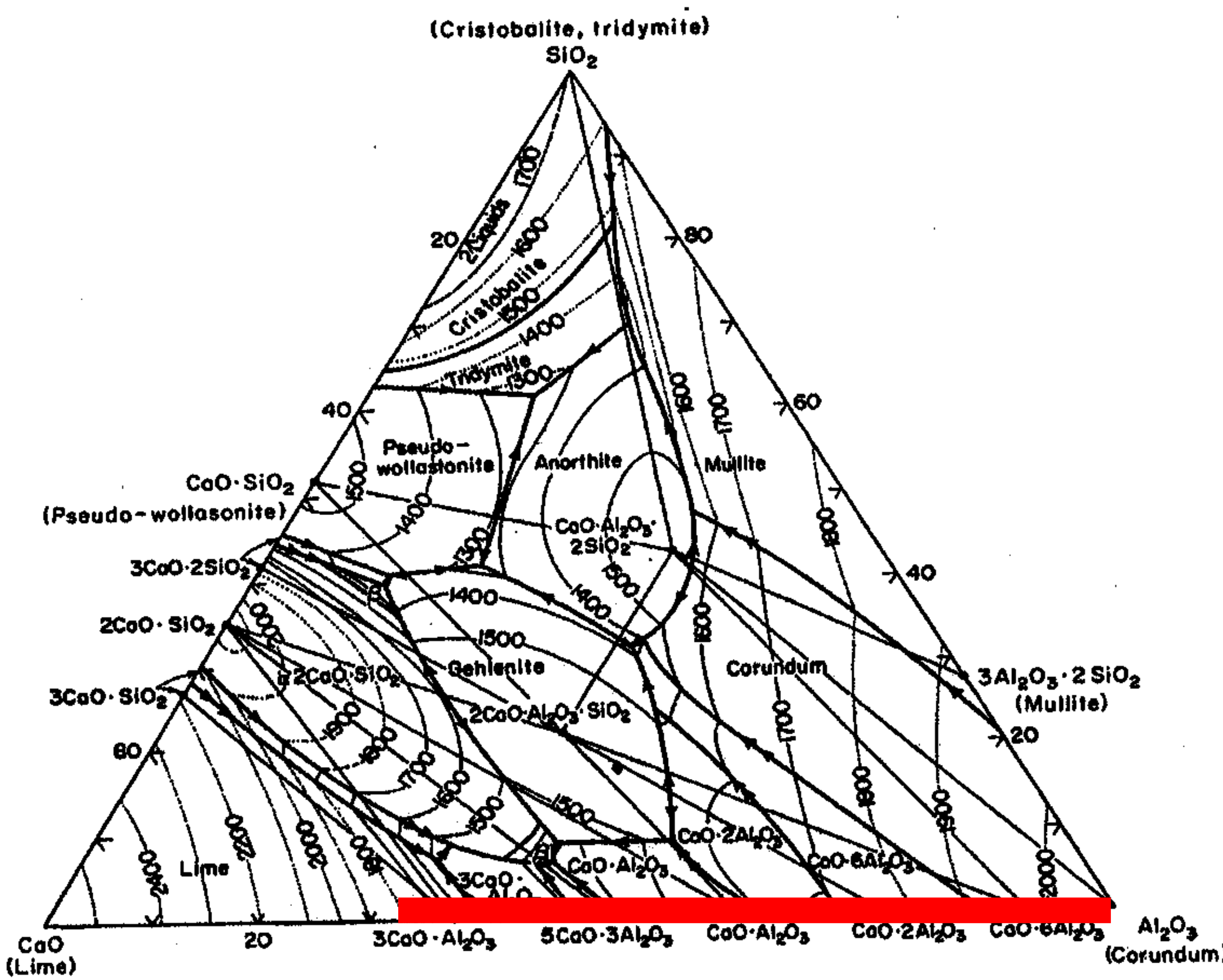


At DLR
May 2013

Aerodynamic levitator furnace for measuring thermophysical properties of refractory liquids

