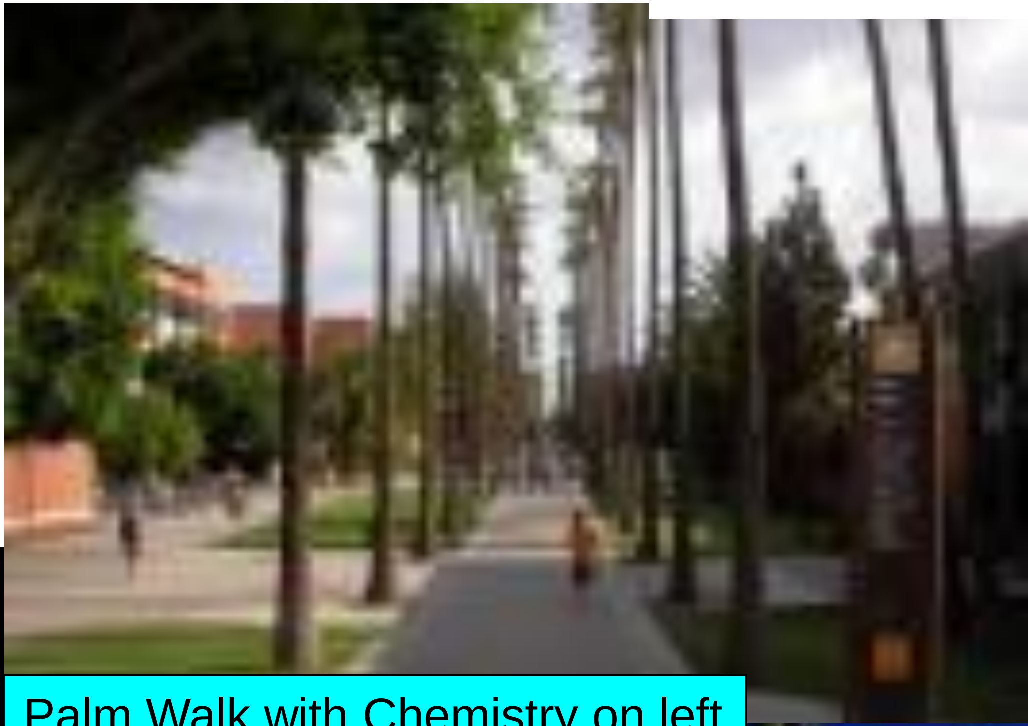
ARIZONA STATE U.



Palm Walk with Chemistry on left

Sun Devil Stadium, from
Tempe Town lake

Outline

1. Backround. Other languages and people

   What is and wot isn't fragile" or strong" behavior …Some misuses or misconceptions

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   Athermal systems. Fragilities for different polydispersivities and shapes.

   * hard ellipsoids

3. Thermal systems: (a) van der Waals ellipsoids, and "hysterisis peaks".

   (b) Ergodicity breaking and fragility

   (c) Strong-fragile transitions and polyamorphism

4. What determines the "fragility" – many ideas, and the roots

5 Physics of vibrational entropy, hence maybe fragility.

Beginnings

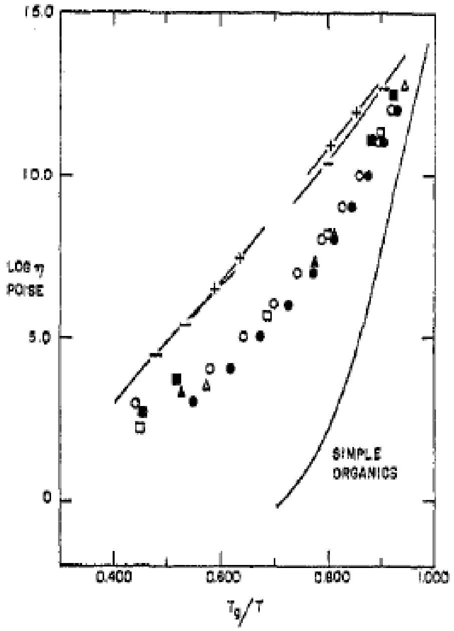
Gustav
Tammann
(Göttingen, 1926)

$$\log_{10}(x(T)) = A + B/(T - T_0),$$

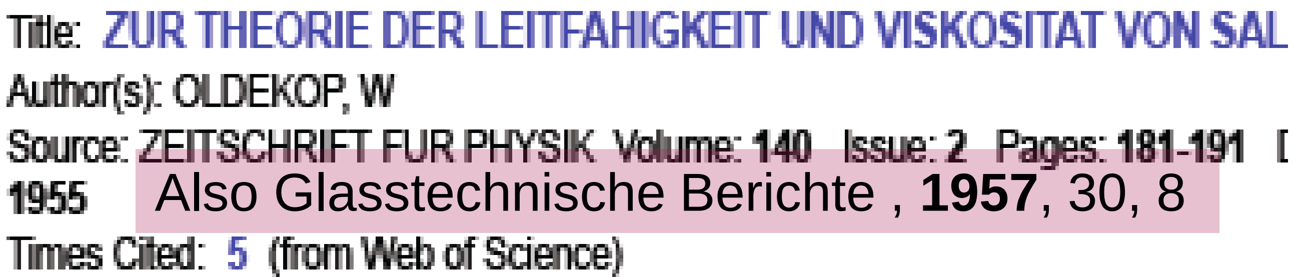
“Long” and “short” glasses

And many other profound contributions

W. T. Laughlin and D. R. Uhlmann



T_g/T normalization for inorganic oxide



Title: ZUR THEORIE DER LEITFAHIGKEIT UND VISKOSITAT VON SAL

Author(s): OLDEKOP, W

Source: ZEITSCHRIFT FUR PHYSIK Volume: 140 Issue: 2 Pages: 181-191

1955

Also Glasstechnische Berichte , **1957**, 30, 8

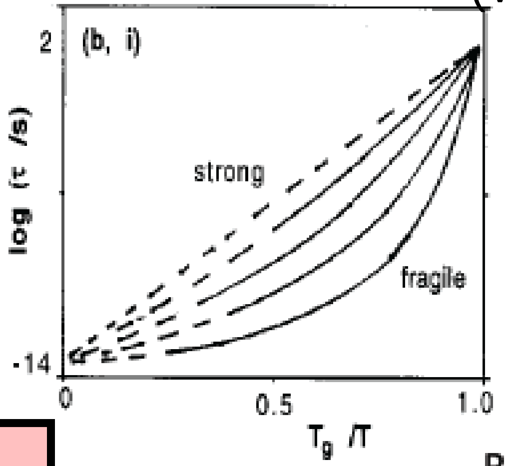
Times Cited: 5 (from Web of Science)

CAUTION

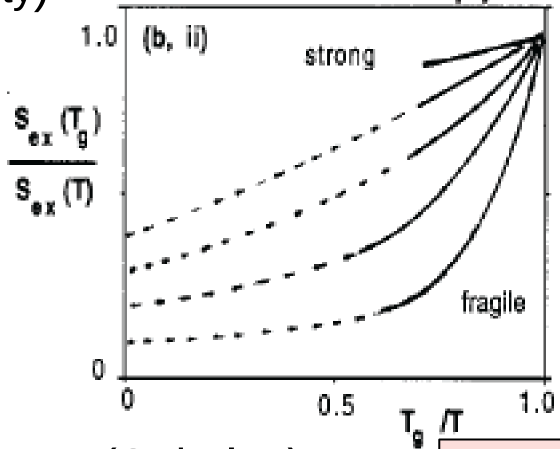
What is [:-)] and wot isn’t [:-( ]

Fragility manifestations

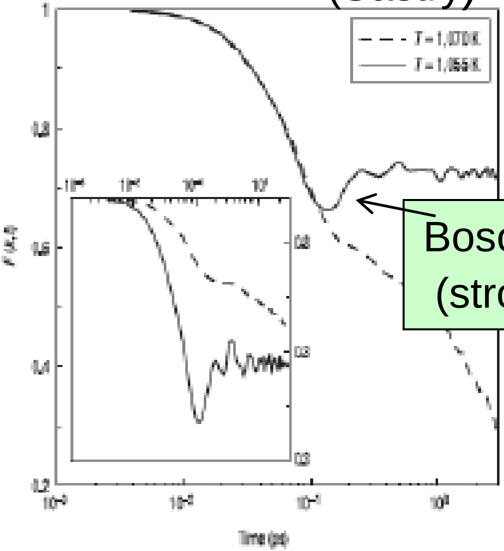
Relaxation time (Viscosity)



Excess entropy



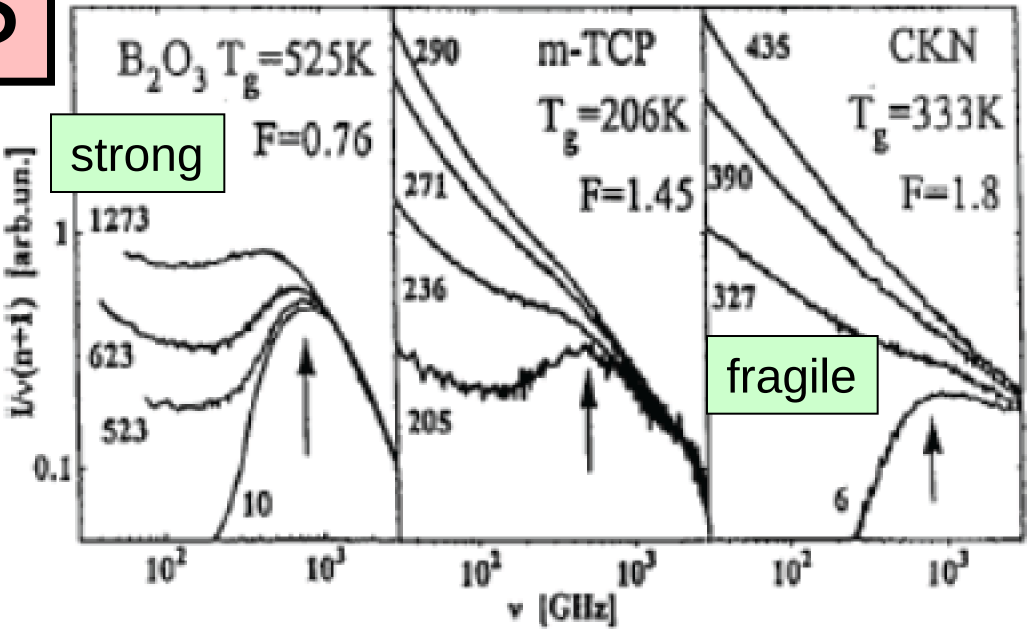
Dynamic structure factor (Sastry)



Boson Dip (strong)

