Viscosity of glass-forming liquids

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Outline

- Background and motivation
- Viscosity models
- Iso-structural viscosity
- Non-Newtonian flow
- Fragile-to-strong transition

Background and motivation

About flow

Haraclitus:
"*everything is in a state of flux*".

Confucius (孔夫子) stood by a river:
"*Everyting flows like this, without ceasing, day and night*".

Deborah:
"*Everything flows if you wait long enough, even the mountains*".

Flow is everywhere!

Flow is remarkable, but sometimes dangerous!

How to judge whether a substance is liquid or solid?

A fundamental number of rheology: Deborah number (D_e)

$$D_e = \frac{\tau}{t}$$

τ — Time of relaxation

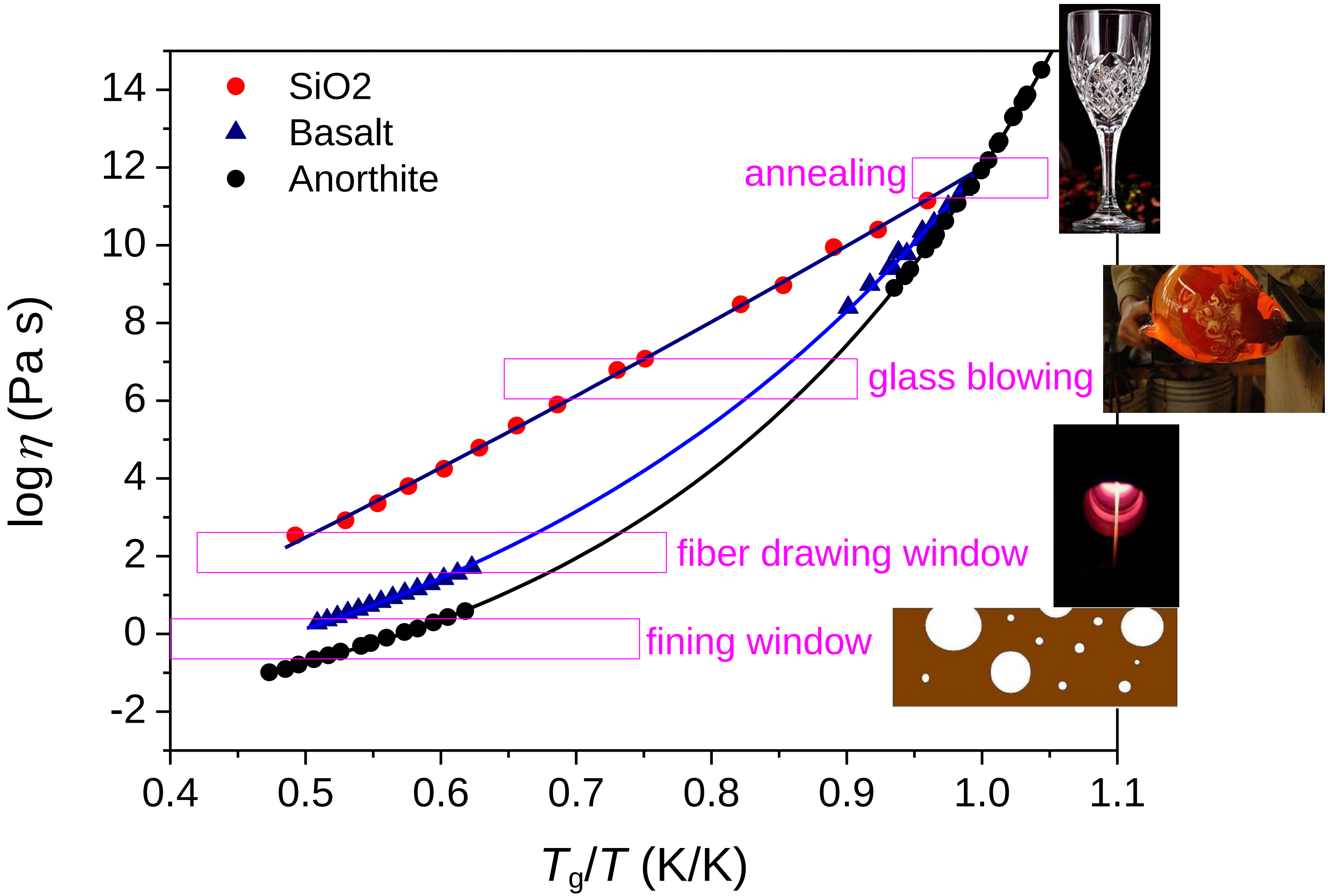
t — Time of observation

If $\tau < t$, a substance is a liquid, otherwise, a solid!

Some liquids flow easily, some not.
How to quantify this?
Measure **Viscosity** by viscometers:

- Concentric Cylinder
- Parallel-Plate Compression
- Capillary
- Beam Bending
- Fiber Elongation
- Sphere penetration
- Melt containerless levitation
- ……..

Viscosity is a crucial quantity of glass technology.



Viscosity determines

- Melting conditions
- Fining behaviour
- Working ranges
- Annealing range
- Upper temperature of use
- Devitrification rate
- Glass forming window
- Glass fiber drawing window

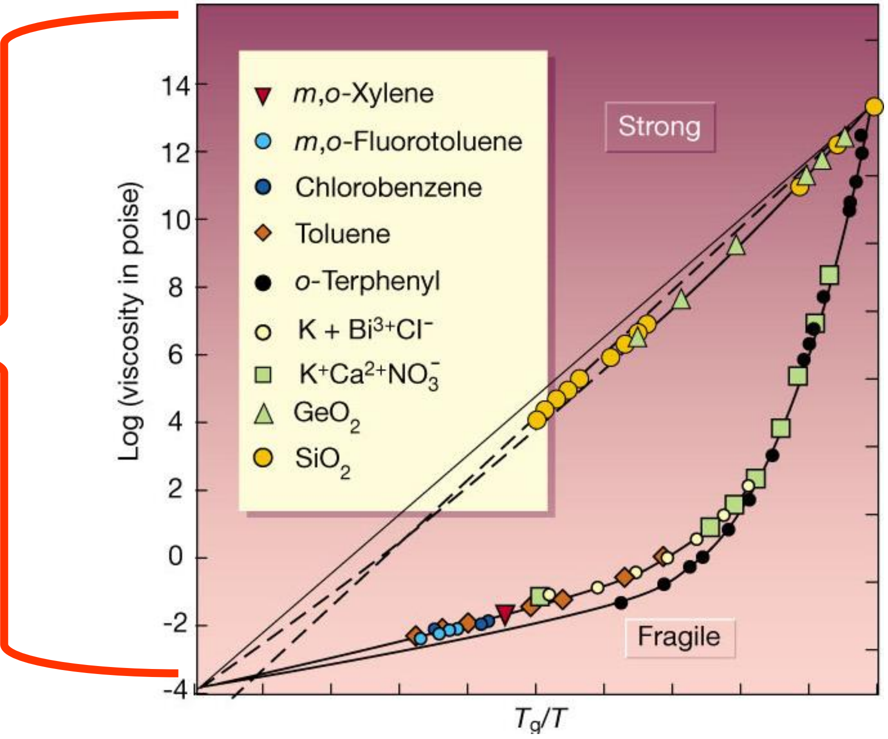
- Every step of industrial glass formation depends critically on the viscosity.
- The glass product relaxation depends on the nonequilibrium viscosity of the glass, which is a function of composition, temperature, and thermal history.

Viscosity is a key quantity of glass science.

It provides information on

- Glass dynamics
- Transport properties
- Glass structure
- Liquid fragility
- Thermodynamics
- Geology
- Crystallization
- ……..

Angell plot

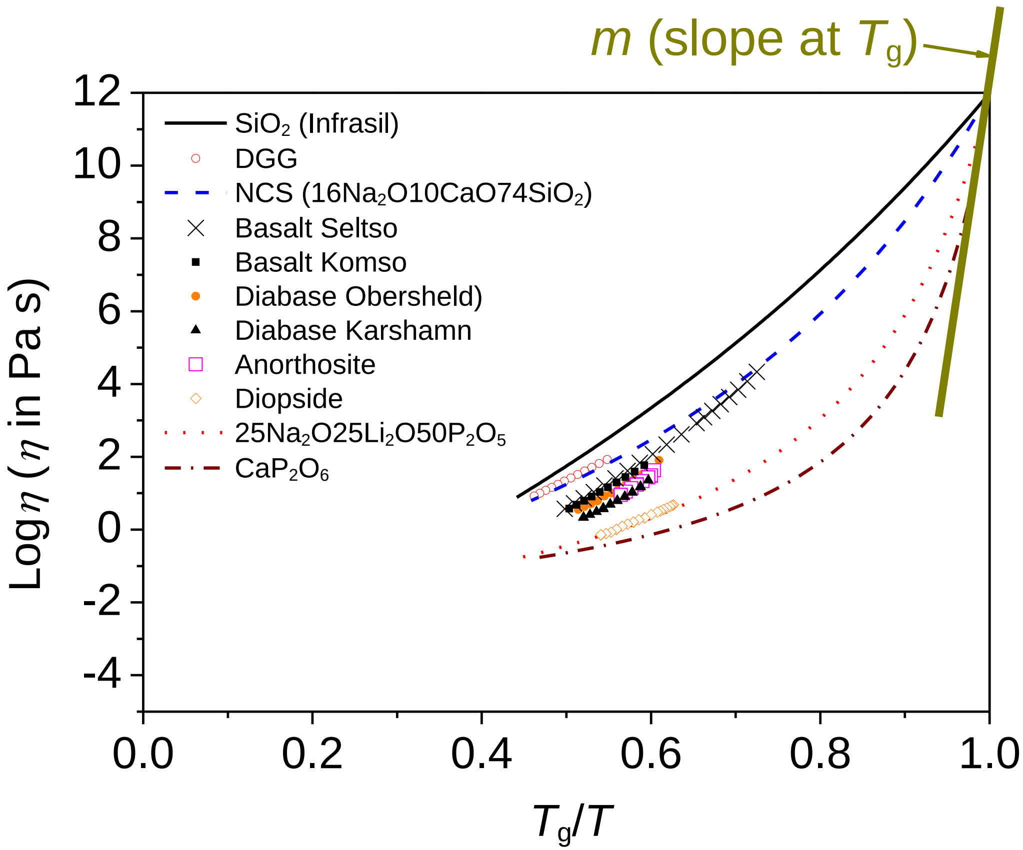


Viscosity of a melt varies with

- **Temperature**
- **Time**
- **Deformation rate**
- Pressure
- **Composition**
- Hydroxyl
- Crystallization
- Phase separation
- Inclusions
- …….

The non-Arrhenian behavior of liquids is described by liquid fragility.

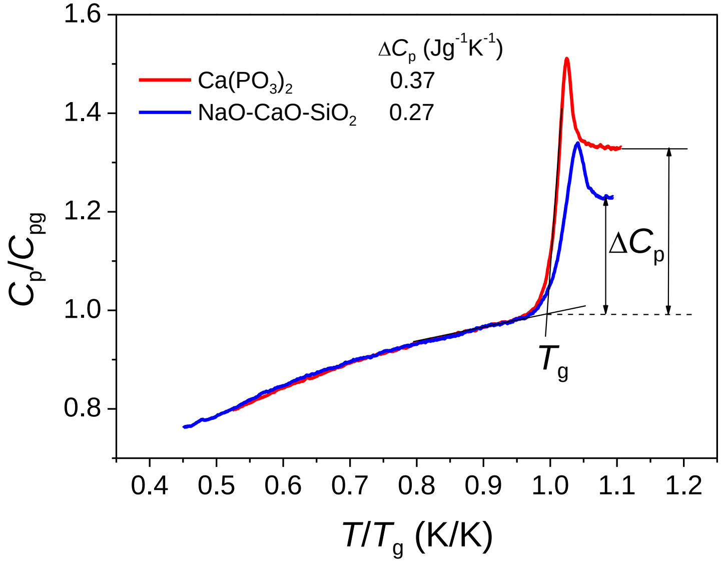
It is quantified by the kinetic liquid fragility index *m*.

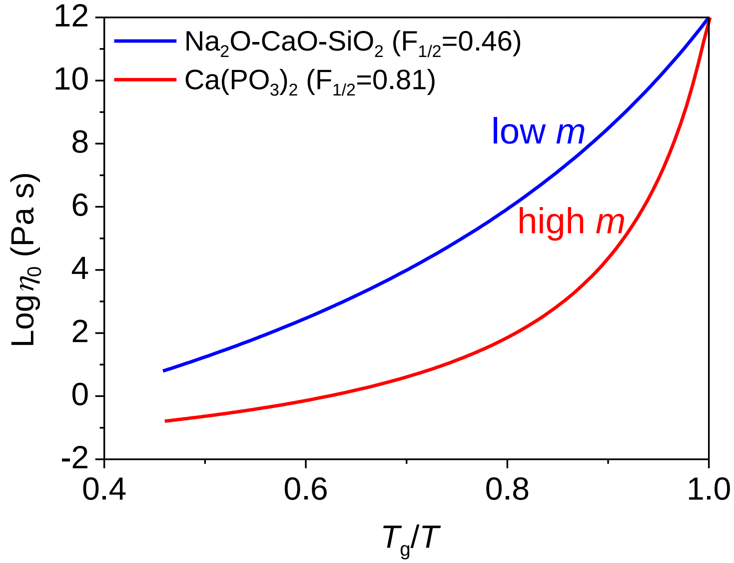


$$m = \left.\frac{d \log \eta}{d(T_g / T)}\right|_{T=T_g}$$

- It is defined as the rate of the viscosity or relaxation liquid at T_g upon cooling.
- It is an important dynamic parameter of glass-forming liquids.