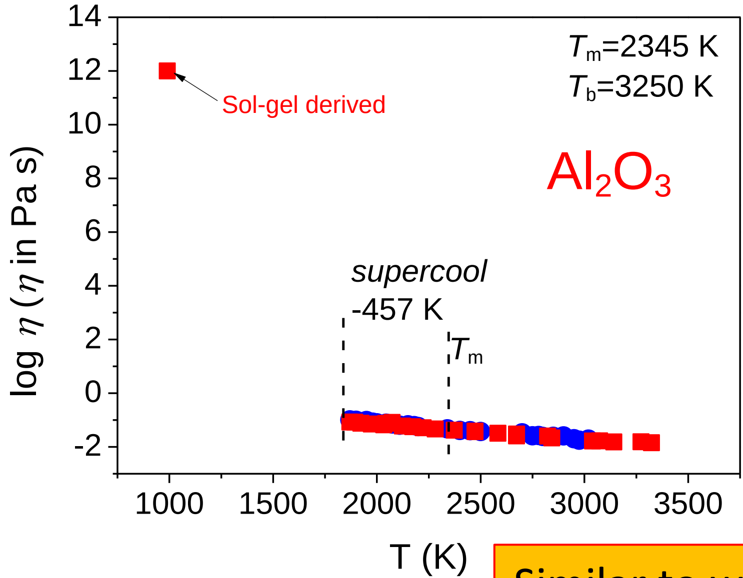
Langstaff, et al. Rev. Sci. Instrum. 2013

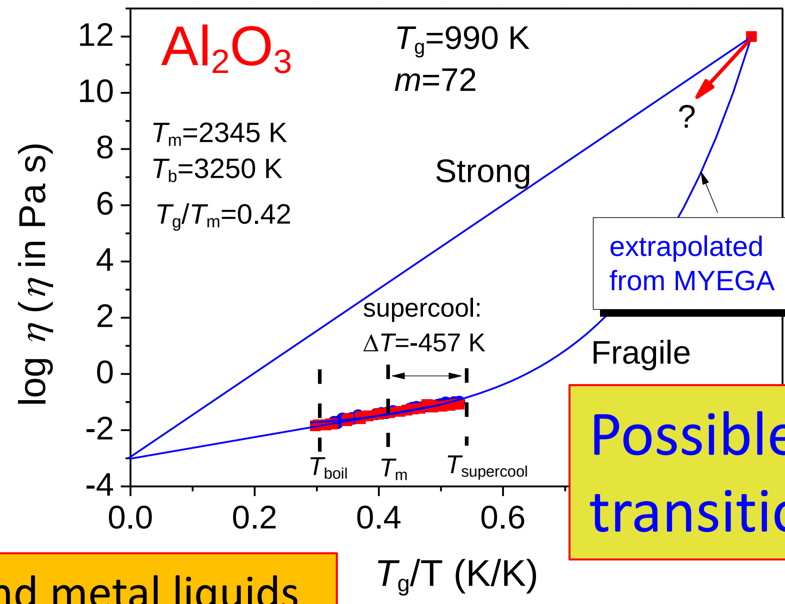
SiO_2-Al_2O_3-CaO phase diagram



Deep supercooling to access possible F-S transitions of refractory oxides, e.g.

Al_2O_3 liquid and other aluminate liquids





Possible F-S transition?

Similar to water and metal liquids

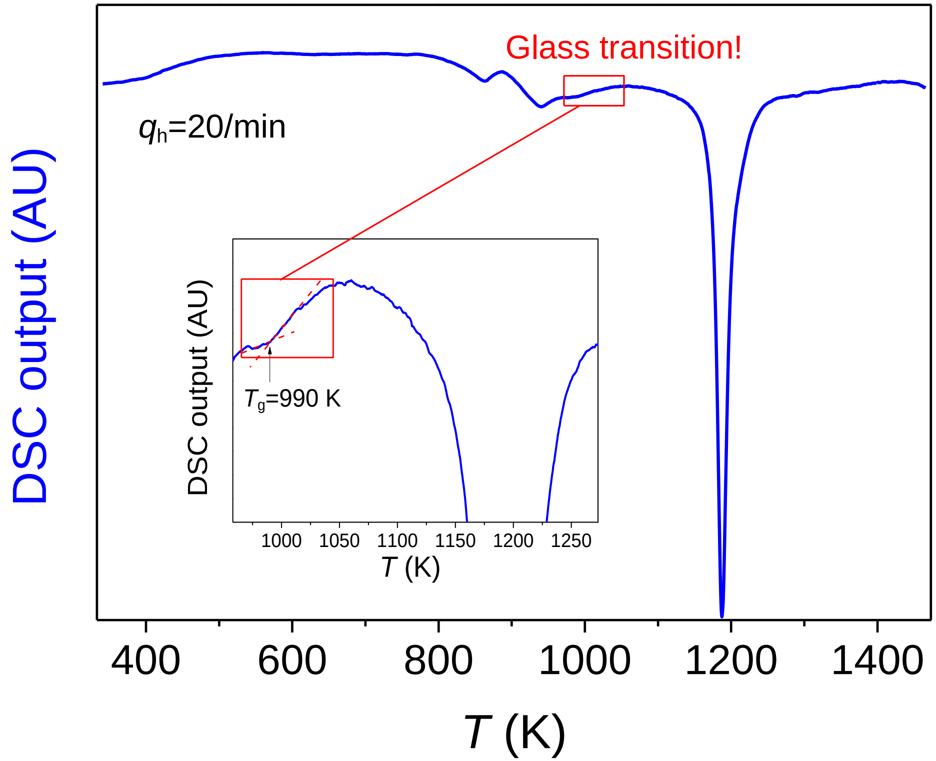
By using the containerless aerodynamic–levitation and laser-heating techniques,

- Dive deeply into No-Man's land
- Determine the Angell Plot of Al_2O_3.