IS

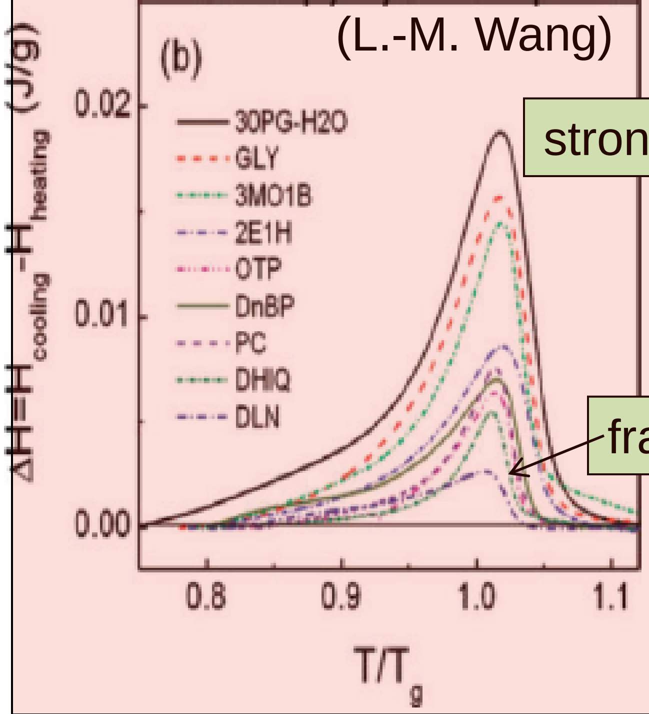
Boson peak (Sokolov)



strong

fragile

Enthalpy hysterisis peak (L.-M. Wang)



strong

fragile

ISN'T

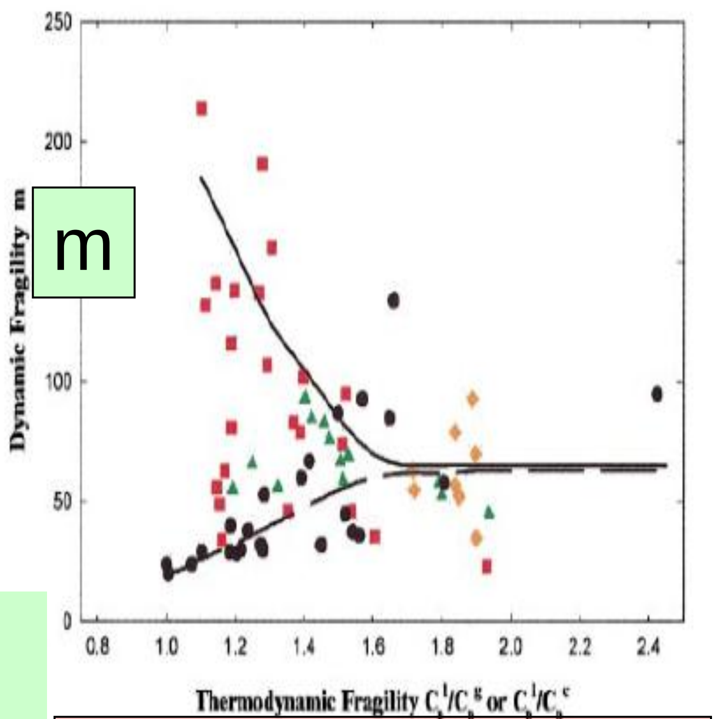
Heat capacity misconceptions: the need for scaling

Example:

JOURNAL OF CHEMICAL PHYSICS VOLUME 114, NUMBER 13

New insights into the fragility dilemma in liquids

Dinghai Huang and Gregory B. McKenna[a]
Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409



Thermo fragility C_p^l/C_p^g :(

The problem is: you can't use an unscaled quantity, and expect sensible correlations.

expansivity $\alpha = 1/V(\partial V/\partial T)_p$

compressibility $\kappa_T = 1/V(\partial V/\partial P)_T$

BUT, heat capacity is $(\partial H/\partial T)_p$ ***unscaled*** **(WHY?)**

We need a quantity with absolute values, to scale by

$(\partial H/\partial T)p = (\partial S/\partial \ln T)_p$

$c_p^* = 1/S(\partial S/\partial \ln T)_p$

No more "beads"

$(\partial S/\partial \ln T)_p = \partial H/T/\partial \ln T)p = \partial[(H/T)/(dT/T)]p$

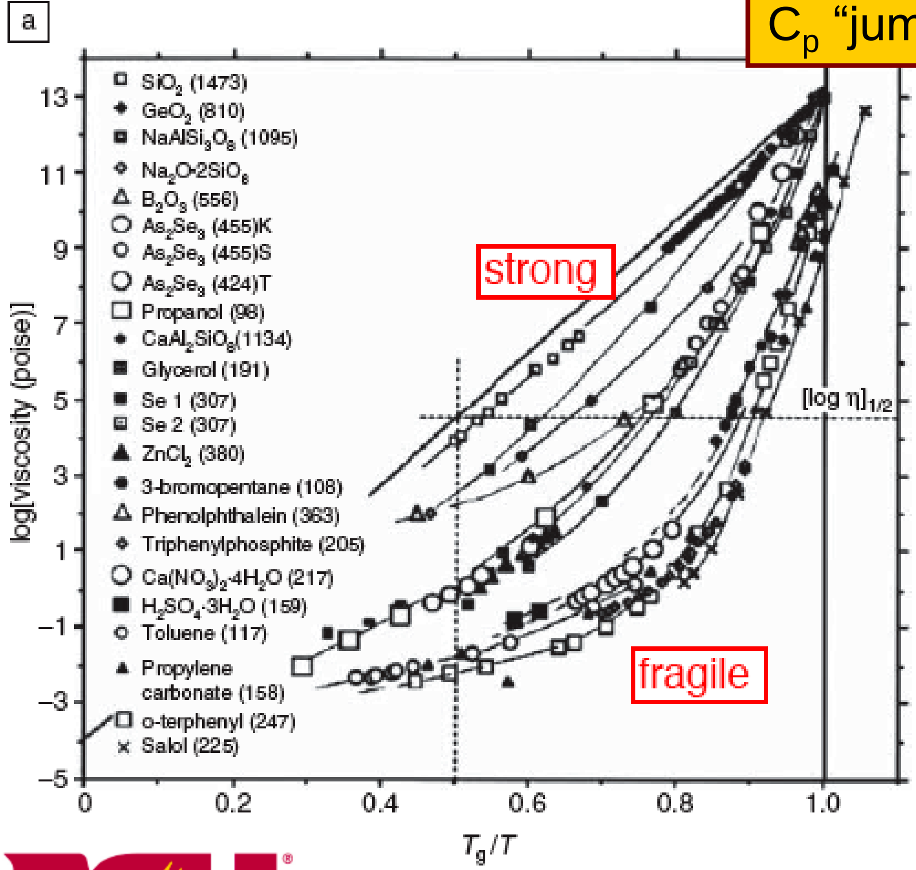
Same pattern for **entropy** generation above T_g

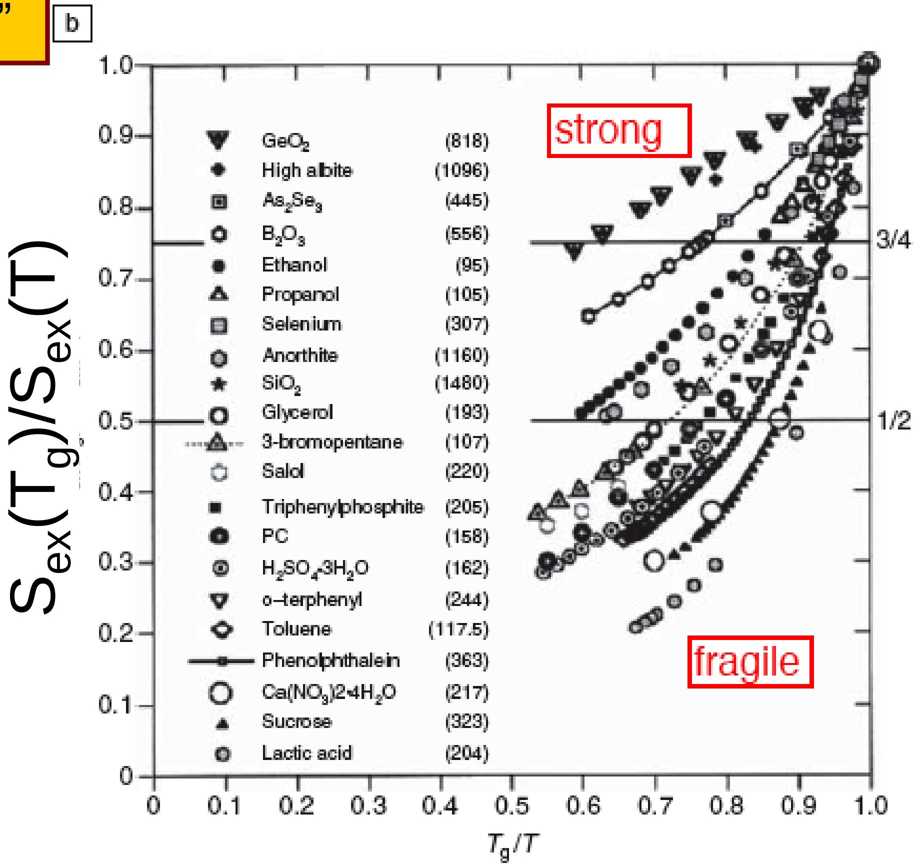
The liquids shown, and their ordering, are the same

Dynamics (viscosity)

Tg now from T of C_p “jump”

Thermodynamics (XS entropy [scaled]