Connection between fragility index (m) and heat capacity jump (ΔC_p) in glass





$$\Delta C_p = \frac{A}{T_g}\left(\frac{m}{m_0} - 1\right)$$

Smedskjaer, et al. J. Phys. Chem. B, 2011

Viscosity models

Vogel-Fulcher-Tamman (VFT) Model

$$\eta = \eta_\infty \exp\left(\frac{A'}{T - T_0}\right)$$

where η_∞ is the high temperature limit of viscosity, and A and T_0 are constants. Or

$$\log \eta = \log \eta_\infty + \frac{A}{T - T_0}$$

$T_0 = T_k$? This is a debating problem.

Vogel, *Phys. Zeit.* **22** (1921) 645; Fulcher, *J. Am. Ceram. Soc.* **8** (1925) 339
Tammann, Hesse, *Z. Anorg. Allg. Chem.* **156** (1926) 245

Adam-Gibbs (AG) Model (Entropy model)

$$\eta = \eta_\infty \exp\left(\frac{B'}{TS_c(T)}\right)$$

where η_∞ is the high temperature limit of viscosity, B is constant, and $S_c(T)$ is the configurational entropy as a function of temperature:

$$S_c(T) = \Delta C_p \ln\left(\frac{T}{T_K}\right)$$ This is a problem too.

Adam and Gibbs, *J. Chem. Phys.* **43** (1965)139

Avramov-Milchev (AM) Model

$$\log \eta = \log \eta_{\infty} + B_{AM} \left(\frac{T_g}{T}\right)^F$$

where η_{∞} is the high temperature limit of viscosity, B_{AM} constant, and T_{g} the glass transition temperature, and F is a measure of liquid fragility.

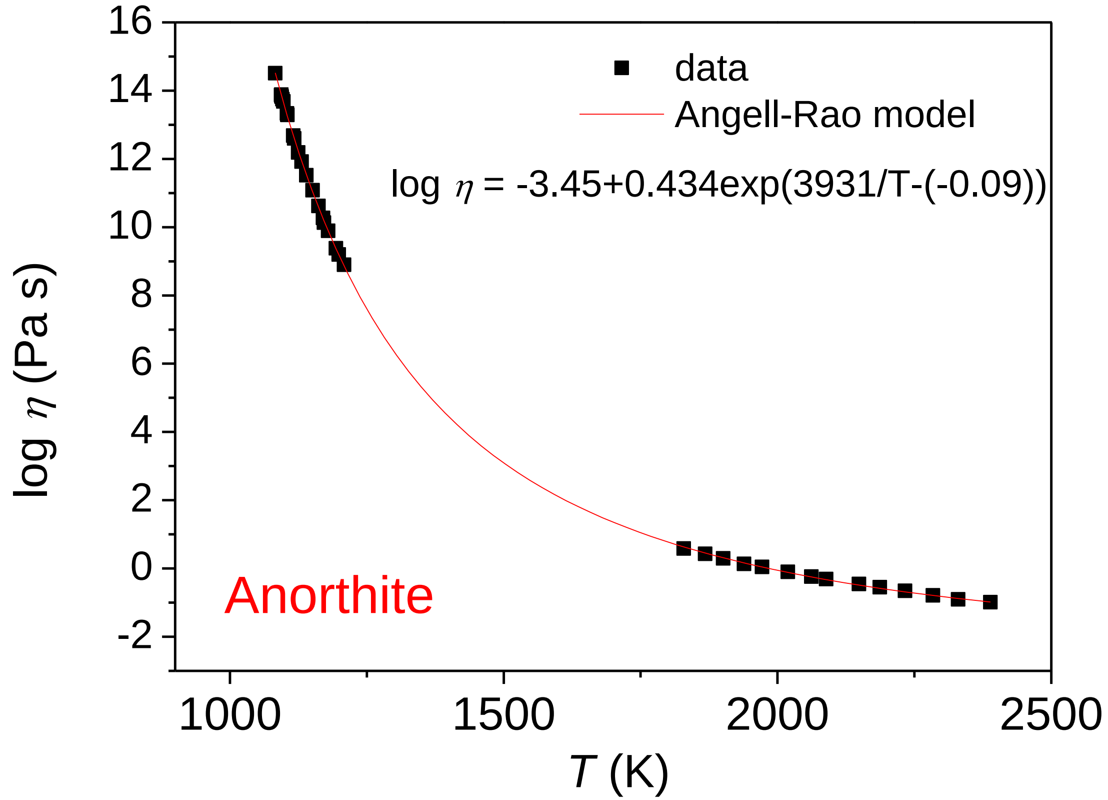
$F=m/B_{\mathrm{AM}}$, where m is the Angell fragility index

Avramov and Milchev, *J. Non-Cryst. Solids* **104** (1988) 253

Angell-Rao (AR) model

Angell and Rao, JCP (1972)

$$log\eta = log\,\eta_\infty + Aexp(\frac{B}{T} - C)$$



This 4-parameters model with fits the data excellently and bears physical meaning.

Other models

- **Free volume model**
- **Doremus model**
- **Shoving model**
- **Sanditov model**
- **Parabolic model**
- **.......**

See recent reviews:

M. I. Ojovan, *Adv. Condensed Mat. Phys.*, 2008,

S.V. Nemilov, *J. Non-Cryst. Solids*, 2011

Q. Zheng, J.C. Mauro, *J. Am. Ceram. Soc.*, 2017.

Derivation of our new model (MYEGA)

$$\log \eta = \log \eta_\infty + \frac{K}{T}\exp\left(\frac{C}{T}\right)$$

$$\log \eta = \log \eta_\infty + \frac{B_3}{TS_c}$$

Adam-Gibbs expression

The configurational entropy

$$S_c = fNk\ln\Omega$$

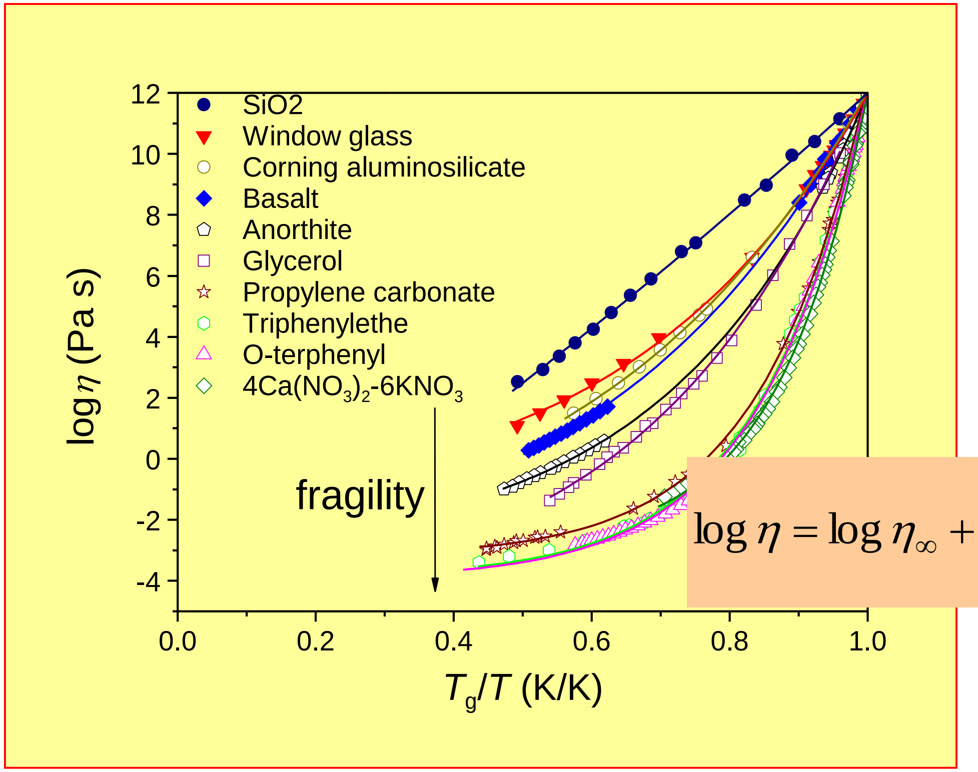
Topological degrees of freedom
A simple two-state system

$$f = 3\exp\left(-\frac{H}{kT}\right)$$

Mauro, Yue, Ellison, Gupta, Allan, *PNAS* 106 (2009) 19780

The viscosity-temperature relation for ***most*** liquids can be described by VFT and AM models, even better by MYEGA:

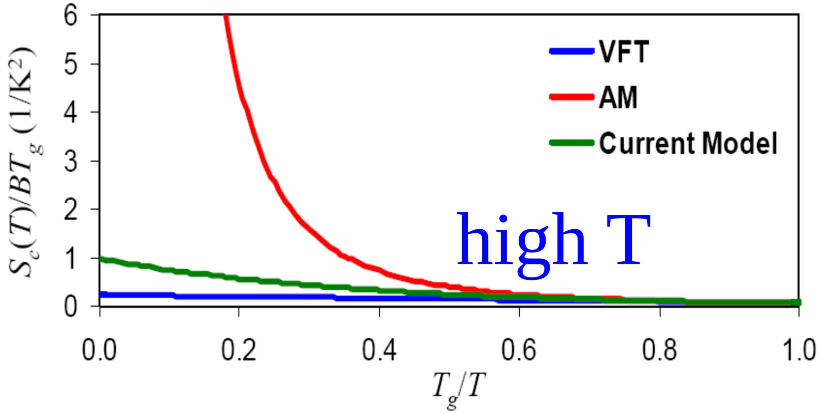
$\eta \sim T$ relation for oxide, ionic and molecular liquids

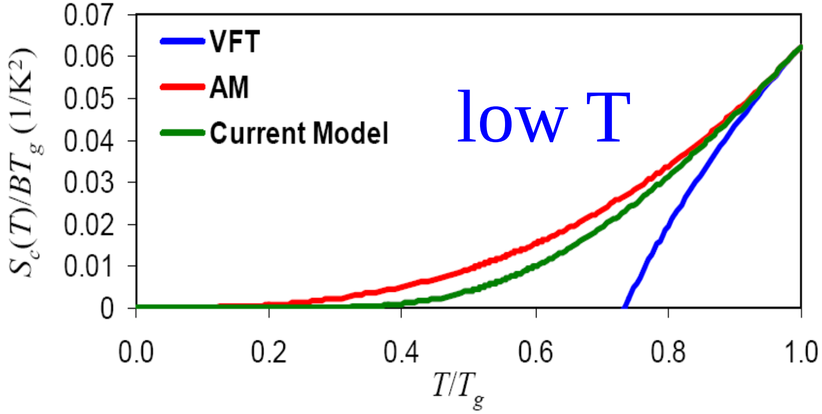


$$\log \eta = \log \eta_\infty + \frac{B}{T}\exp\left(\frac{C}{T}\right)$$

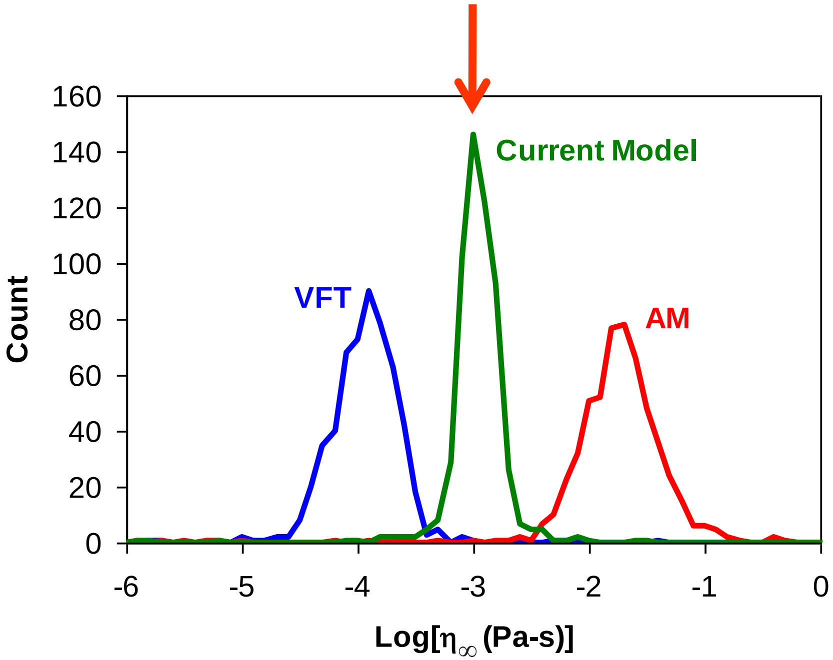
$$\log \eta = \log \eta_\infty + (12 - \log \eta_\infty)\frac{T_g}{T}\exp\left[\left(\frac{m}{12 - \log \eta_\infty} - 1\right)\left(\frac{T_g}{T} - 1\right)\right]$$