Note: T_g was measured on thhe sputtering derived Al_2O_3 to get. It is a challenge to prepare the fused Al_2O_3 glass, but we'll try…

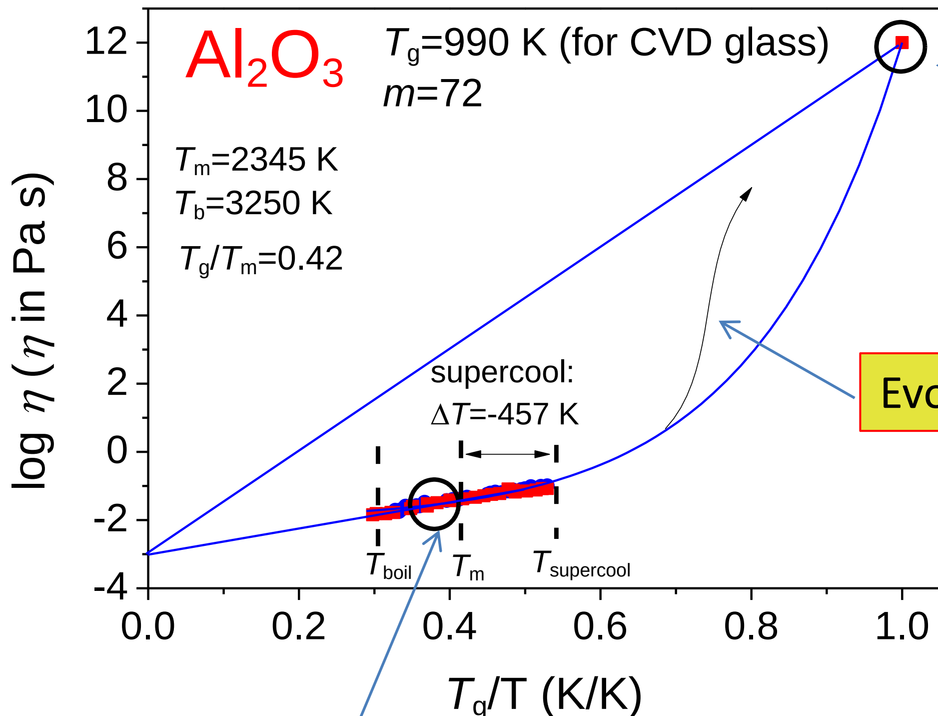
Greaves, Kargl, Pan, Yue, et al. in progress

Glass transition of Al_2O_3



- Small C_p jump – implication of small *m*?
- Caution: Sputtering dereived film– water influence
- Thermal history needs to be known.

Structure of Al_2O_3 liquid and glass



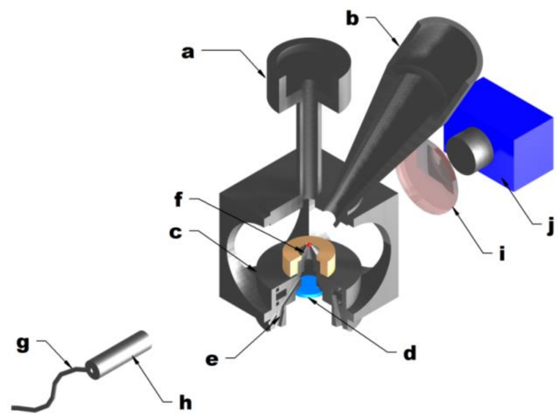
55% AlO_4, 42% AlO_5, and 3% AlO_6 units

Oxygen triclusters are found.

S.K. Lee, et al. PRL 2009

We'll measure high T_f glasses

Evolution of clusters in medium range?