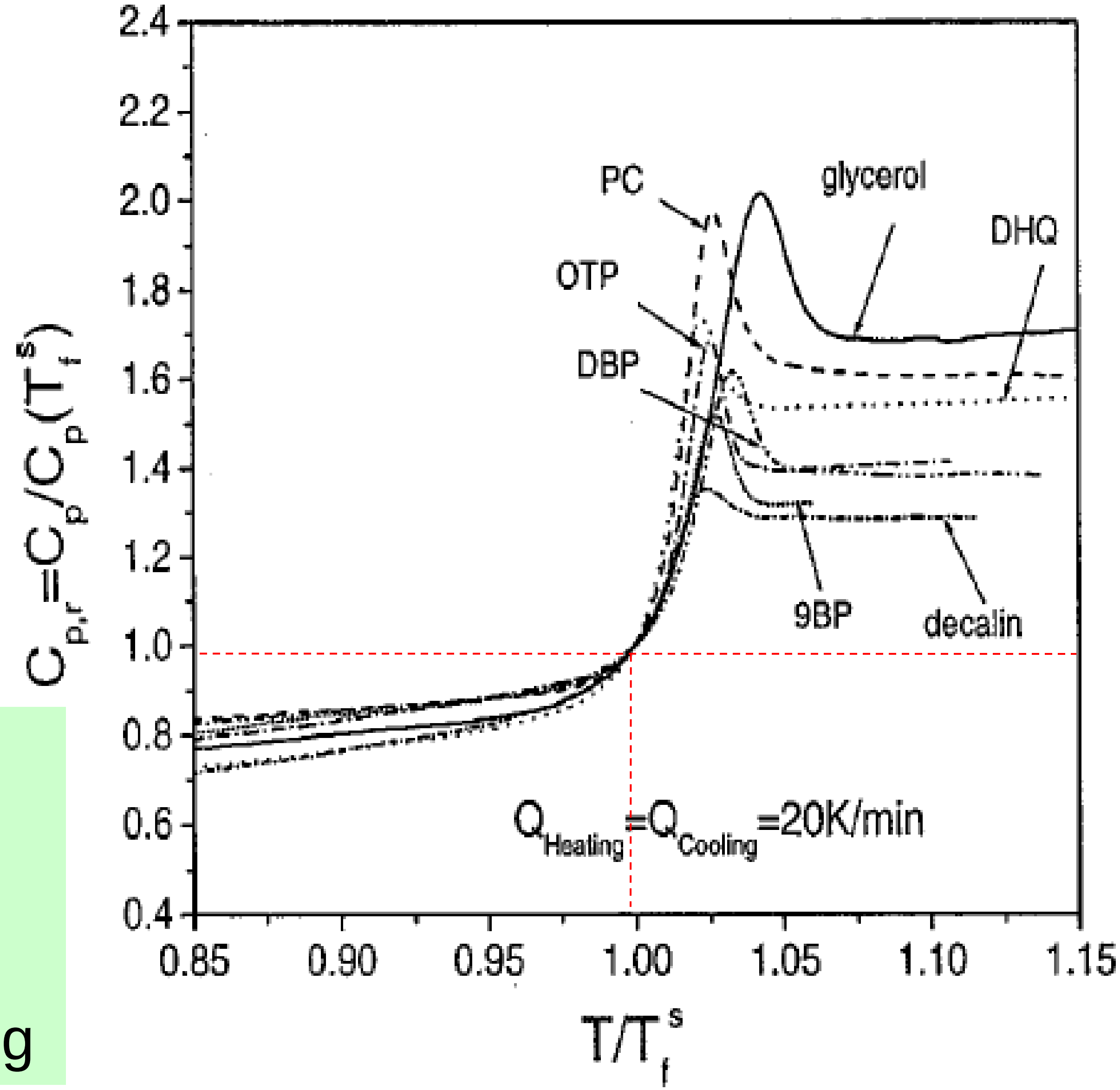


Martinez and CAA, Nature, 2001

How BAD is the ΔC_p correlation?
Smallest ΔC_p (decalin) has ***largest*** fragility

Work of Limin Wang
JCP 2002

(One of my three) attachments



The C_p jump at the standard Tg (fictive temperature for 20K/min cooling) – normalized to C_p at Tg

When is a liquid a “strong” liquid?

e.g. one reads:
“salol undergoes a fragile-to-strong transition above T_g”

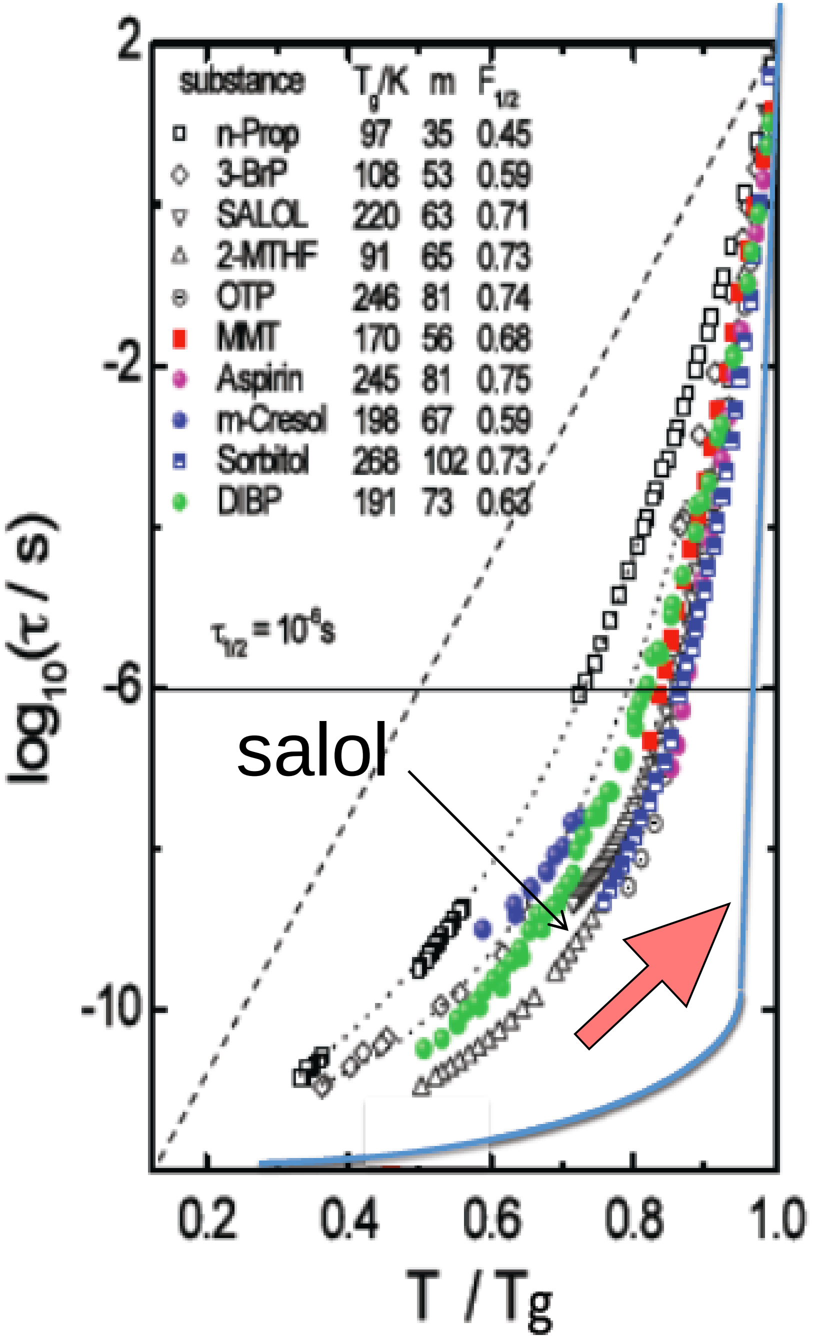
(back to Arrhenius near Tg) :-(:-(

Reductio ad absurdum

Is this (*arrow*) a strong liquid? It has 10 orders of magnitude of Arrhenius behavior approaching T_g.

Surely not. Consider the m value and ***pre-exponent*** !

A “strong” liquid is a simple activated system. It has a pre-exponent typical of lattice vibration time (10^{-14} s). This is the (inverse) frequency of attempts to escape its neighbors, and the slope of the plot gives the barrier opposing the attempt.

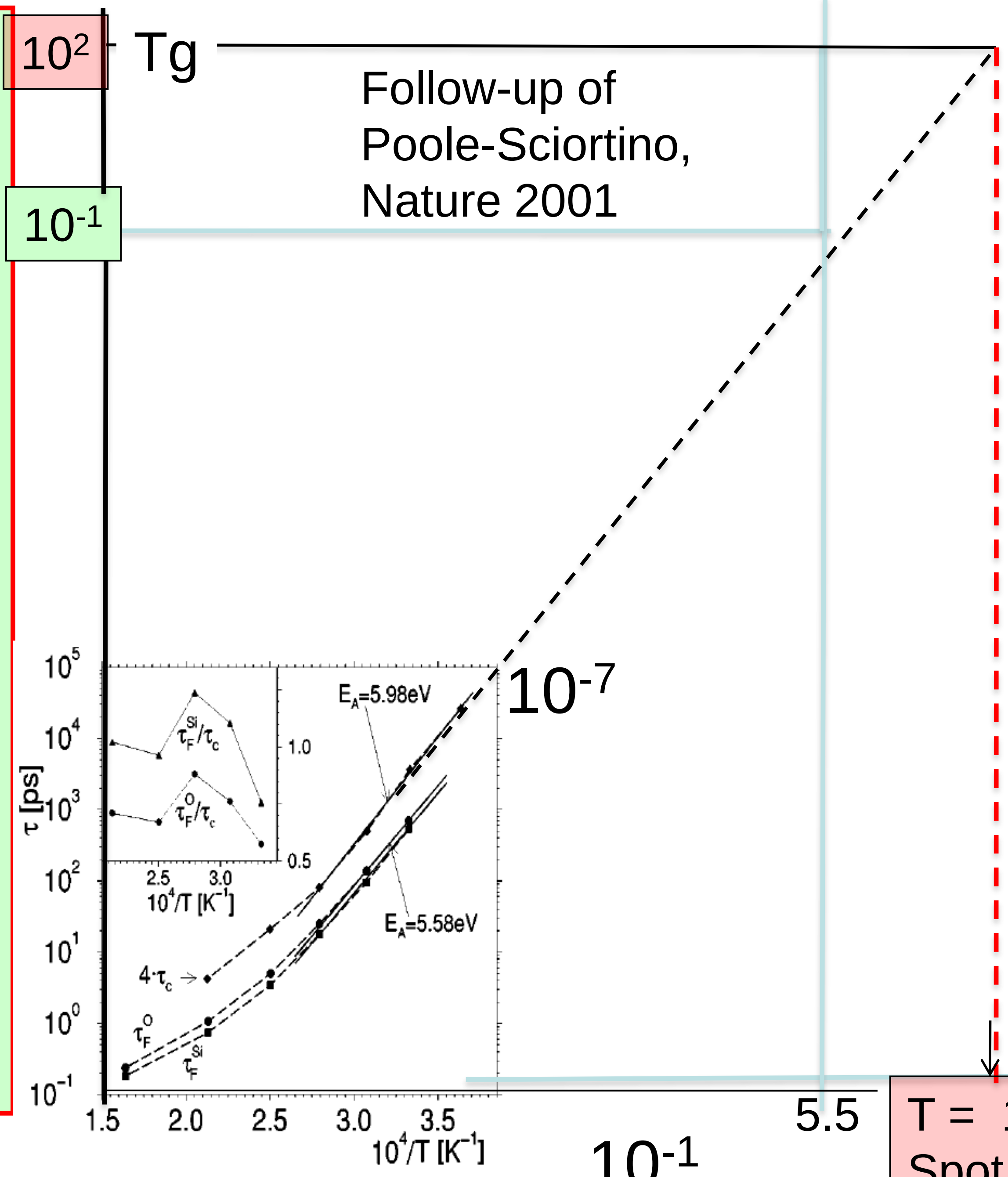


BUT this is OK

From Horbach, Kob and Binder

Fragile-to-Arrhenius transition in BKS silica, showing five order of magnitude change in tau, extrapolating to correct T_g of laboratory silica