The new model is physically reasonable. (Fitting results based on 1000 glasses)





$\log \eta_\infty$=-3

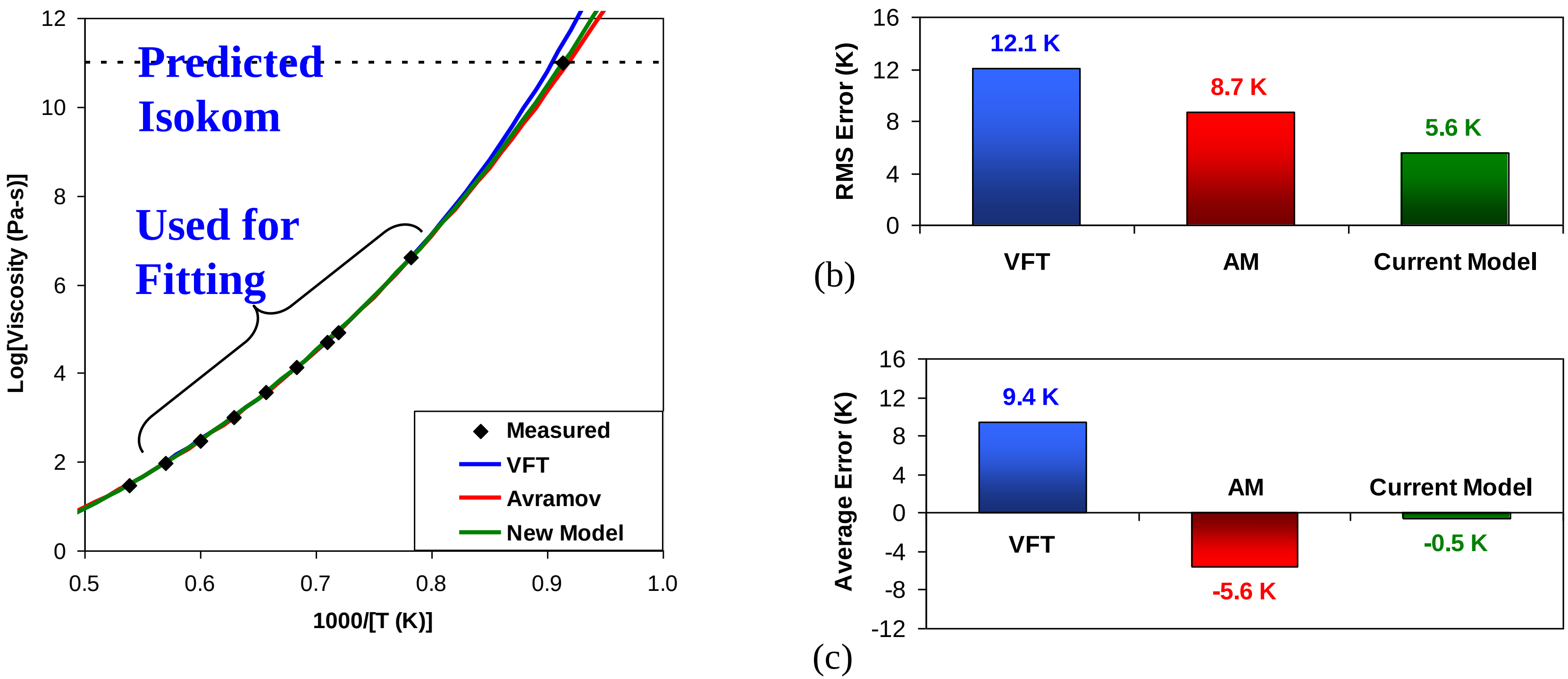


New model:

- S_c converges at T=∞
- S_c = 0 at T=0

- $\log \eta_\infty$: *the narrowest distribution*
- $\log \eta_\infty$=-3: A universal value?

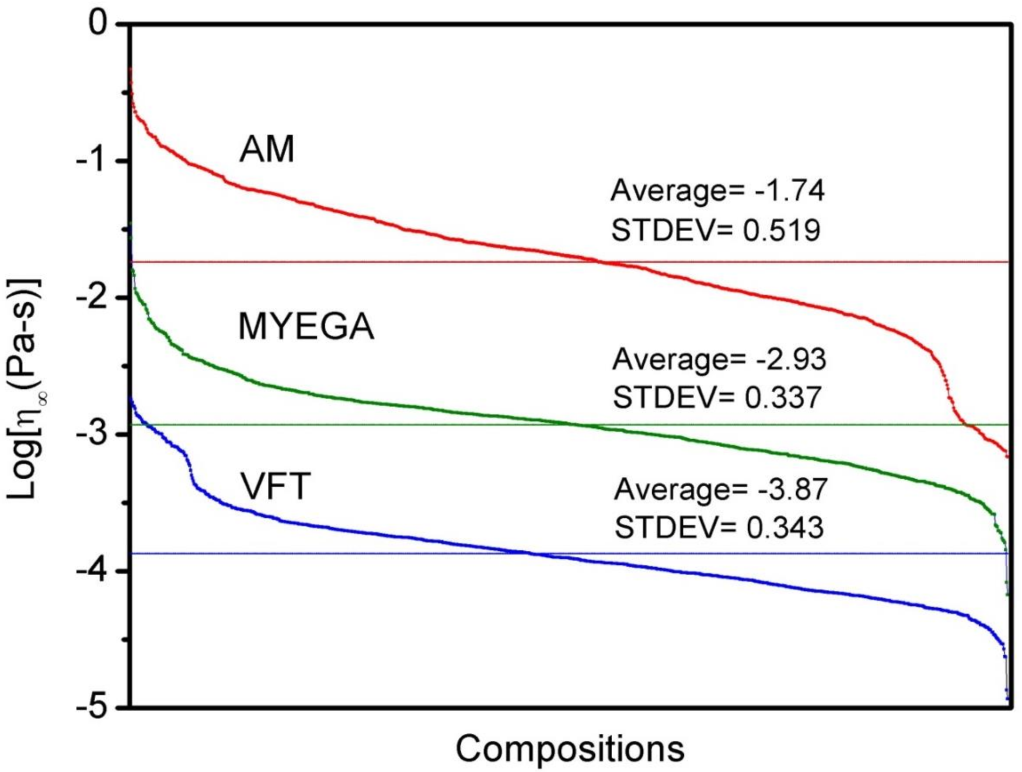
The new model is practically useful.



The new model shows stronger ability to predict low *T* viscosity data from high *T* viscosity data than the other 3-parameter models.

Is there a universal log η_∞ value?

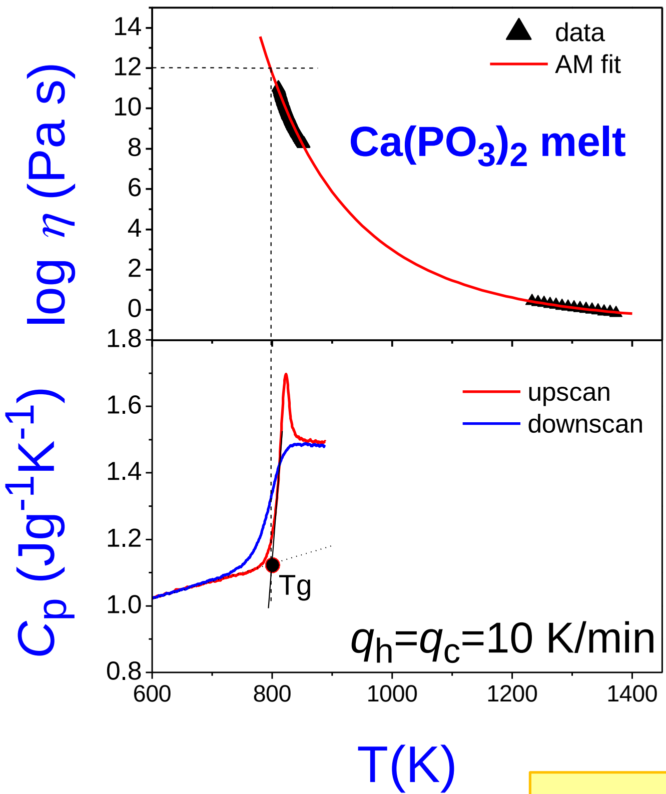
Results on 946 Corning compositions

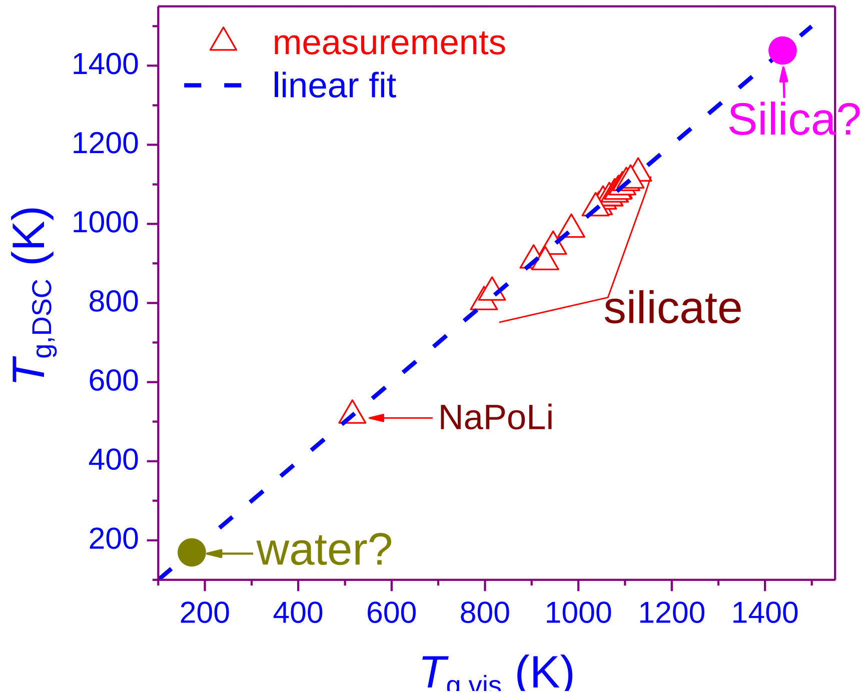


It is about -3!

Zheng, et al. *Phys. Rev. B* 2011

$T_{g,vis}$ (from viscosity) and $T_{g,DSC}$ (from DSC)





$$T_{g,10K/min} = T_{\log\eta=12}$$

Y. Z. Yue, *J. Non-Cryst. Solids* 2008, 2009

Practical use of the MYEGA

$$\log\eta = \log\eta_\infty + \frac{B}{T}\exp\left(\frac{C}{T}\right)$$

$$m = \frac{d\log\eta}{d(Tg/T)}\Bigg|_{T=Tg}$$

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

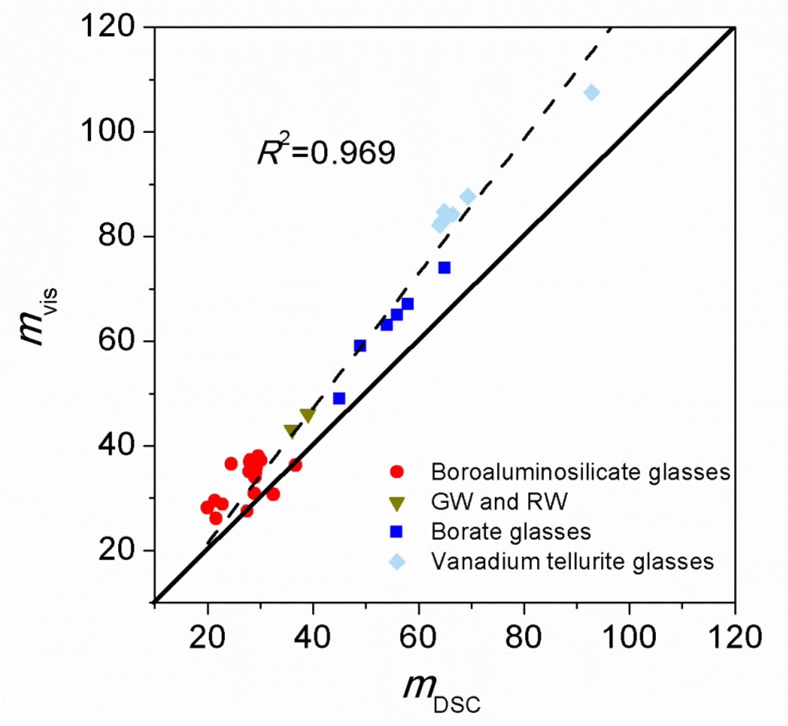
For inorganic systems
$\boldsymbol{\eta_\infty \approx 10^{-3}}$ **Pa s**

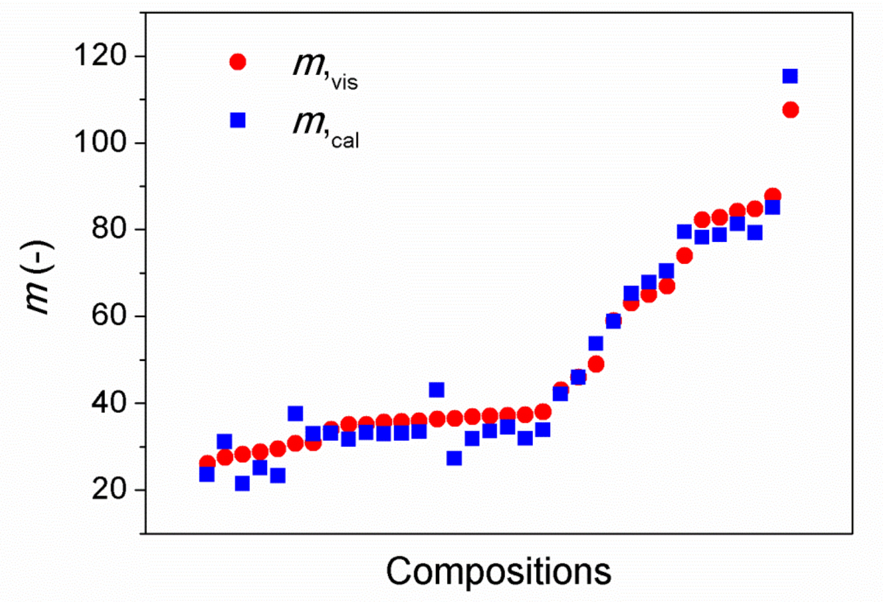
For inorganic systems
$\boldsymbol{\eta_{Tg} \approx 10^{12}}$ **Pa s**

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

Now, only two parameters, m and T_g, remain. Meaning: the entire $\log\eta$~T relation can be estimated just by DSC!