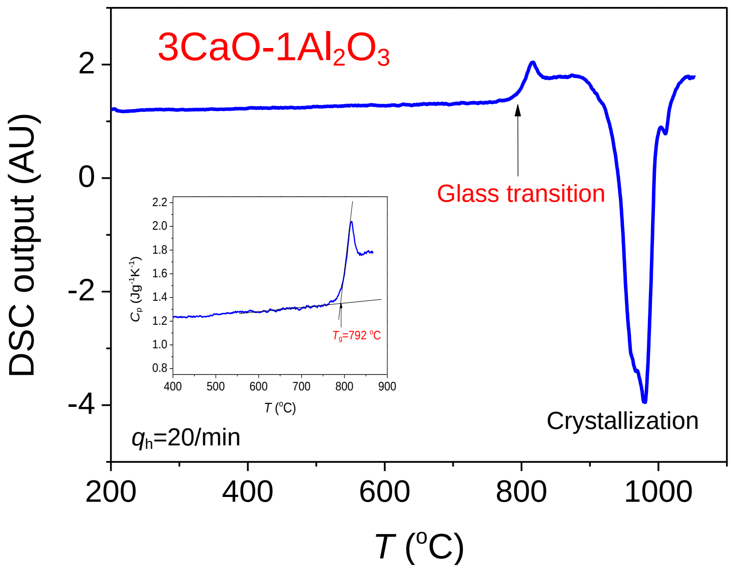
NMR: 57.5% AlO_4, 34.7% AlO_5, and 4.3% AlO_6 and 3.5% AlO_3, units

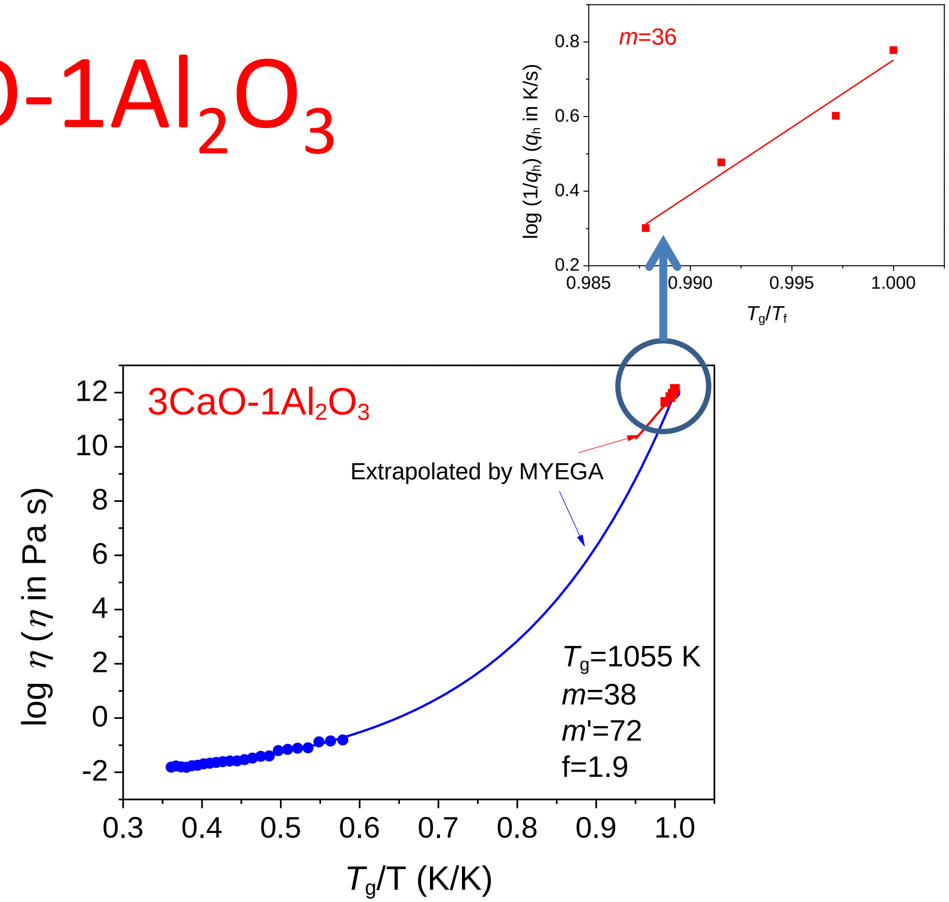
L.B. Skinner, et al. PRB 2013

G.N. Greaves, et al. Science 2008

Yue, Kargl, G.N. Greaves, et al, in progress

Fragility of $3CaO\text{-}1Al_2O_3$





- Surprisingly, stable glassy C_3A glass could be obtained by quenching.
- A slight F-S transition is implied.
- Structure will be measured.

Perspective

- Conduct dynamic measurements during supercooling
- Increase the T_f as high as possible
- *In-situ structural characterization (on-going)*
- Theoretical approach and simulation

Acknowledgements

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Ruikun Pan - *Wuhan University of Technology*

Guang Yang - *Xi-An Jiaotong University*

Yanfei Zhang – *Qilu University of Shandong*

Mette Solvang - *Rockwool International A/S*

My co-workers….

Thank you for your attention!