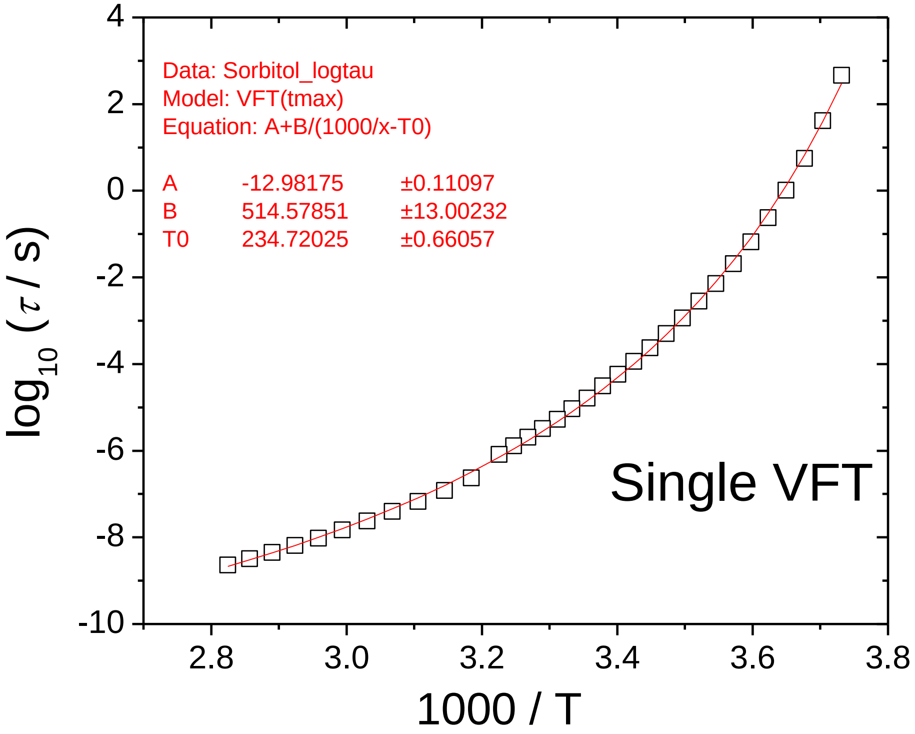
5000K



Follow-up of Poole-Sciortino, Nature 2001

T = 1500K
Spot on!!

Dynamic feature of Sorbitol

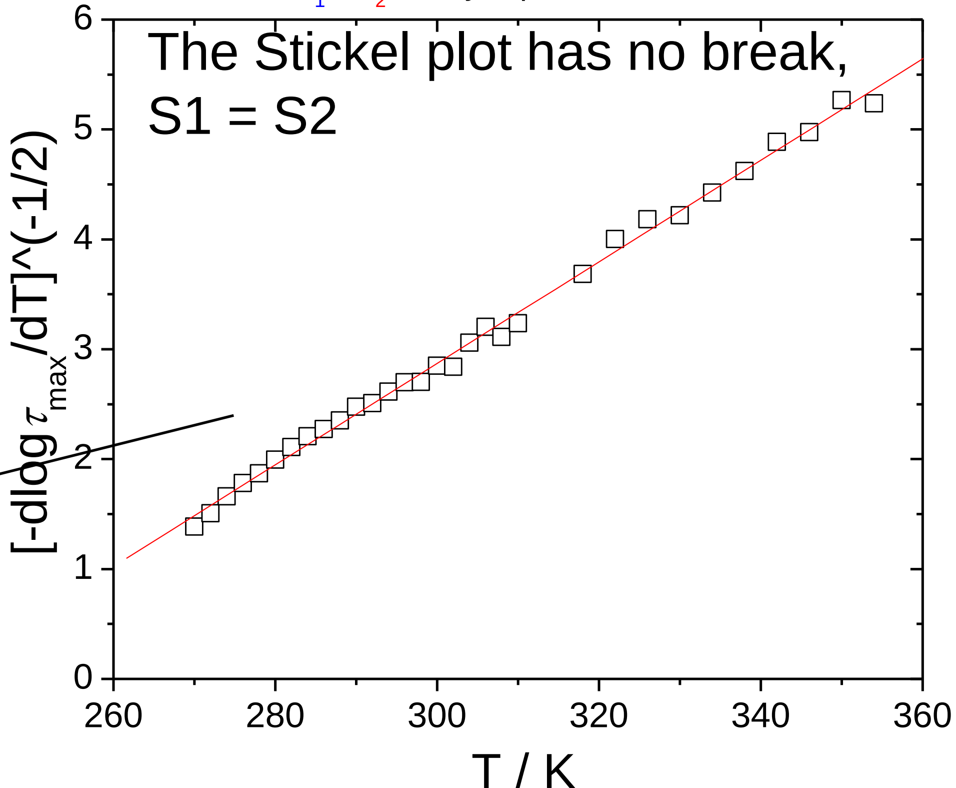


Single VFT

Stickel plots.

A sensitive way to detect crossover behavior. In ideal fragile liquid cases, **like dibutyl phthallate and sorbitol,** there is no crossover. Mostly it is a crossover from one VFT function to a second. If an Arrhenius function takes over at low temperatures the Stickel plot goes flat.

S_1 / S_2 neally equals to 1

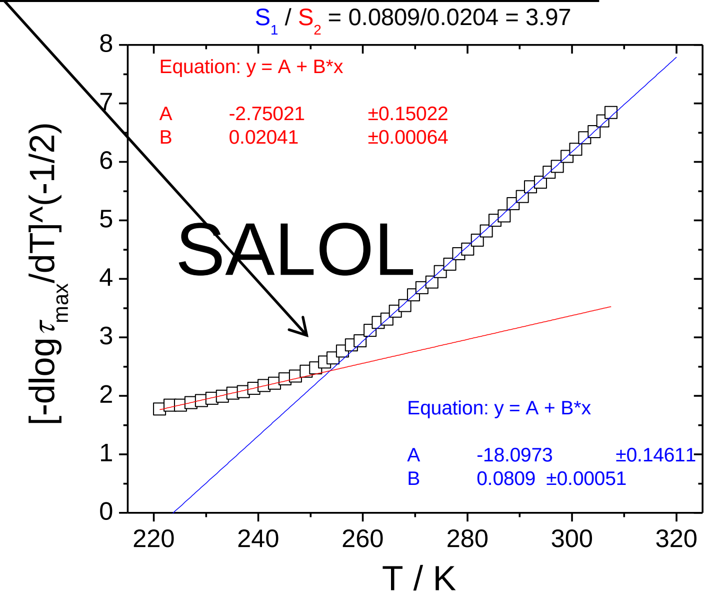


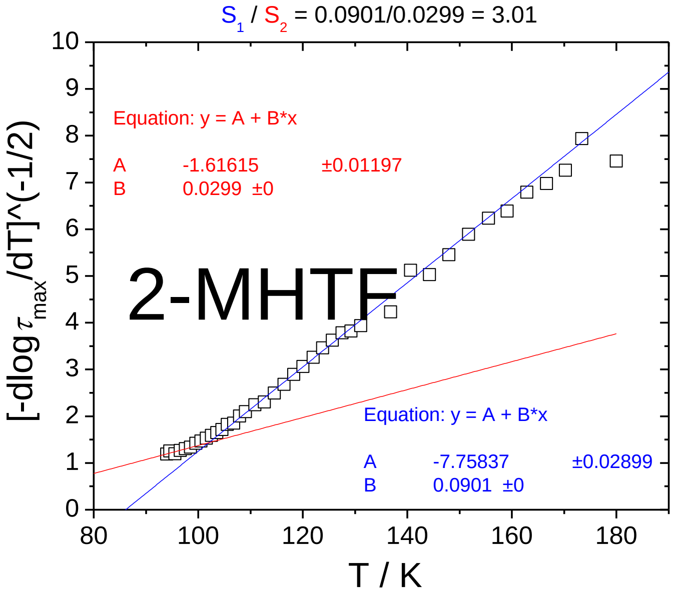
The Stickel plot has no break,
S1 = S2

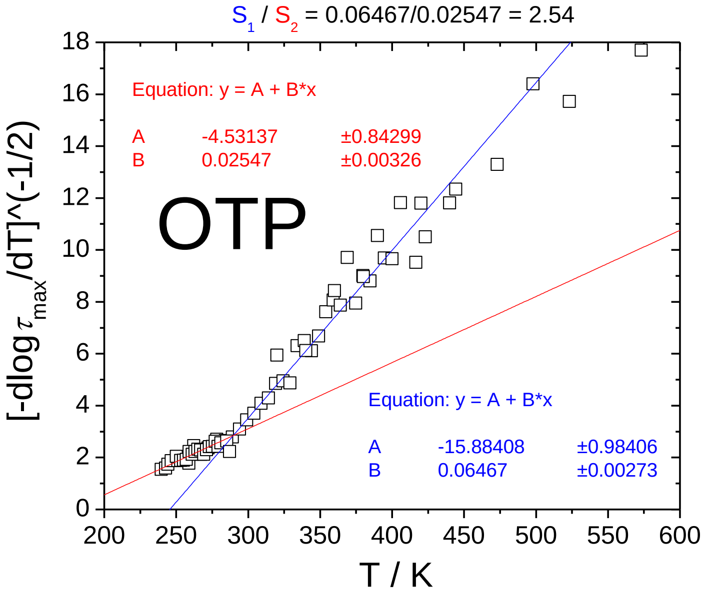
No crossover temperature T_B can be identified from this plot, also because single VFT can fit the data well.