Be careful with the difference between m_{vis} and m_{DSC}





- $m_{vis} > m_{DSC}$
- m_{vis} - m_{DSC} due to Arrhenian approximation of non-Arrhenius behavior
- $m_{vis} - m_{DSC}$ increases as fragility increases

A model:

$$m_{vis} - m_0 = (m_{DSC} - m_0)[1 + f(m_{DSC} - m_0)]$$

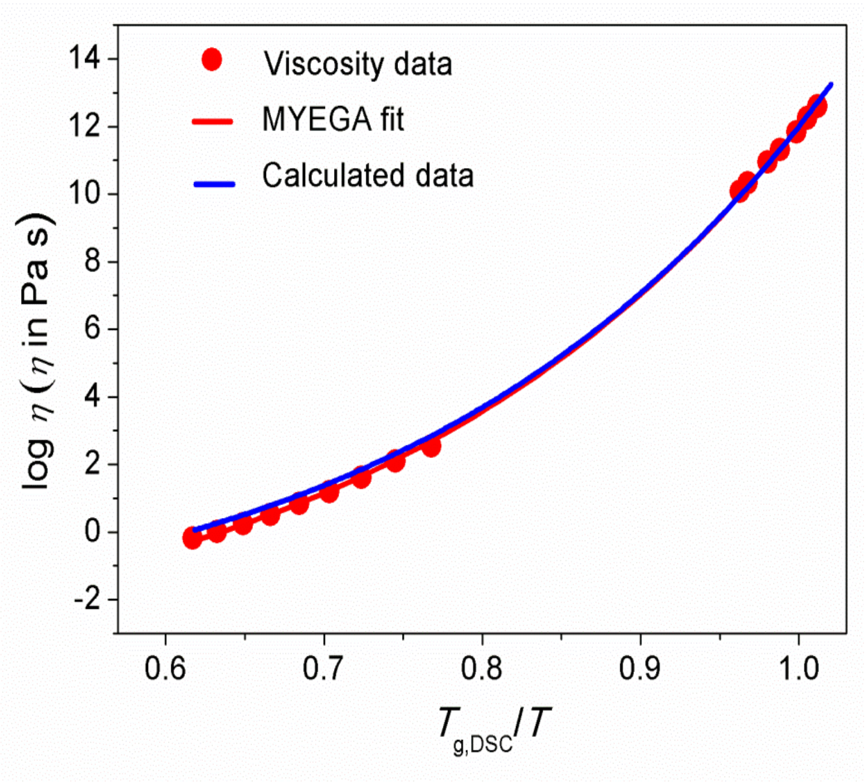
$$m_{vis} = 1.289(m_{DSC} - m_0) + m_0$$

Zheng, Mauro, Yue, *J. Non-Cryst. Solids*. 2017

The entire viscosity-temperature curve can be determined by DSC!

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

Example



Based on the facts:

- *T_g and m_{DSC} are measurable by DSC*
- *m_{DSC} can be converted to m_{vis}.*
- $\log_{10}\eta_\infty$=-3
- *T_g corresponds to 10^{12} Pa s*

Advantages of the DSC method:

- It is simpler.
- Takes much less time than viscometry technique.
- Uses smaller samples.
- Measure both good and poor glass forming systems.

Derivation of VFT from MYEGA

$$\log \eta(T) = \log \eta_\infty + \frac{C}{T}\exp\left(\frac{K}{T}\right)$$

$$= \log \eta_\infty + \frac{C}{T\exp(-K/T)}$$

- In the high temperature limit, -K/T can be expanded in a Taylor series:

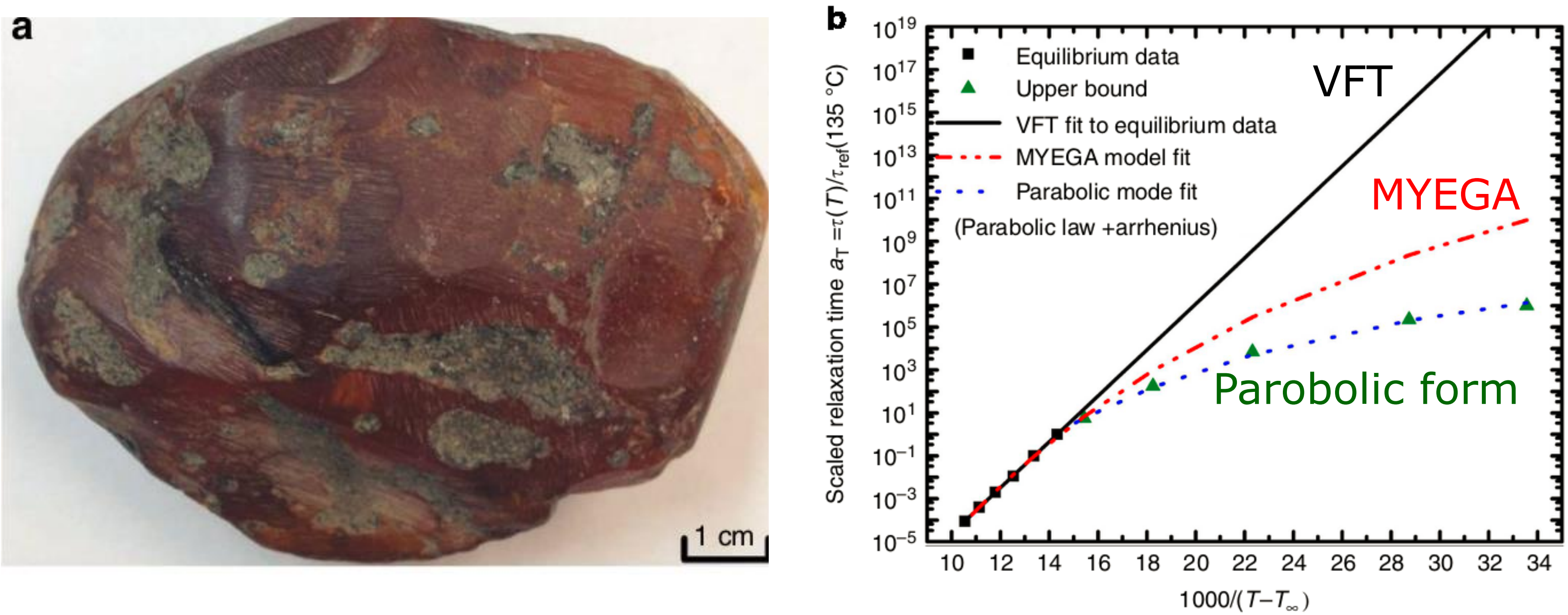
$$\log \eta(T) \approx \log \eta_\infty + \frac{C}{T\left(1 - \frac{K}{T}\right)}$$

$$= \log \eta_\infty + \frac{C}{T - K}$$

M.M. Smedskjaer, J.C. Mauro, Y.Z. Yue, *J. Chem. Phys.* **131**, 244514 (2009).

Divergent at a finite *T* ?

Using 20-million year-old amber, Zhao, et al. provided an implication against the existence of the divergence at a finite *T*.

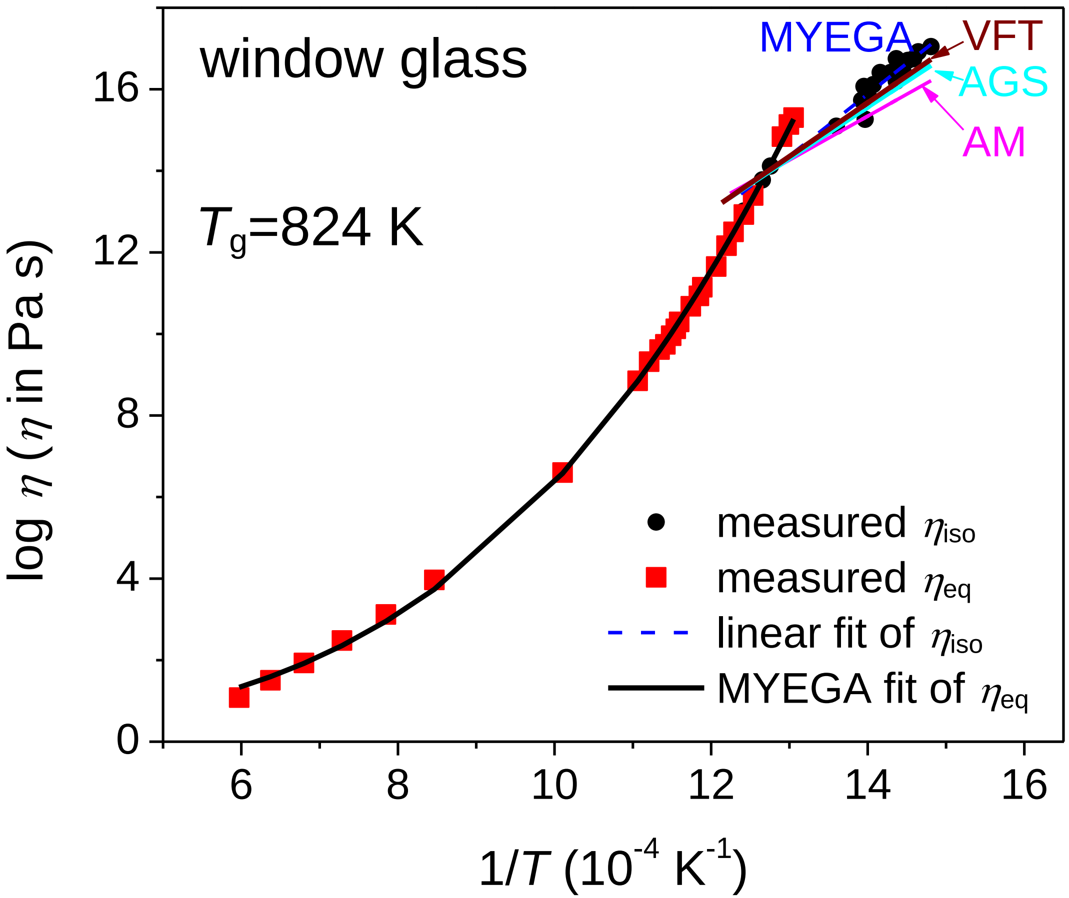


Zhao, Simon, McKenna, *Nature Comm*, (2013)