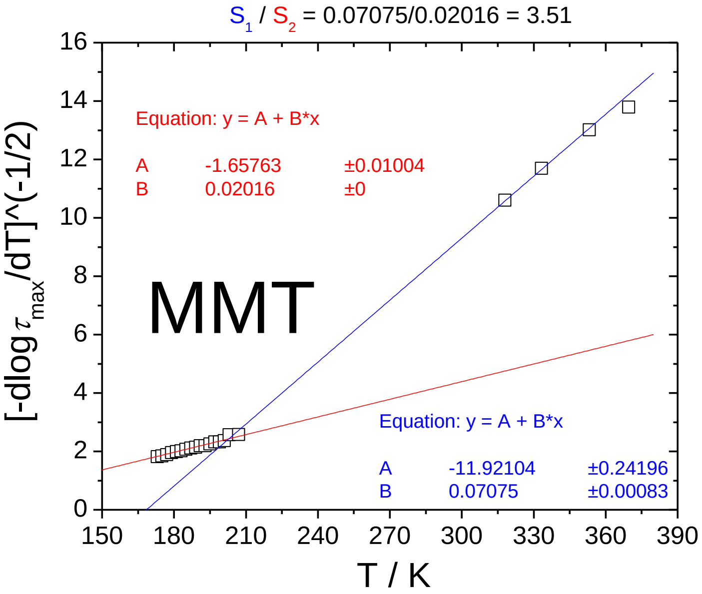
Hydrogen bonding saturated: *next slide*

Stickel plots

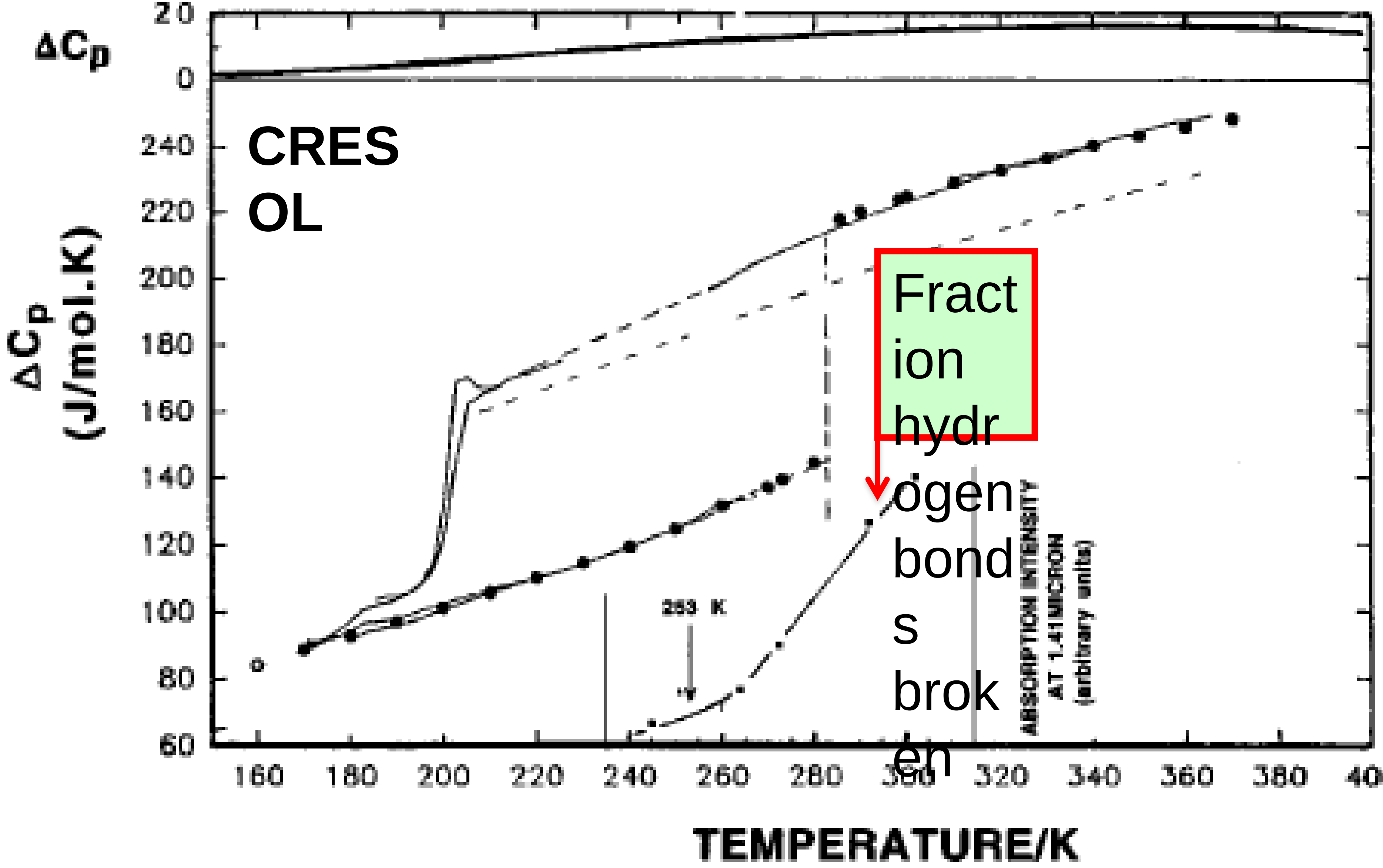








Effect of hydrogen bonds on VFT breakdown



CRESOL

Fraction hydrogen bonds broken

(*Take a break*)

Snapper rocks, Coolangatta, Qld.

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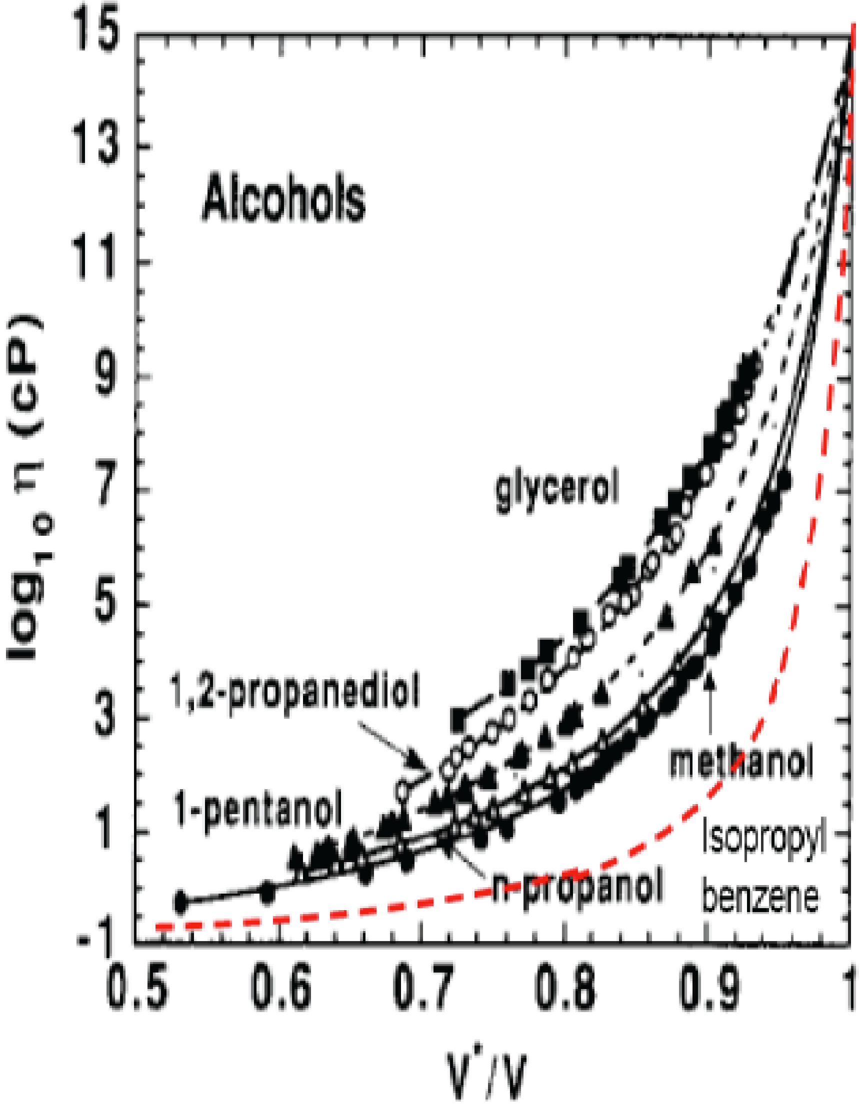
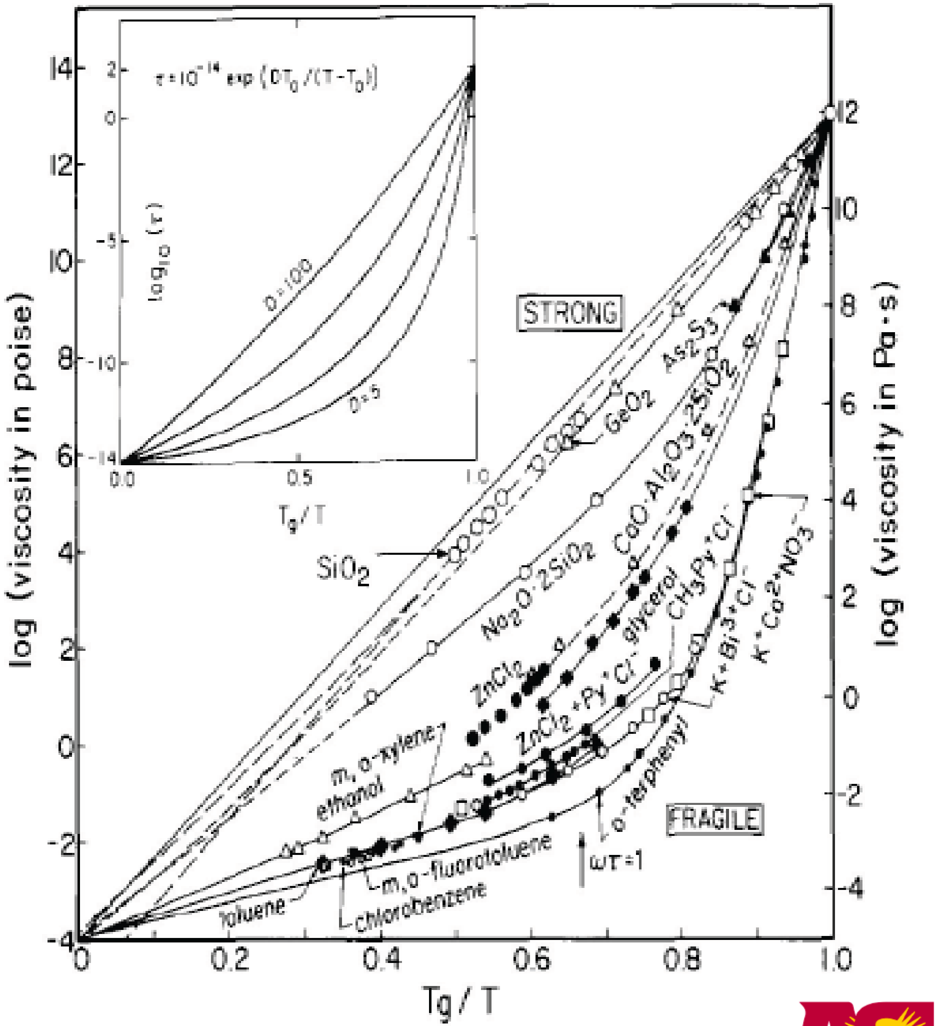
Volume vs thermal manifestations

Herbst and King, 1993
Alicante Ngai-pilgrimmage



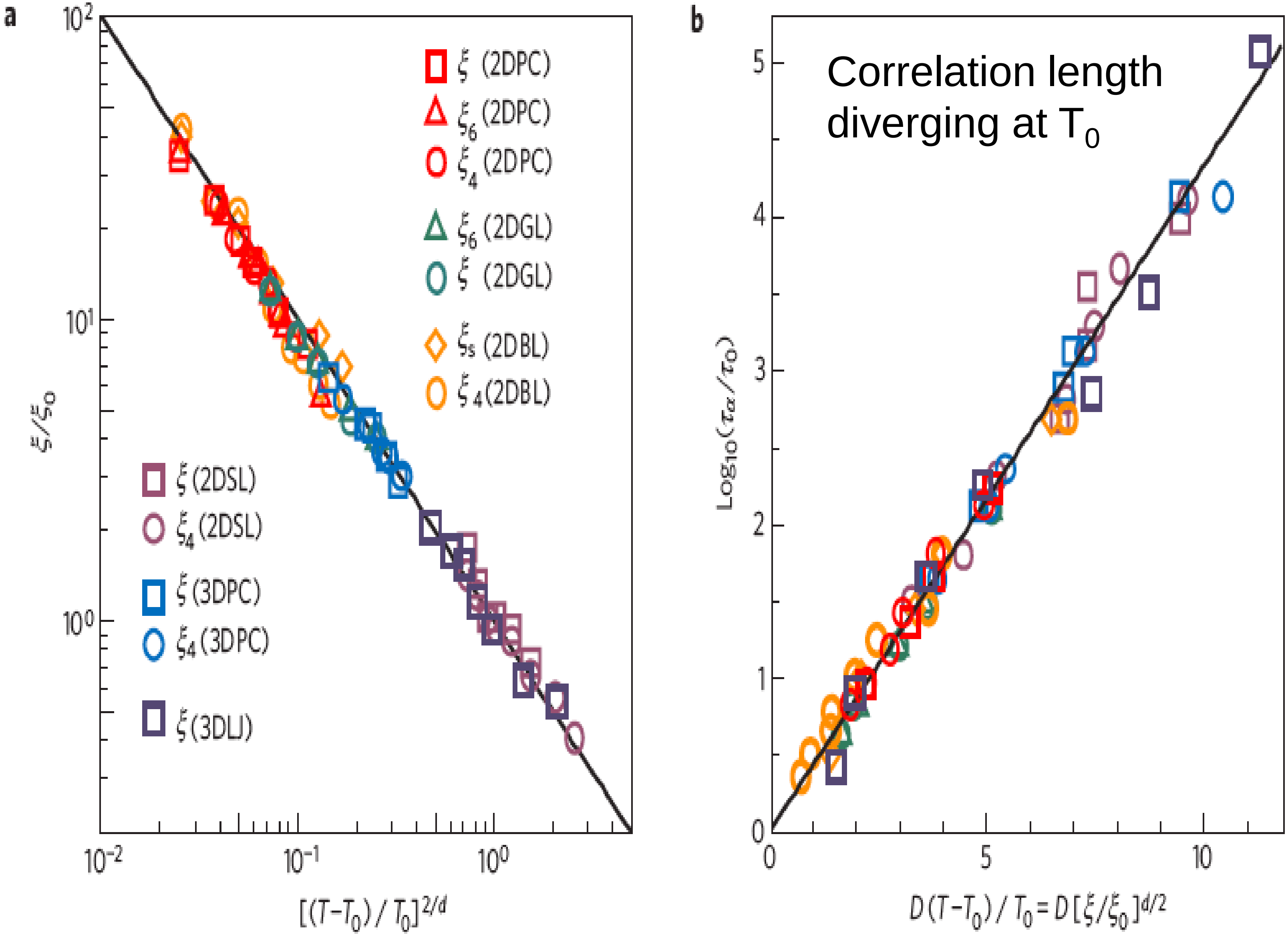
The familiar one



Non-crystallizing polydisperse hard spheres

Tanaka and co., Nature Mater.

(Skip)