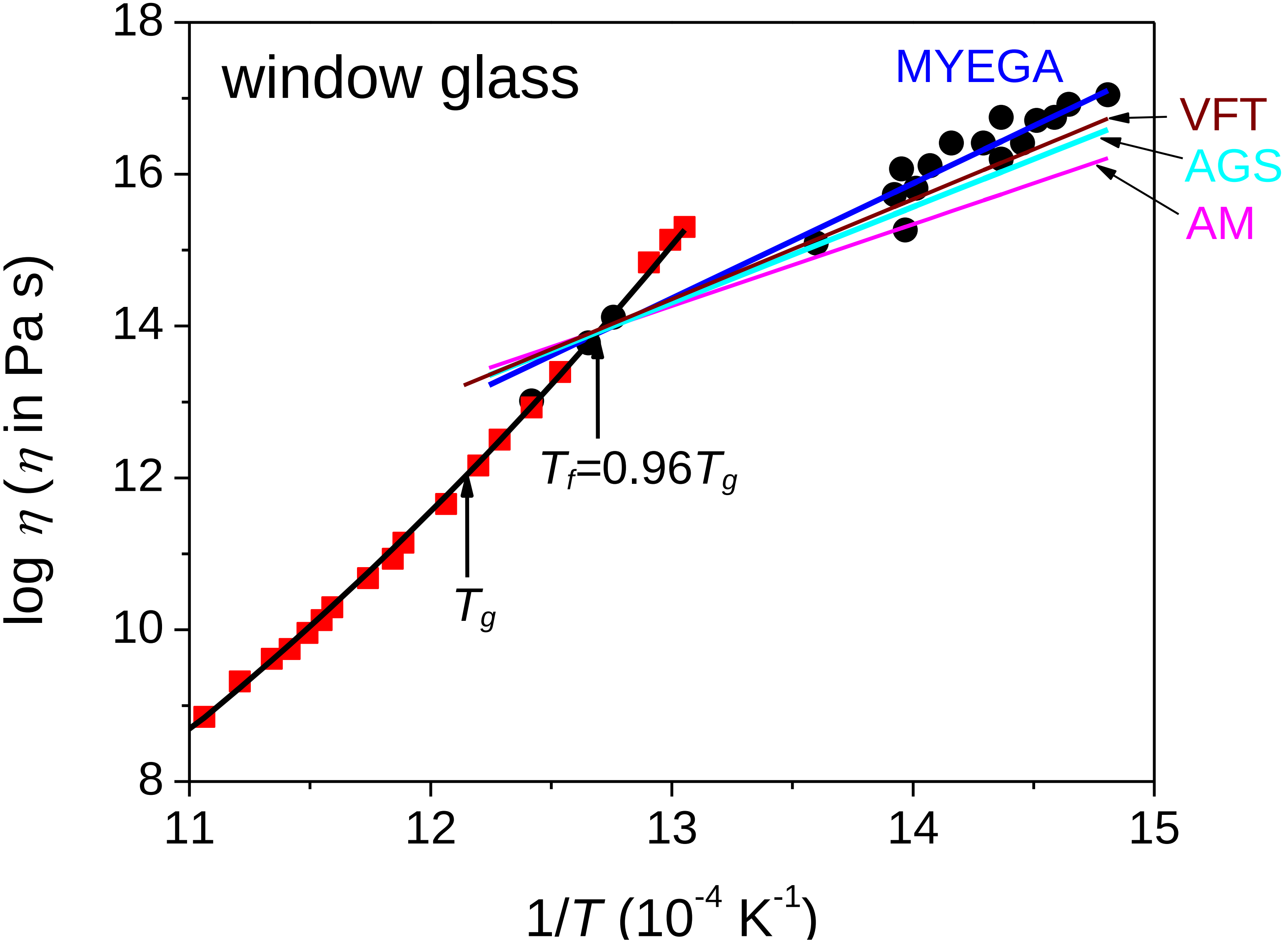
See also Hecksher, et al., *Nature Phys*. (2008)

Iso-structural viscosity or non-equilibrium viscosity

Comparison between the measured η_{iso} data and the η_{iso} data calculated from models

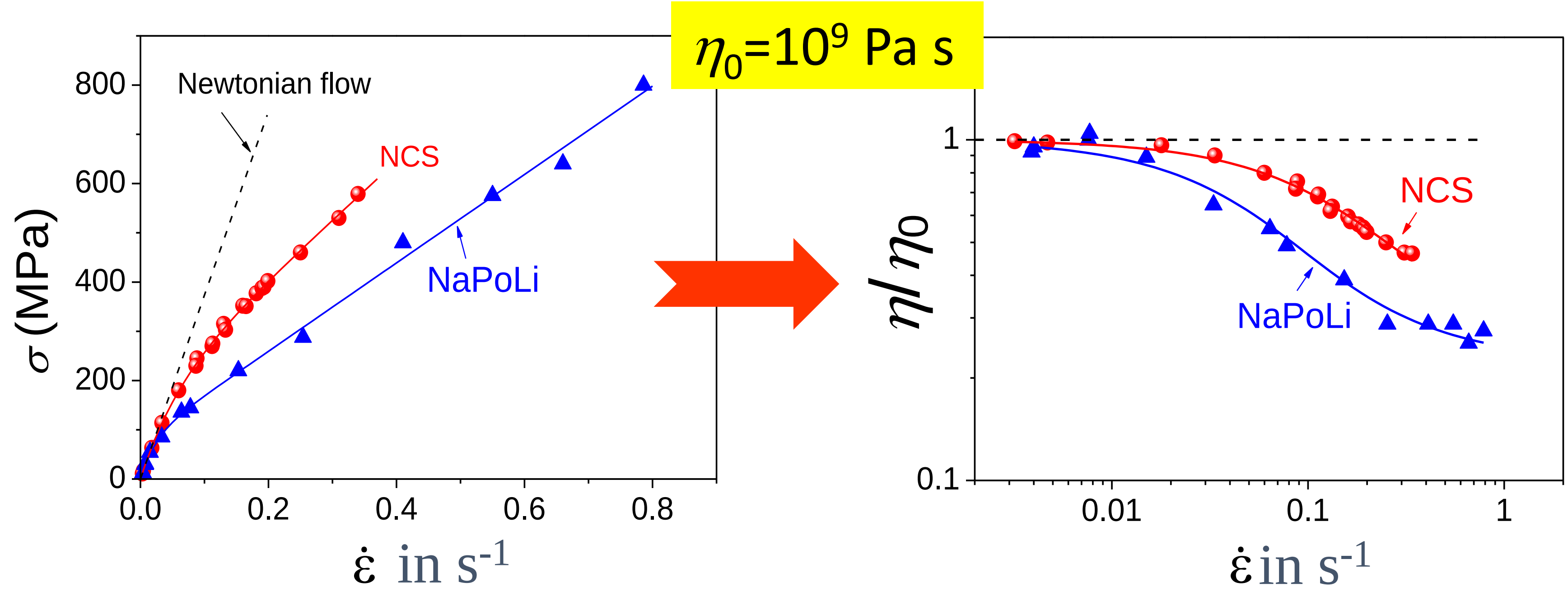


Data from Mazurin (1982)


window glass
MYEGA
VFT
AGS
AM
T_f=0.96T_g
T_g
log η (η in Pa s)
1/T (10^{-4} K^{-1})
18
16
14
12
10
8
11
12
13
14
15

Non-Newtonian flow
(Shear rate dependence of viscosity)
(Shear thinning)

Non-Newtonian shear flow of glass-forming liquids (soda lime silicate vs Li-Na metaphosphate)



$$\sigma = \eta_\infty + (\eta_0 - \eta_\infty)\dot{\varepsilon}_g(1 - \exp(-\frac{\dot{\varepsilon}}{\varepsilon_g}))$$

$$\frac{\eta}{\eta_0} = \frac{\eta_\infty}{\eta_0} + (1 - \frac{\eta_\infty}{\eta_0})\frac{\dot{\varepsilon}_g}{\dot{\varepsilon}}[1 - \exp(-\frac{\dot{\varepsilon}}{\dot{\varepsilon}_g})]$$

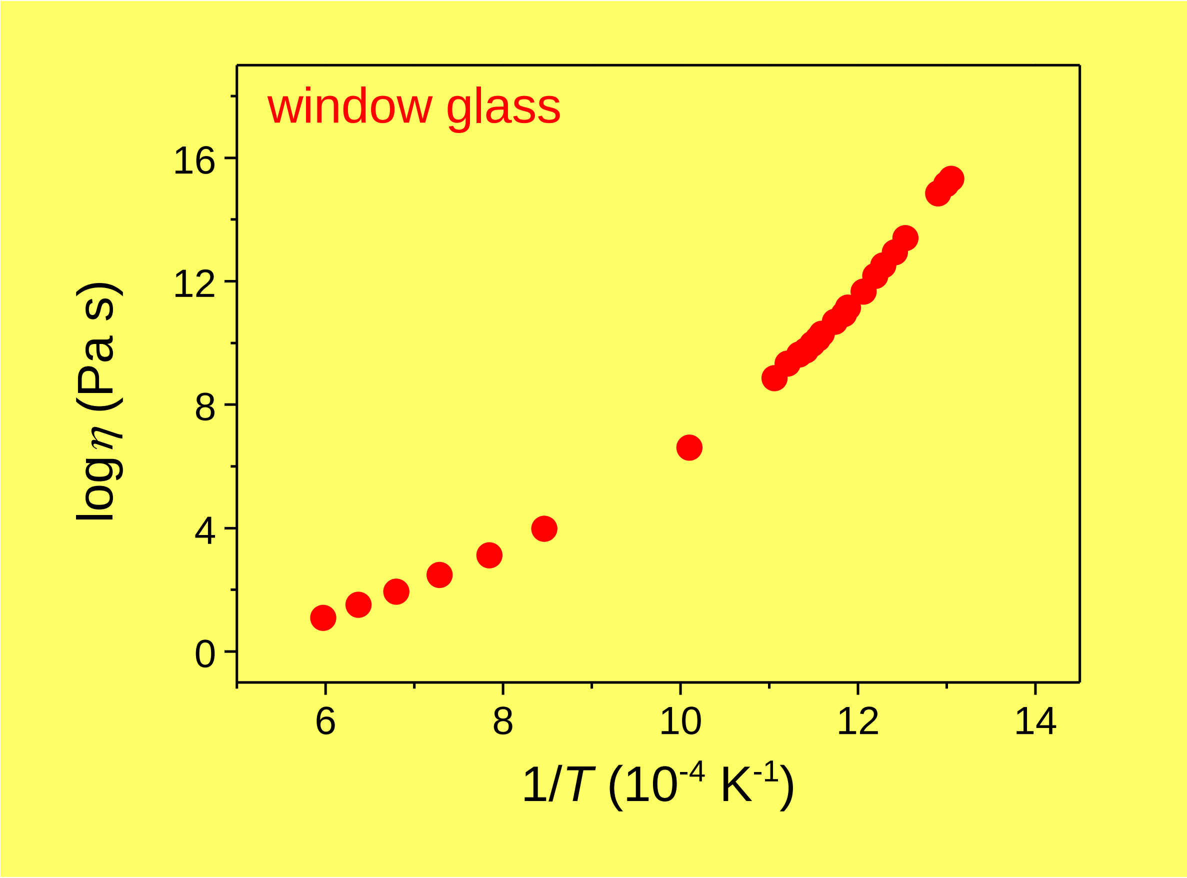
It is attributed to orientation of structural units.

Y.Z. Yue and R. Brückner, J. Non-Cryst. Solids (1994)

Fragile-to-strong transition

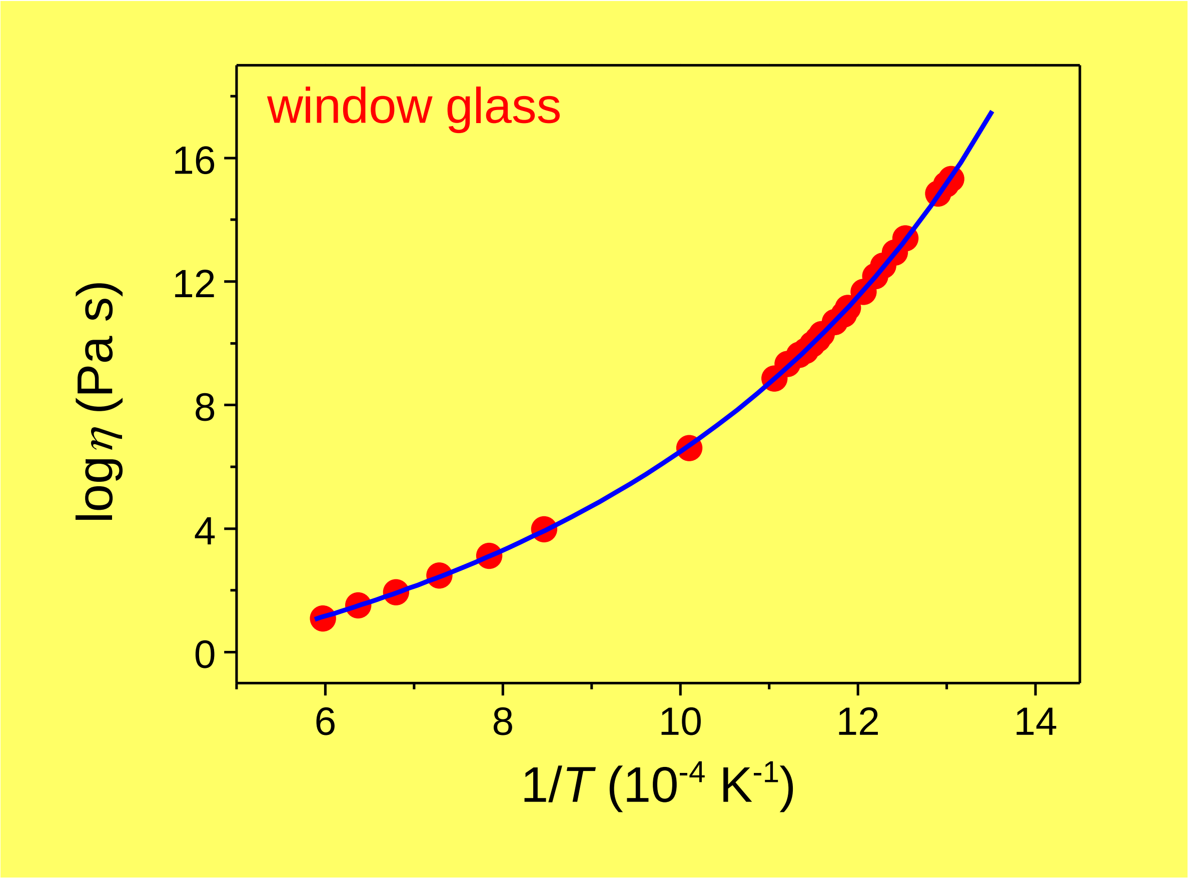
(An abnormal liquid dynamic behaviour)

A normal liquid – a window glass!

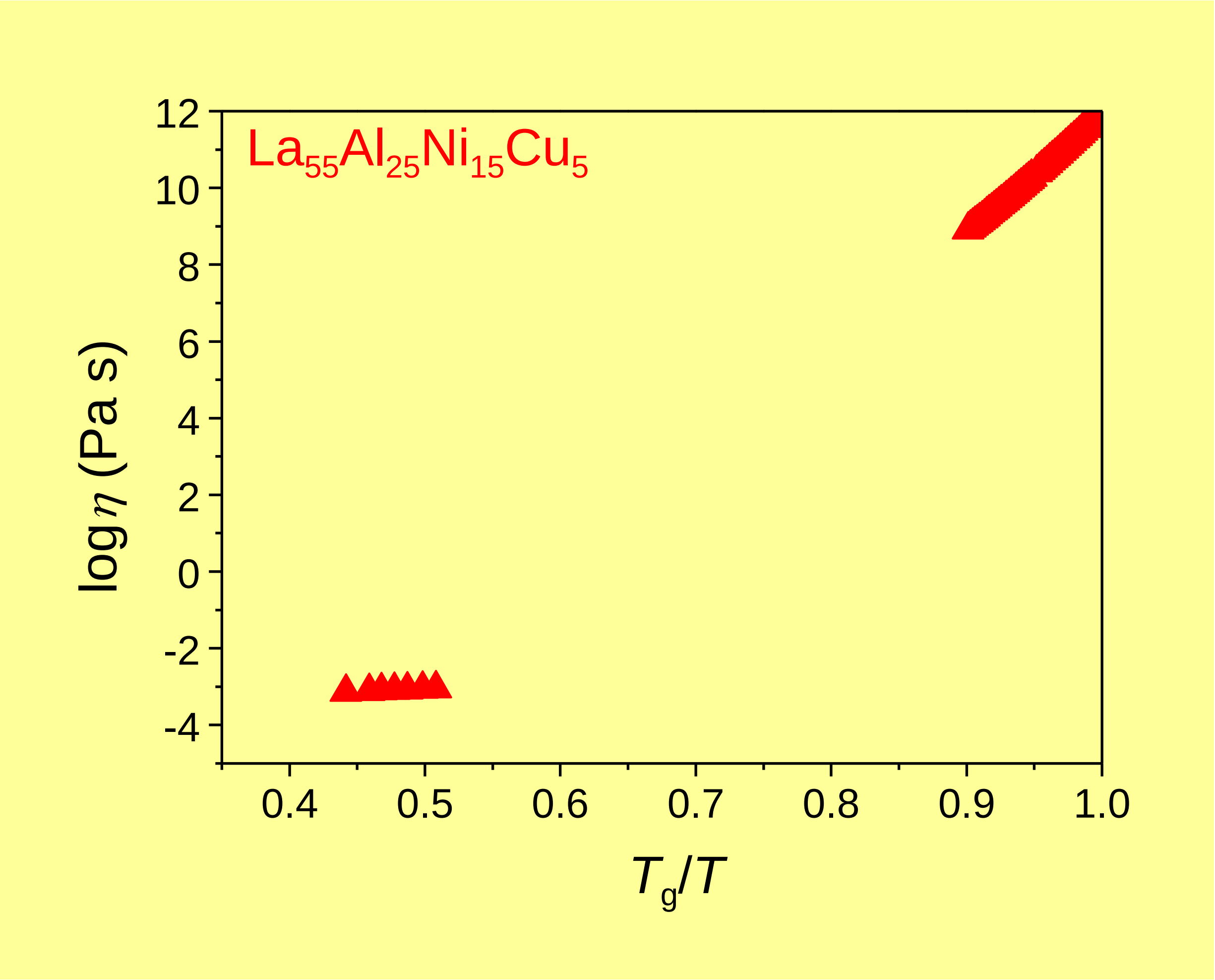


A normal liquid – a window glass!

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

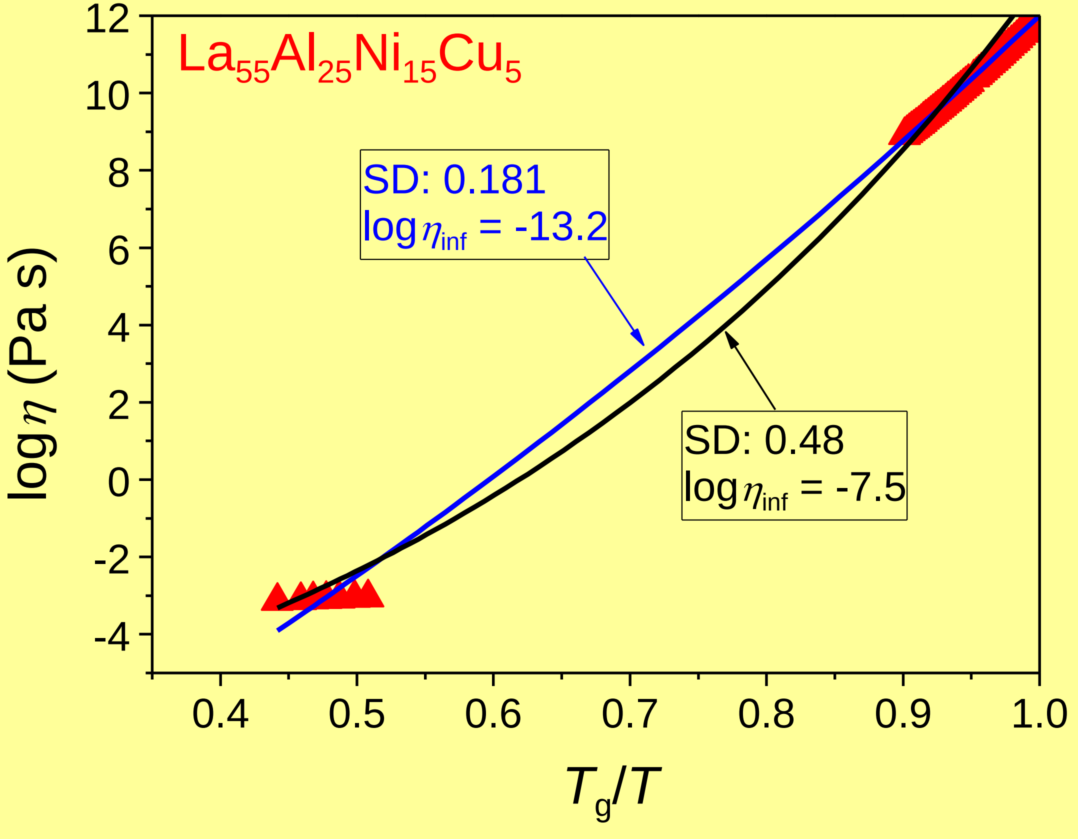


An abnormal case – a metallic liquid!

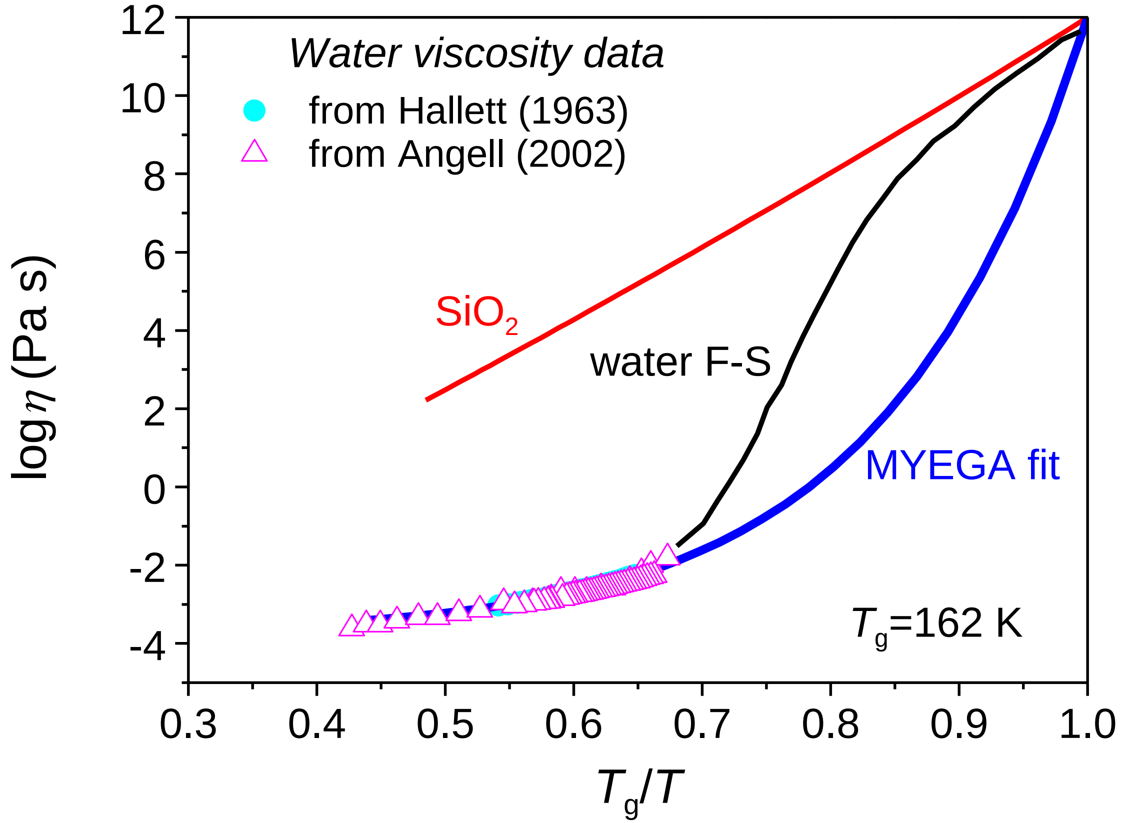


An abnormal case – a metallic liquid!
Its dynamics cannot be decribed by a 3-parameters model.

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

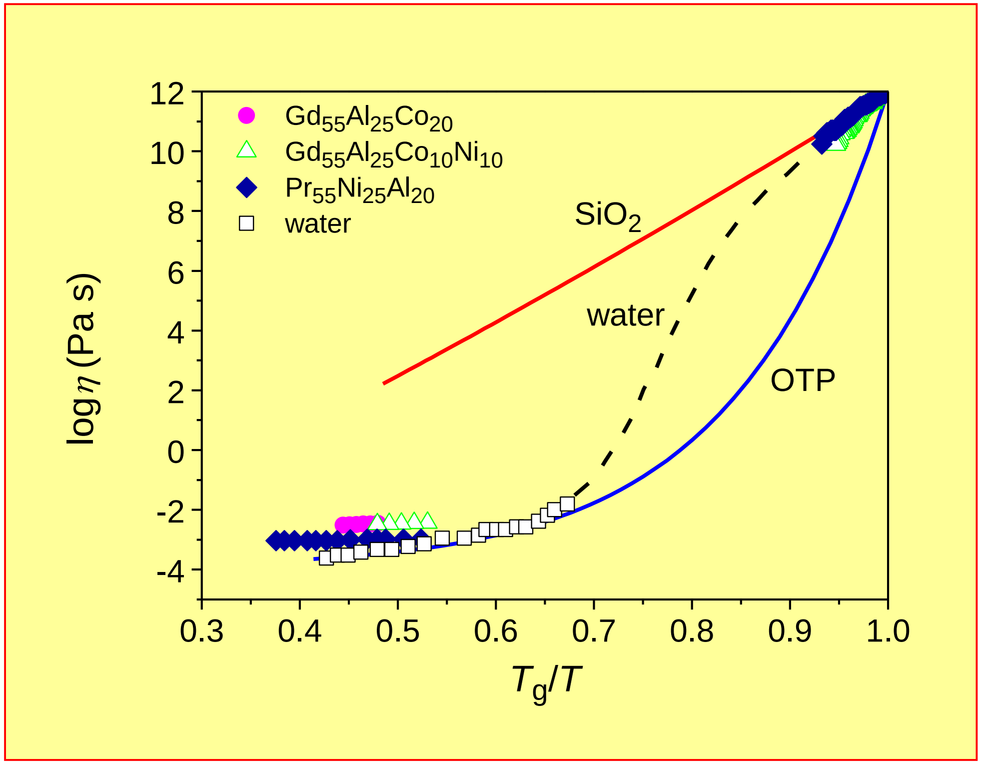


We recall a famous liquid – water, which shows an abnormal dynamic behaviour to – fragile-to-strong transition