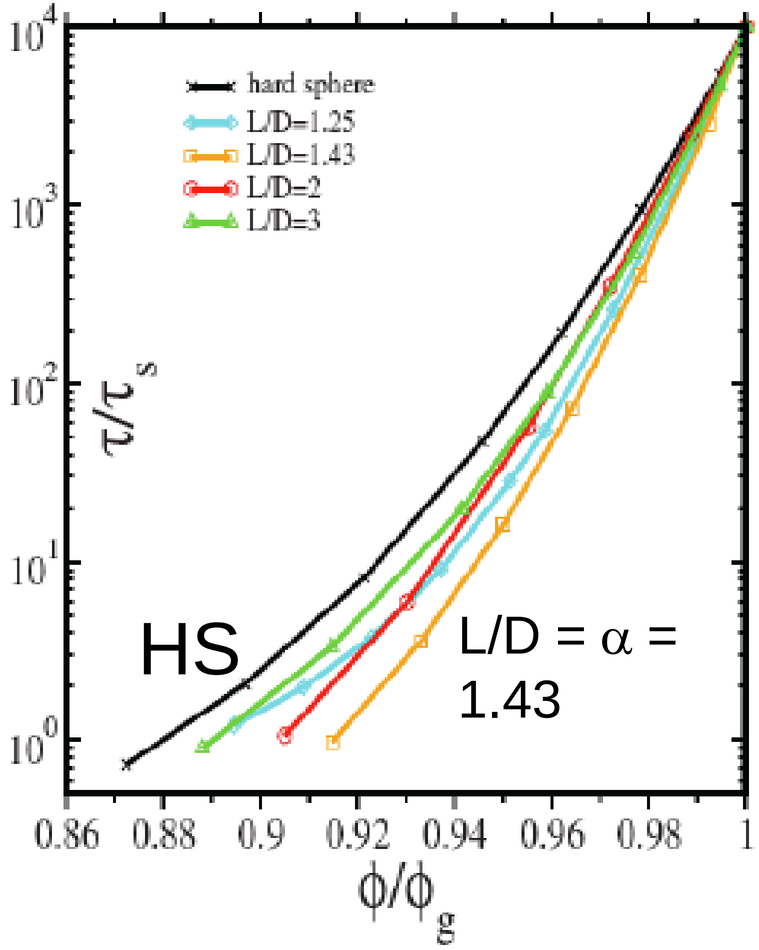


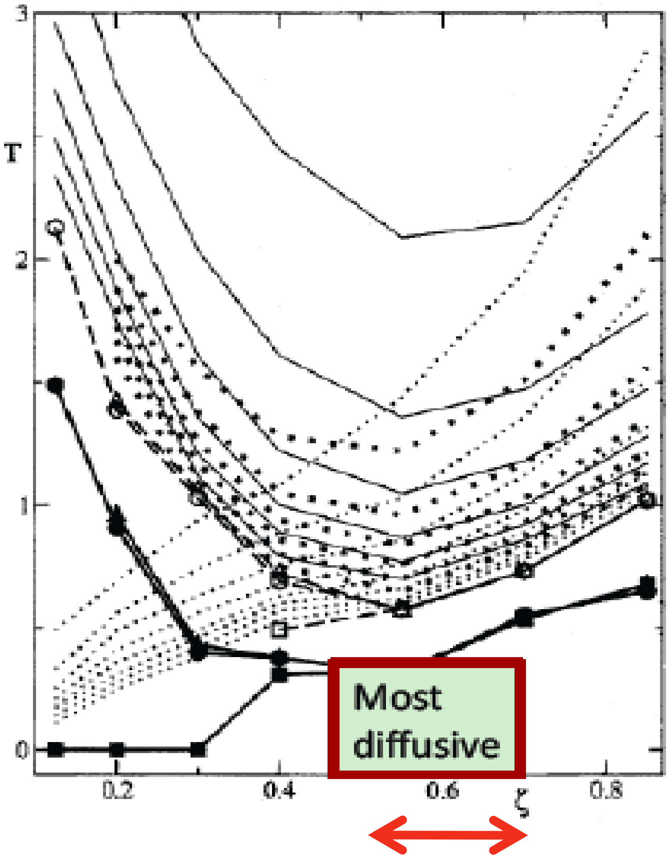
Correlation length diverging at T_0

Asymmetric hard particles

Zhang and Schweitzer, JCPXX, hard rods of different L/D

Sciortino and coworkers hard dumbbells





α = 2.0-1.43

Iso-diffusivity plots

different shapes, Schweitzer et al

244907-5 Influence of colloidal shape on dynamics. II

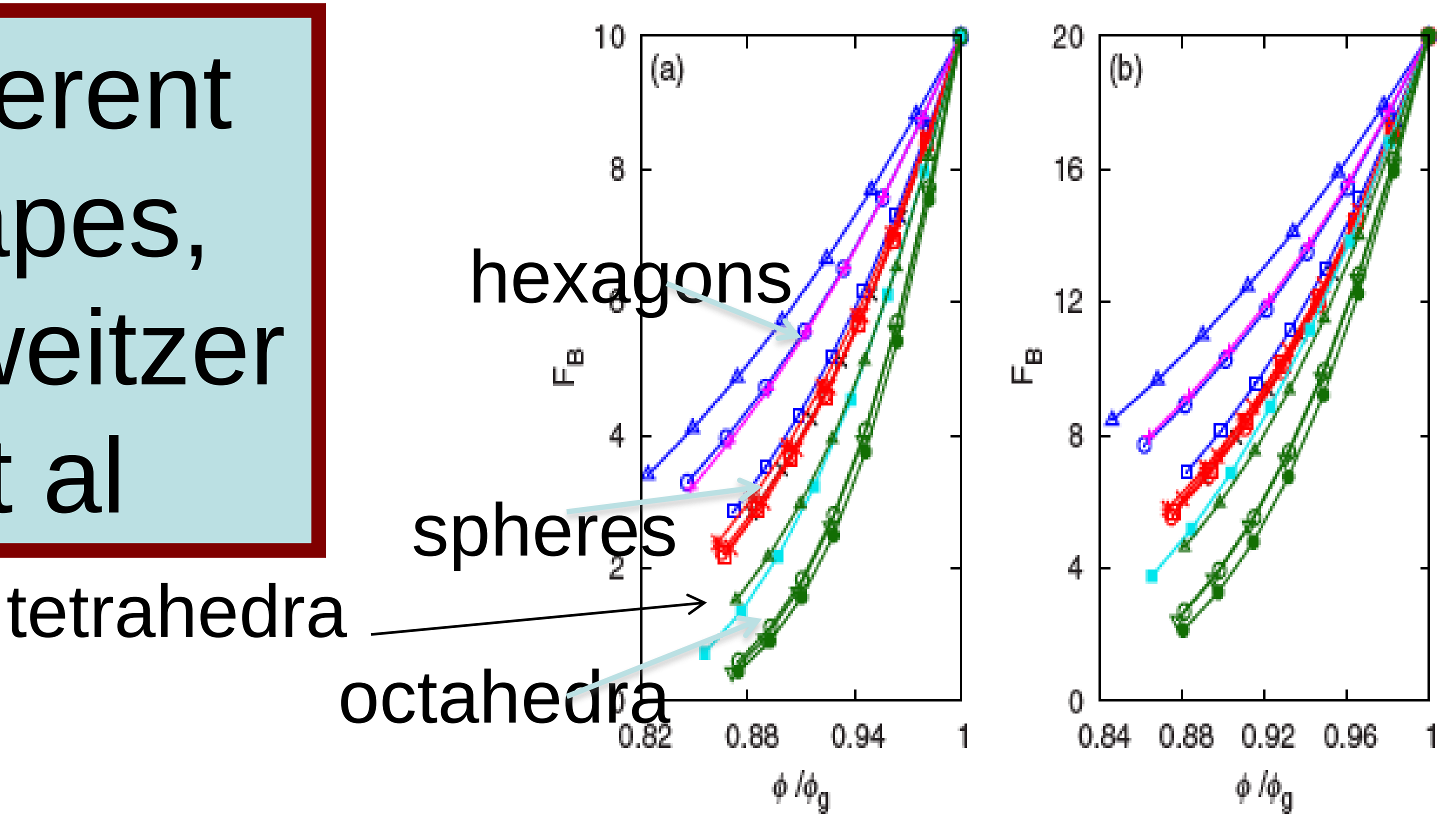
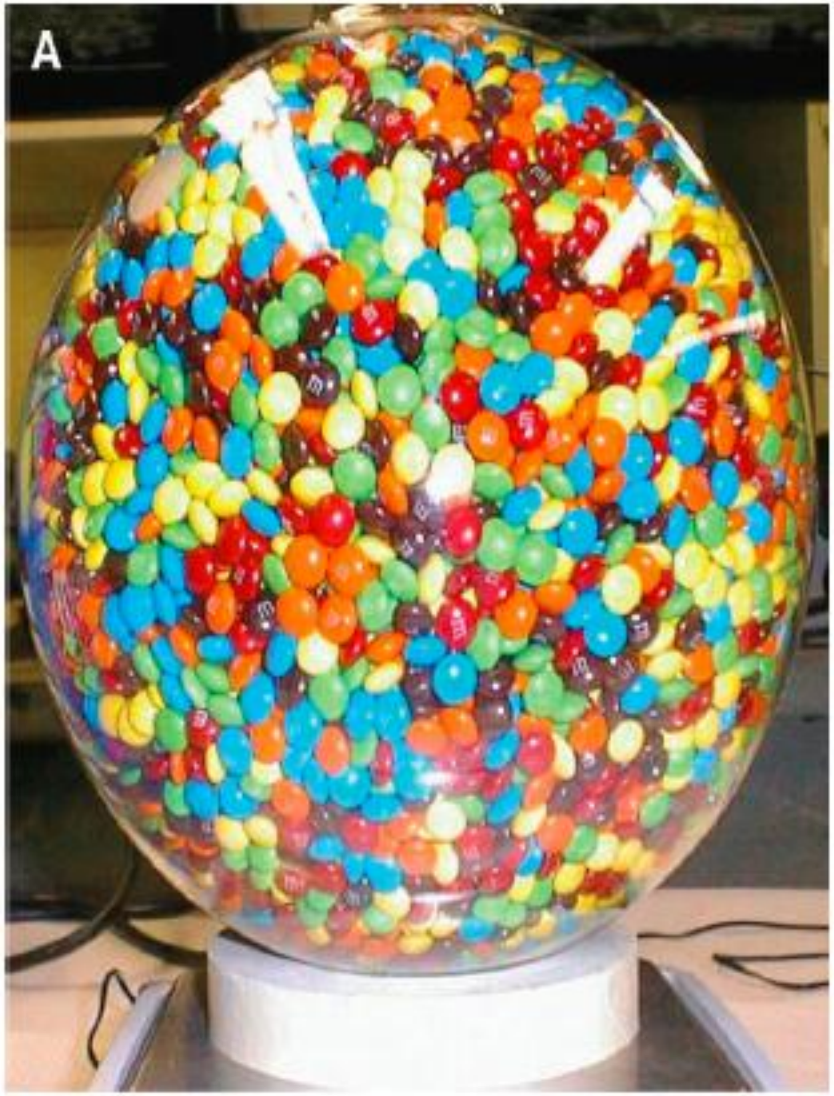


FIG. 7. (Color online) Dynamic fragility plot in the format of barrier height as a function of the scaled variable ϕ/ϕ_g (where ϕ_g is the volume fraction at which $F_B=10kT$ for the left panel and $F_B=20kT$ for the right panel) for the sphere (black crosses), rod of two sites (open, blue squares), rod of six sites (open, blue circles), rod of ten sites (open, blue triangles), hexagon (pink pluses), triangle (red crosses), disk of five sites (open, red squares), disk of seven sites (open, red circles), disk of eight sites (red asterisks), cube (solid, light blue squares), tetrahedron (open, green triangles), octahedron (open, green circles), snub disphenoid (solid, green circles), and gyroelongated square pyramid (open, green up-side-down triangles).

Ellipsoids !!

Donev et al, Science, 2004



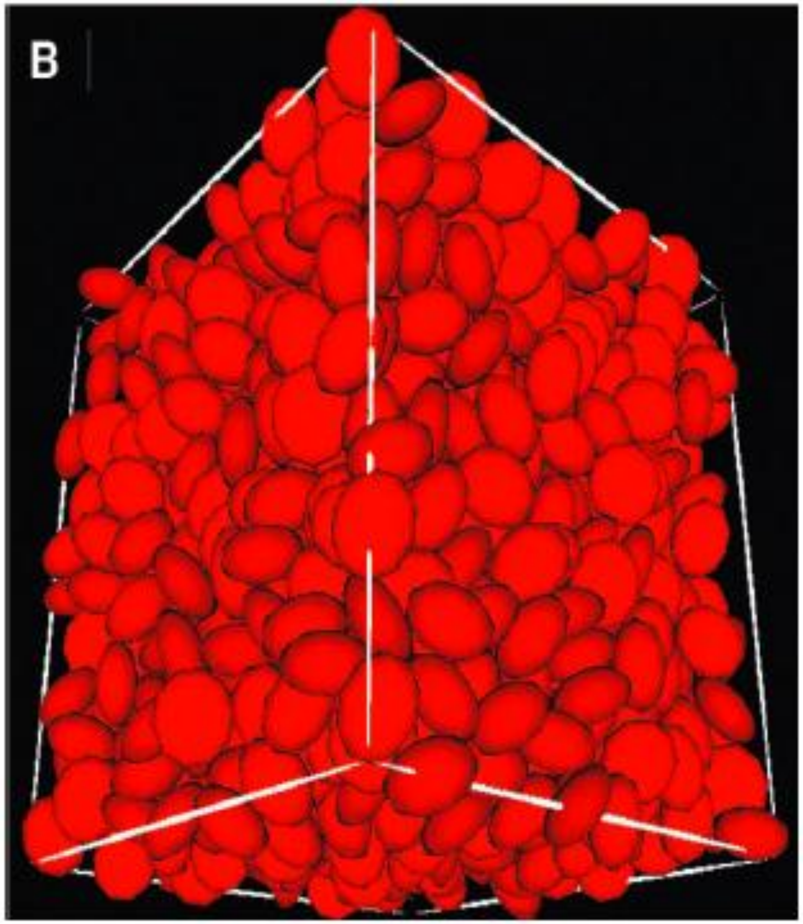
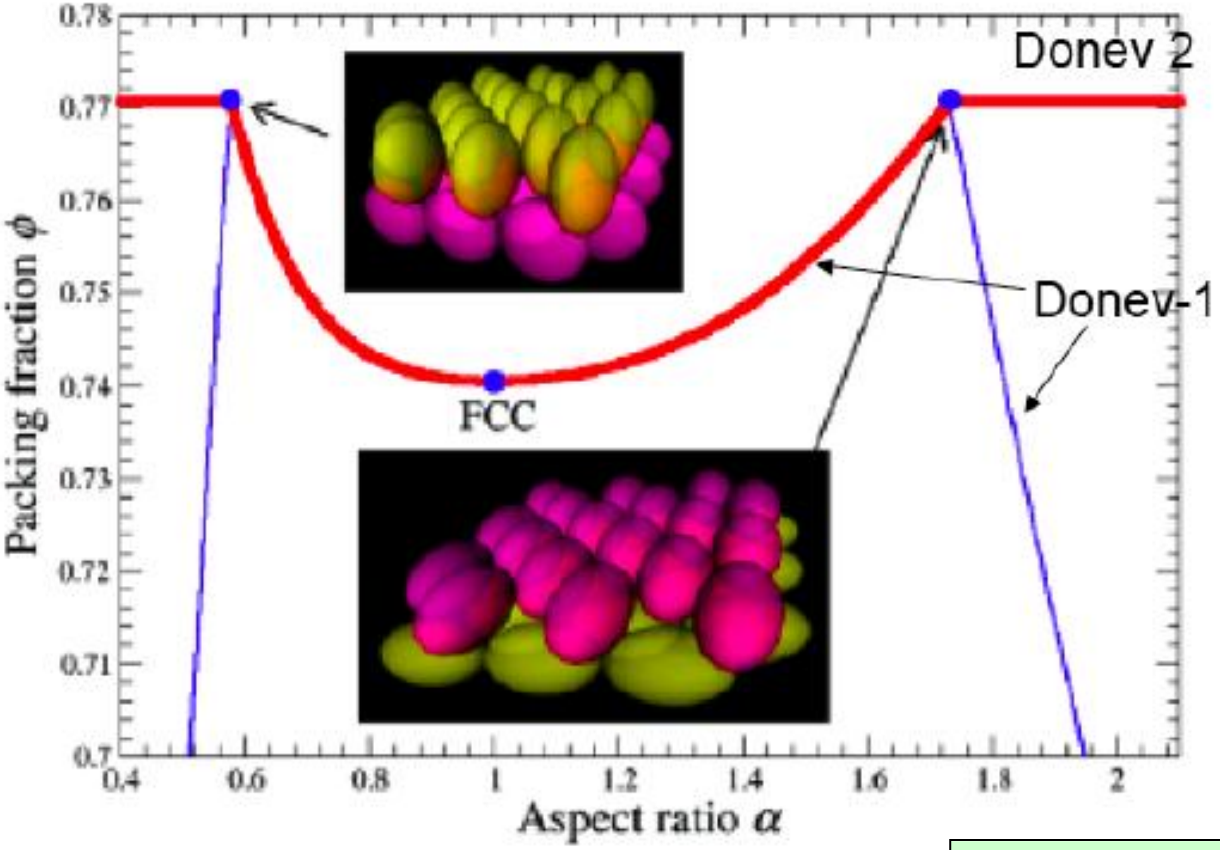


Fig. 1. (**A**) An experimental packing of the regular candies. (**B**) Computer-generated packing of 1000 oblate ellipsoids with $\alpha = 1.9^{-1}$.