Ito, Moynihan, Angell, *Nature* 1999

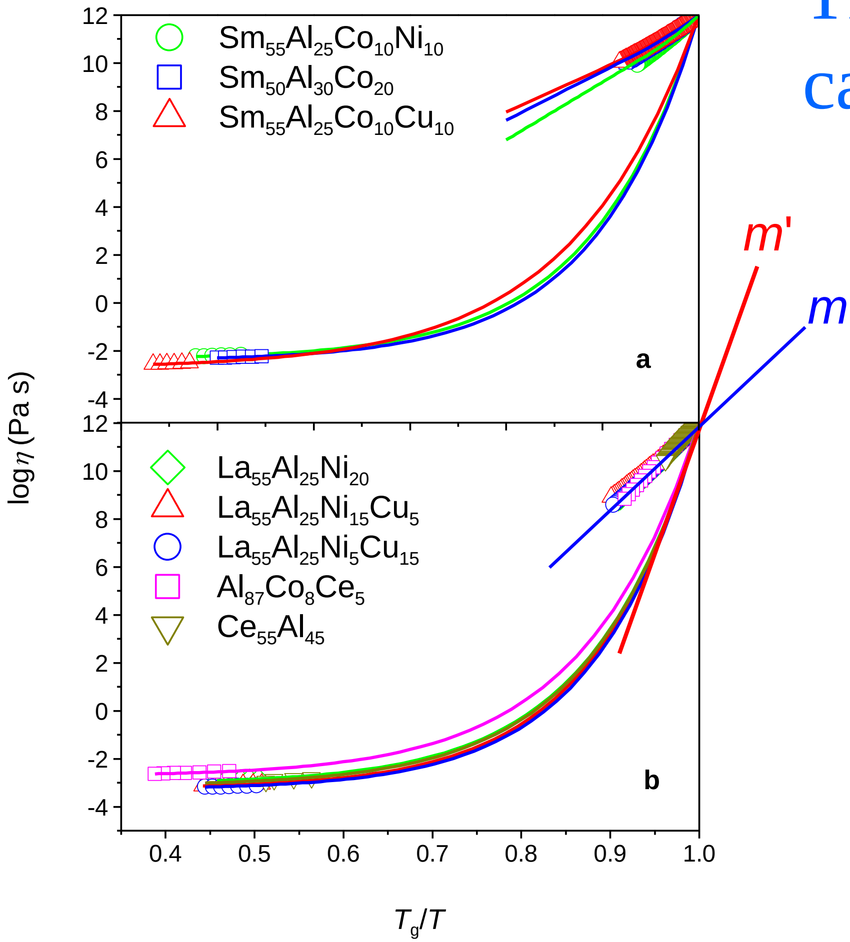
More metallic liquids similar to water, which exhibits Fragile-to-Strong (F-S) Transition



The data of these liquids cannot be described by a single model.

Zhang, Hu, Yue, Mauro, *J. Chem. Phys*. (2010)
Way, Wadhwa, Busch, *ACTA Mater*. (2007)

More….



The extent of the F-S transition can be determined by:

$$f = m'/m$$

$f > 1$: F-S transition

$f = 1$: no F-S transition

$f < 1$: never seen (unphysical?)

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.

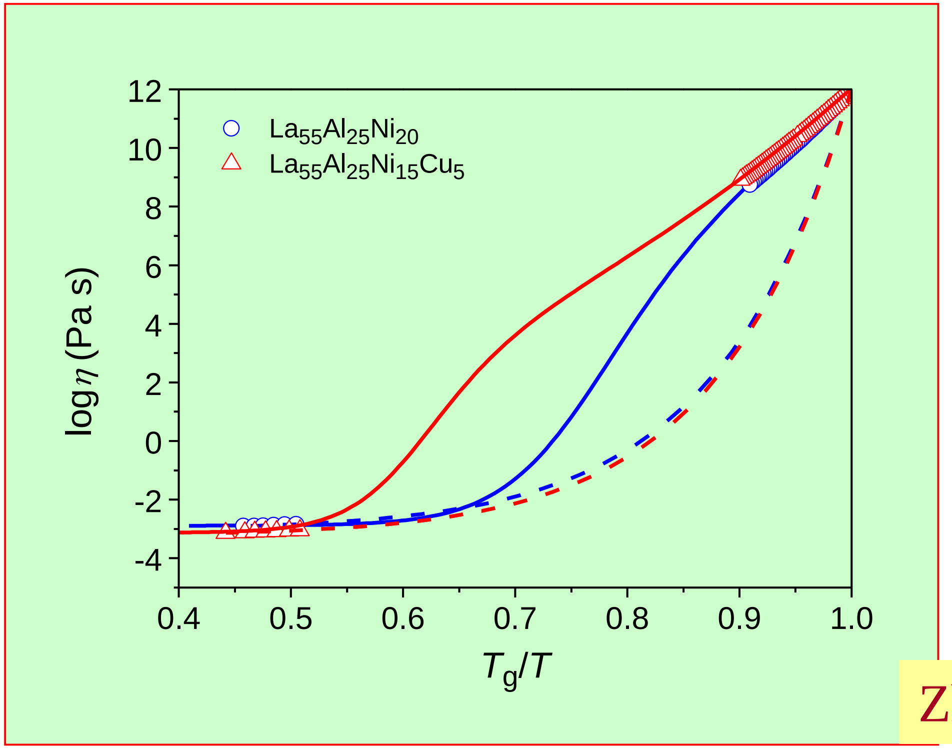
Question:

Is there a model that can describe the abnormal liquid dynamic behaviour?

Yes! But, to do so, the MYEGA has been generalized to the form:

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

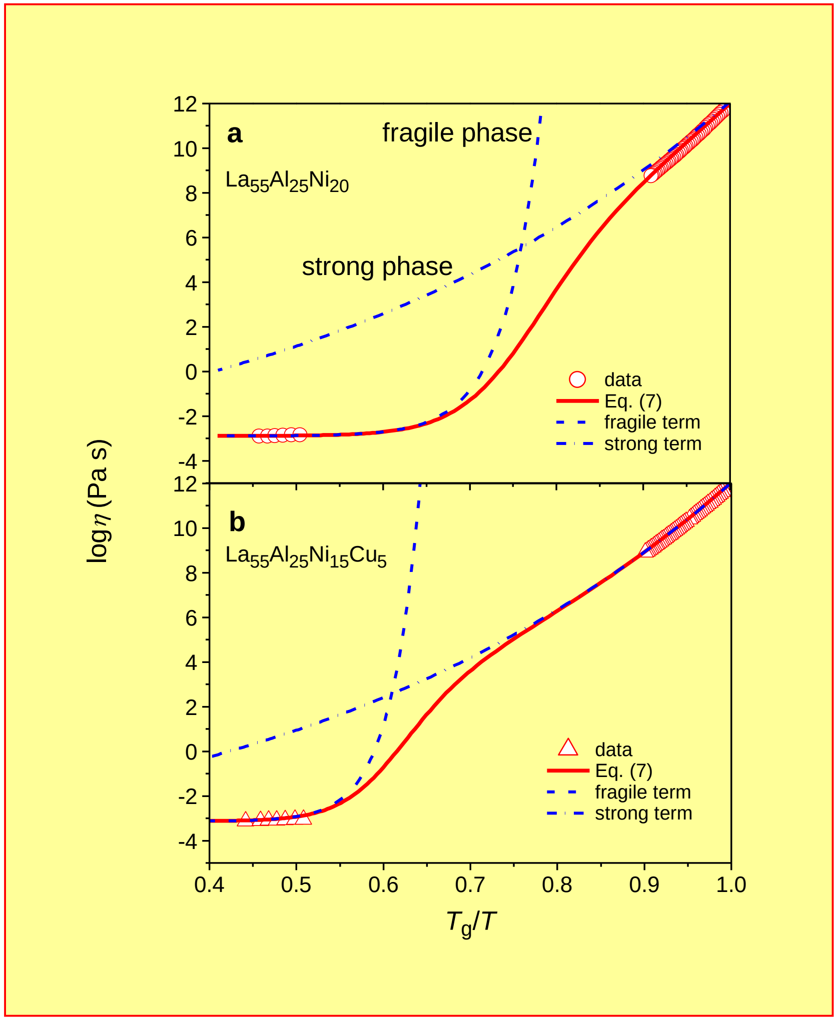
Fragile term   Strong term



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 that for normal liquids.

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

Two “phases” co-exists in the F-S crossover regime: Strong and fragile phases



Fragile phase (LDA):

- higher T_g
- higher activation enthalpy
- higher entropy
- lower density

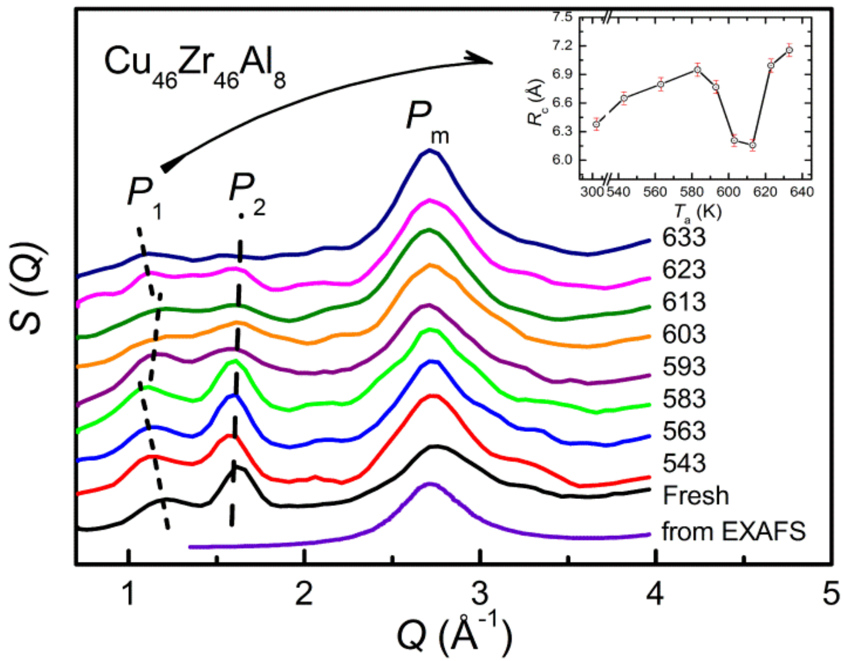
Strong phase (HDA):

- lower T_g, i.e., actual T_g of the mixed liquid
- lower activation enthalpy
- lower entropy
- higher density

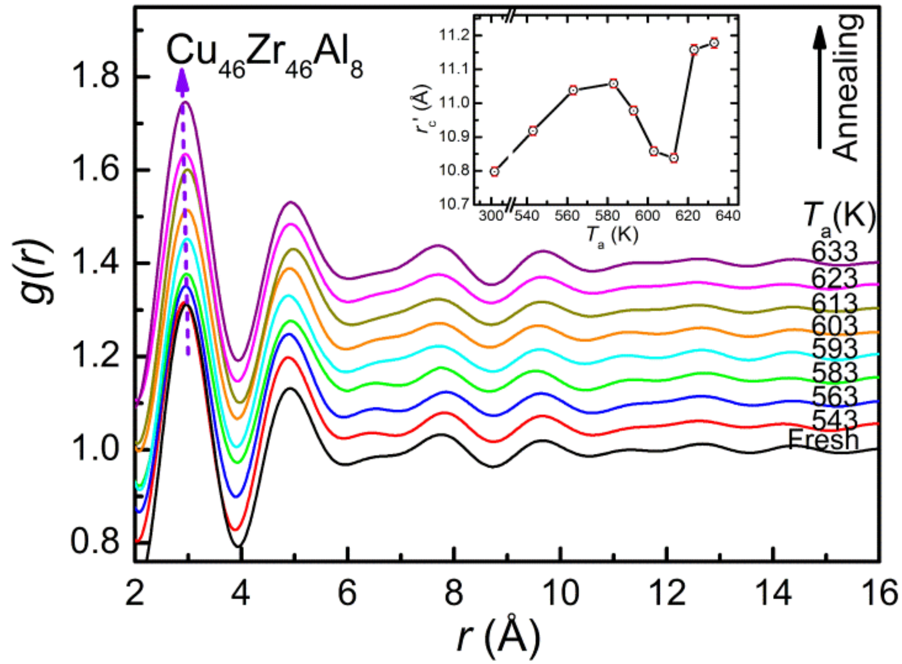
The fragile phase is cooled, the F-S transition intervenes, mitigating the sharp increase in viscosity with decreasing *T*.

Non-montonic structural response to sub-T_g annealing measured by x-ray scattering

Total structural factors



PDF

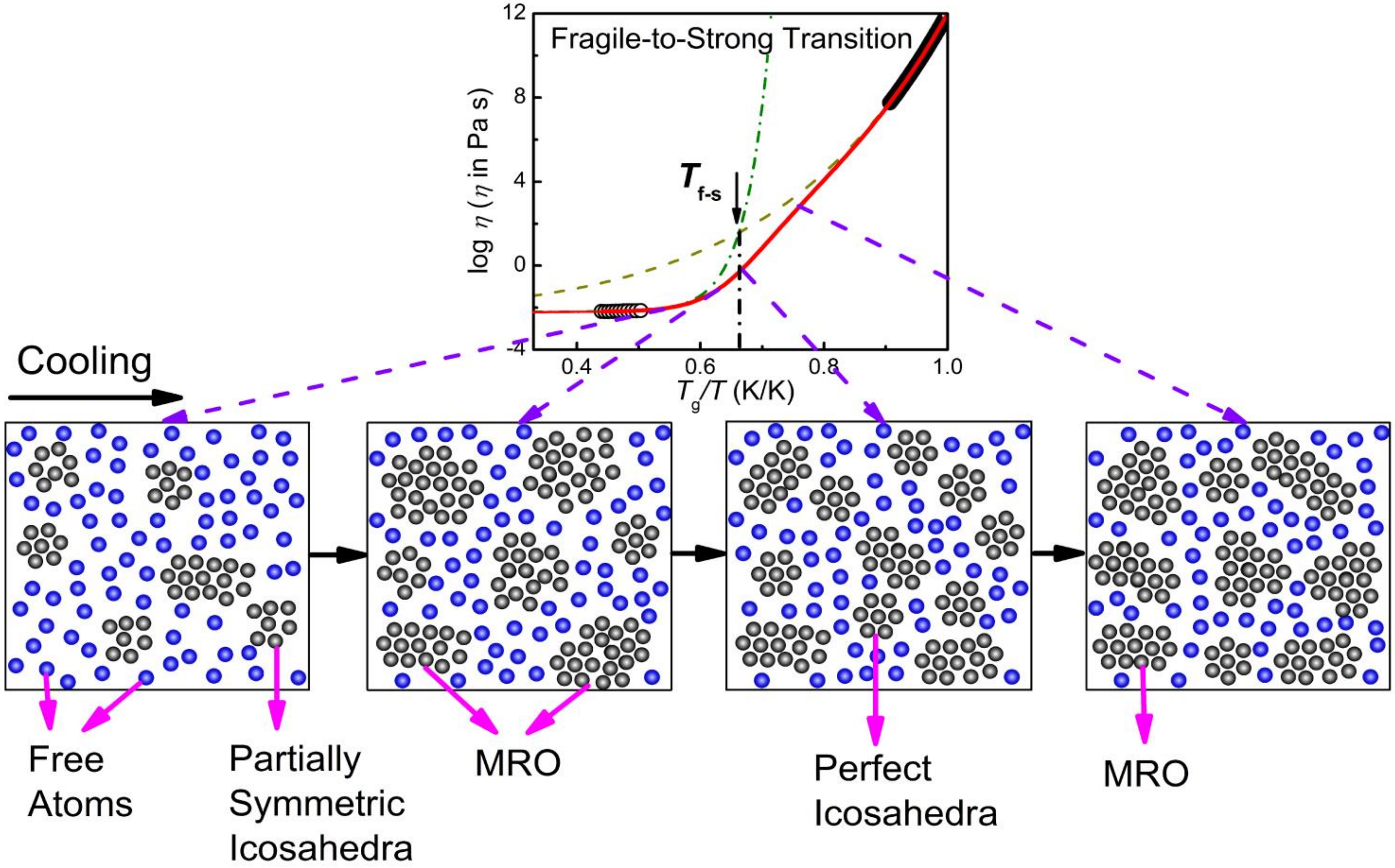


Annealing dependence of the structural unit size

Annealing dependence of the correlation length

Critical temperature for the dramatic decreases in R_c: T_c ~ around 1.3T_g

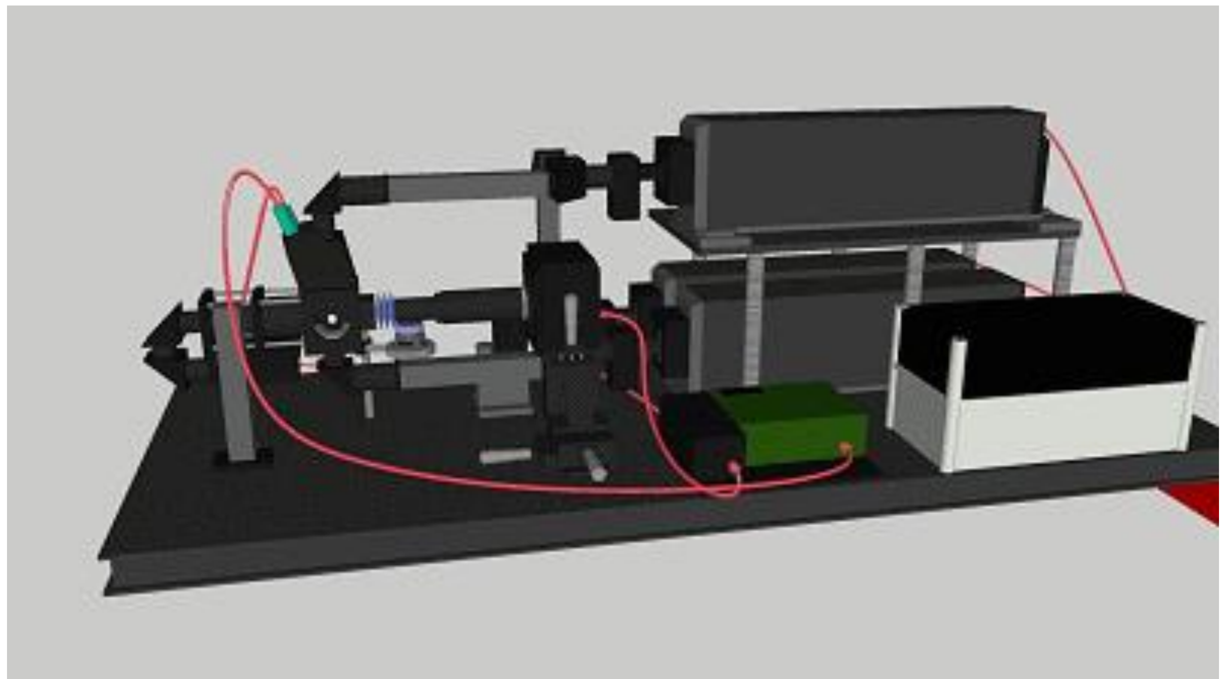
Schematic scenario of the structural evolution during fragile-to-strong transition



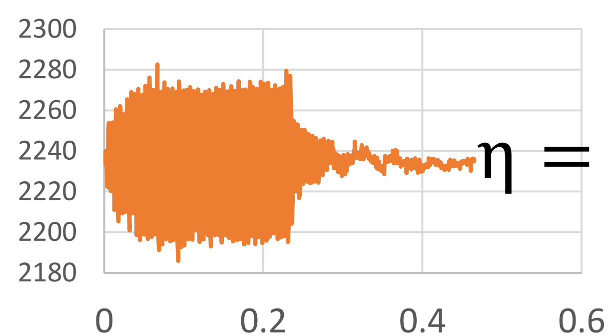
Zhou, et al. *J. Chem. Phys.* (2015)

Containerless aerodynamic levitation (ADL) melting to avoid heterogeneous nucleation

Melting of Al_2O_3



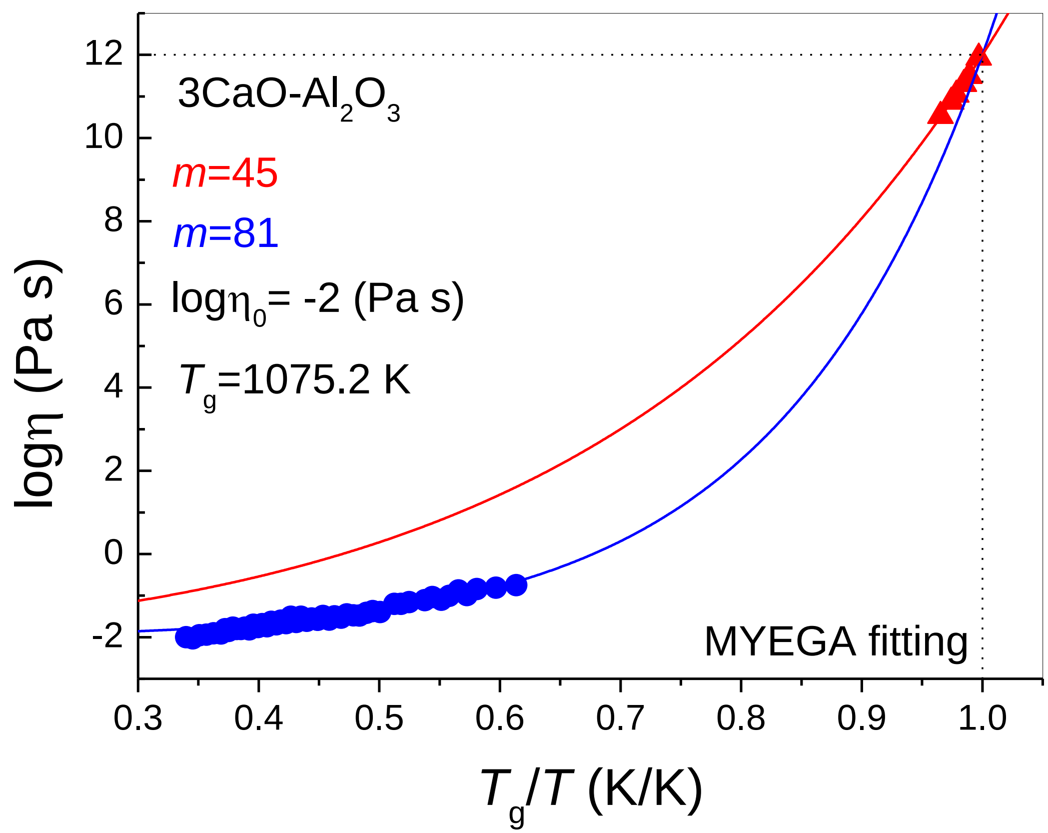
- Extend the supercooled region
- Measure viscosity
- In-situ structural characterization



$$\eta = \frac{3M}{20\pi R}\Gamma$$

Forced oscillation and decay

Fragile-to-strong transition in aluminates



Fitted with

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

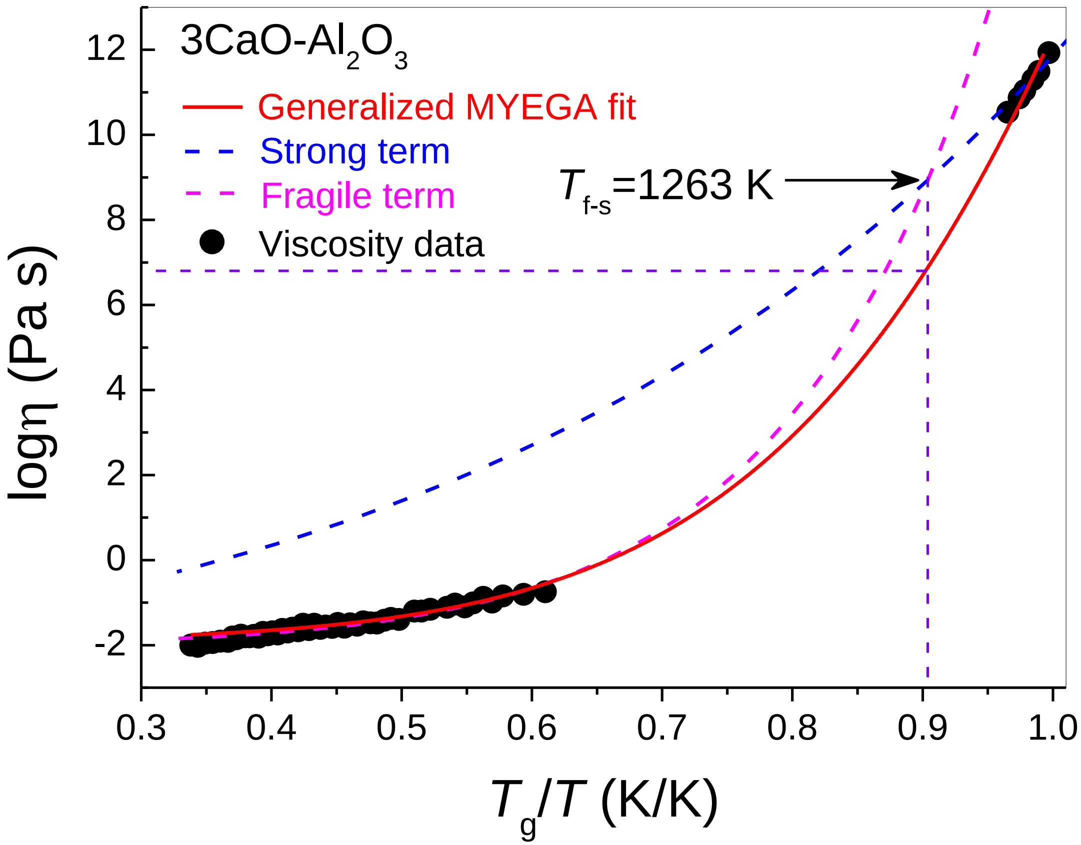
(MYEGA)

The data can be described by the generalized MYEGA

$$log\eta = log\eta_0 + \frac{1}{T[W_1 \exp\left(\frac{-C_1}{T}\right) + W_2 \exp(\frac{-C_2}{T})]}$$

$$T_{f-s} = \frac{C_1 - C_2}{lnW_1 - lnW_2}$$

Parameter	Value
$\log\eta_0$ (Pa s)	-2.039
W_1	0.018
C_1	7324
W_2	1.68E-4
C_2	1407



I would like to all my co-authors and collaborators.

Thank you for your attention!