SI-2: Hard elllipsoid close packing

Donev et al PRL 2004



Packing efficiency much higher than fcc close packing of spheres

But at α =1.4 doesn’t crystallize

Improving the Density of Jammed Disordered Packings Using Ellipsoids
Aleksandar Donev, *et al.*
Science **303**, 990 (2004);

What does it mean?

The rate of change of the “free” volume with total volume becomes a much sharper function of volume when close packing is enhanced? Entropy, again?

$dS = R\,d\ln V$ (ideal gas)

$$\partial S_c / \partial V = R\partial(V_f/V)/\partial V = R\partial(V_f)/\partial \ln V$$

$(\partial S_c / \partial V)_T$ enhanced for $\alpha = 1.4\text{-}1.5$

Rate of entropy change again?

Tsien Shan Mtns, Western China

Crossed on the flight out to the last University in China before hitting Kazakhstan…. 23,000 ft and still glaciated.

846K

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Let’s put in attractive forces

Study ellipsoids by adaptation of the Gay-Berne model for liquid crystals with

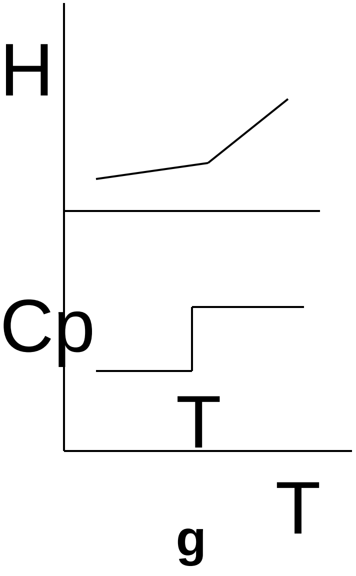
Dmitry Matyushov

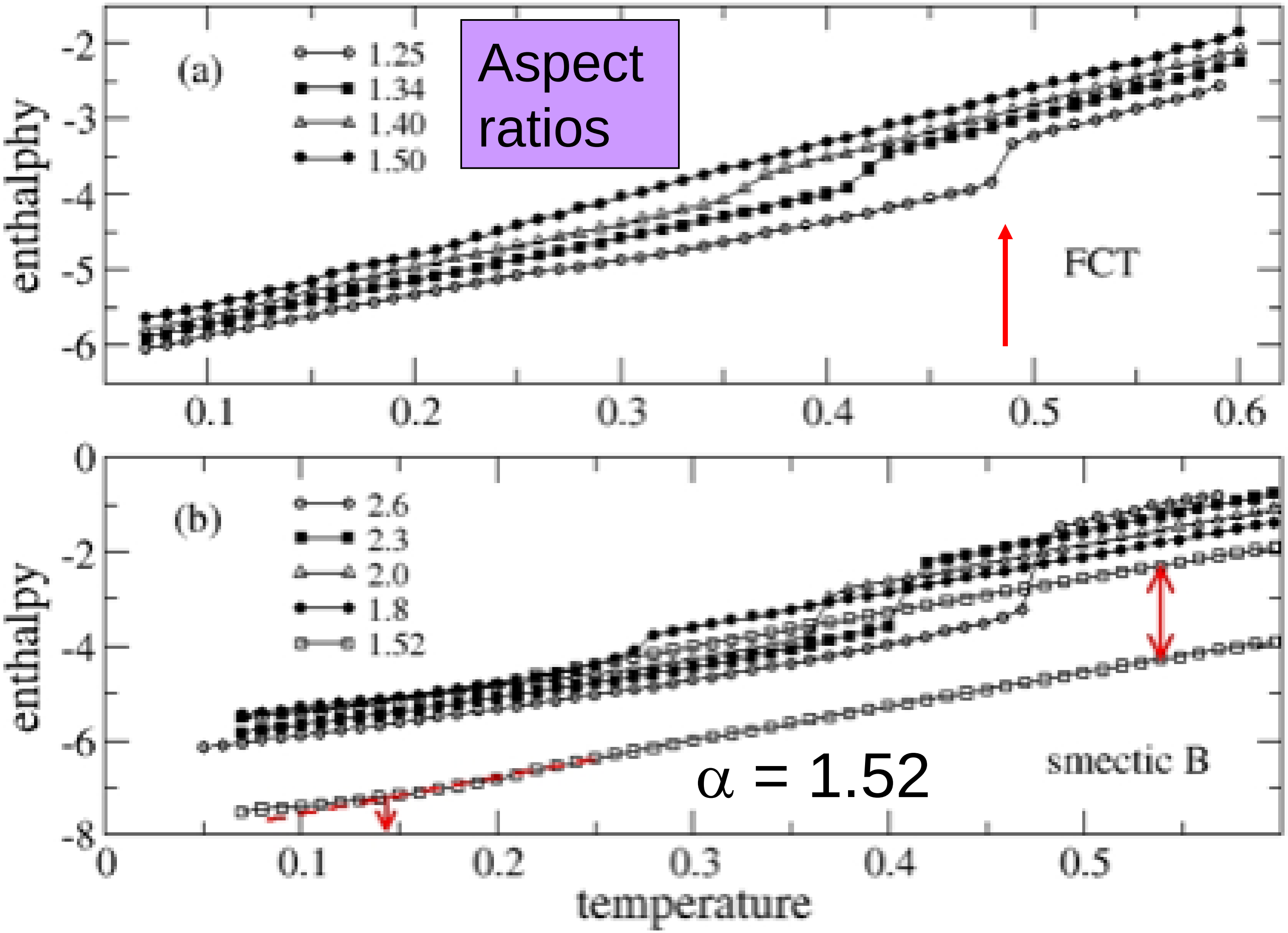
Vitaliy Kapko

Showed how to make E and H a (single parameter) function of aspect ratio

Enthalpy - temperature (melting endotherms)

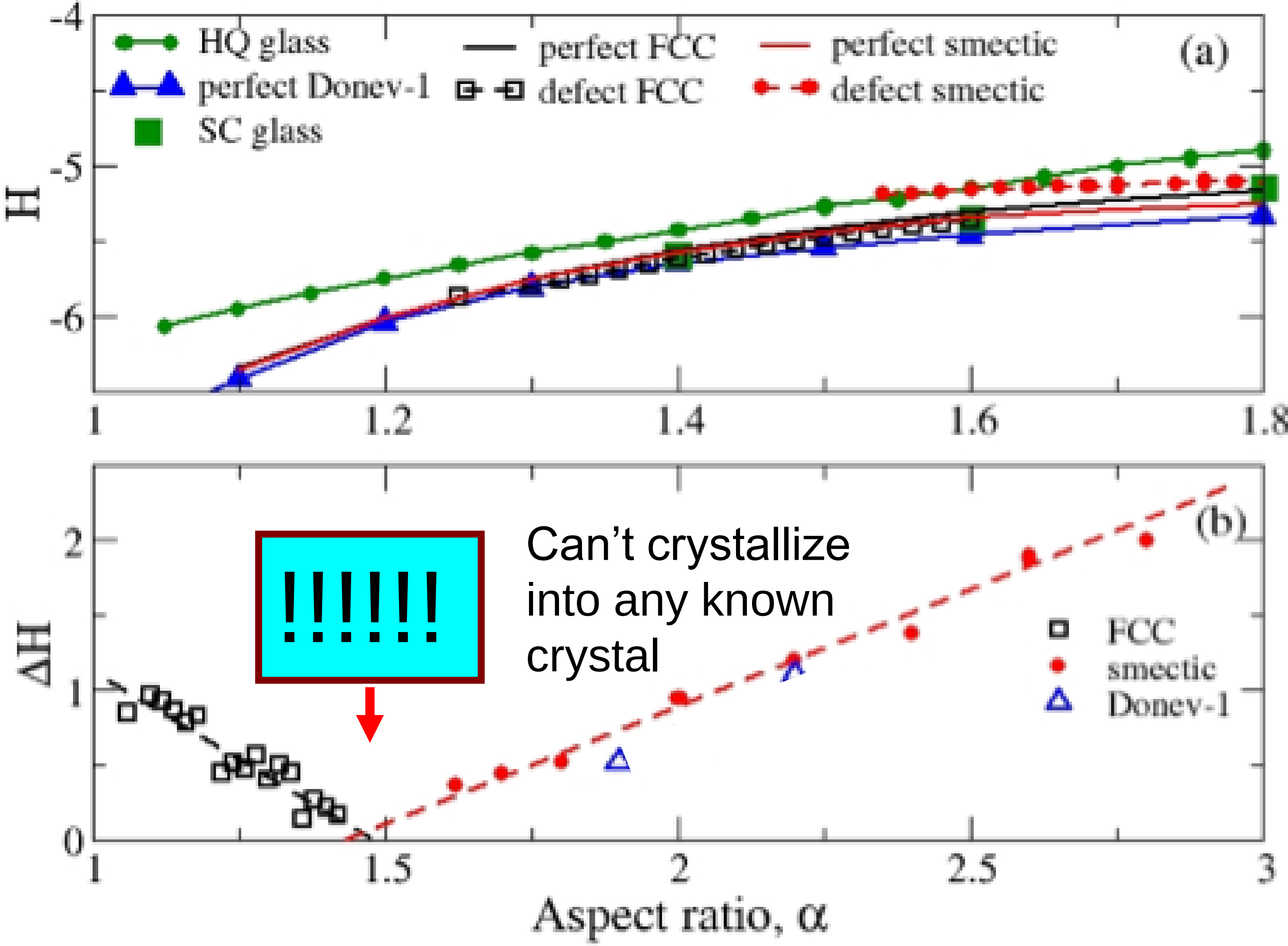
Kapko et al. JPC 2012 (Stanley honor volume)




Aspect ratios

α = 1.52

Energies, at 0 K, of Gay-Berne crystalline phases and glasses



!!!!!!

Can’t crystallize into any known crystal

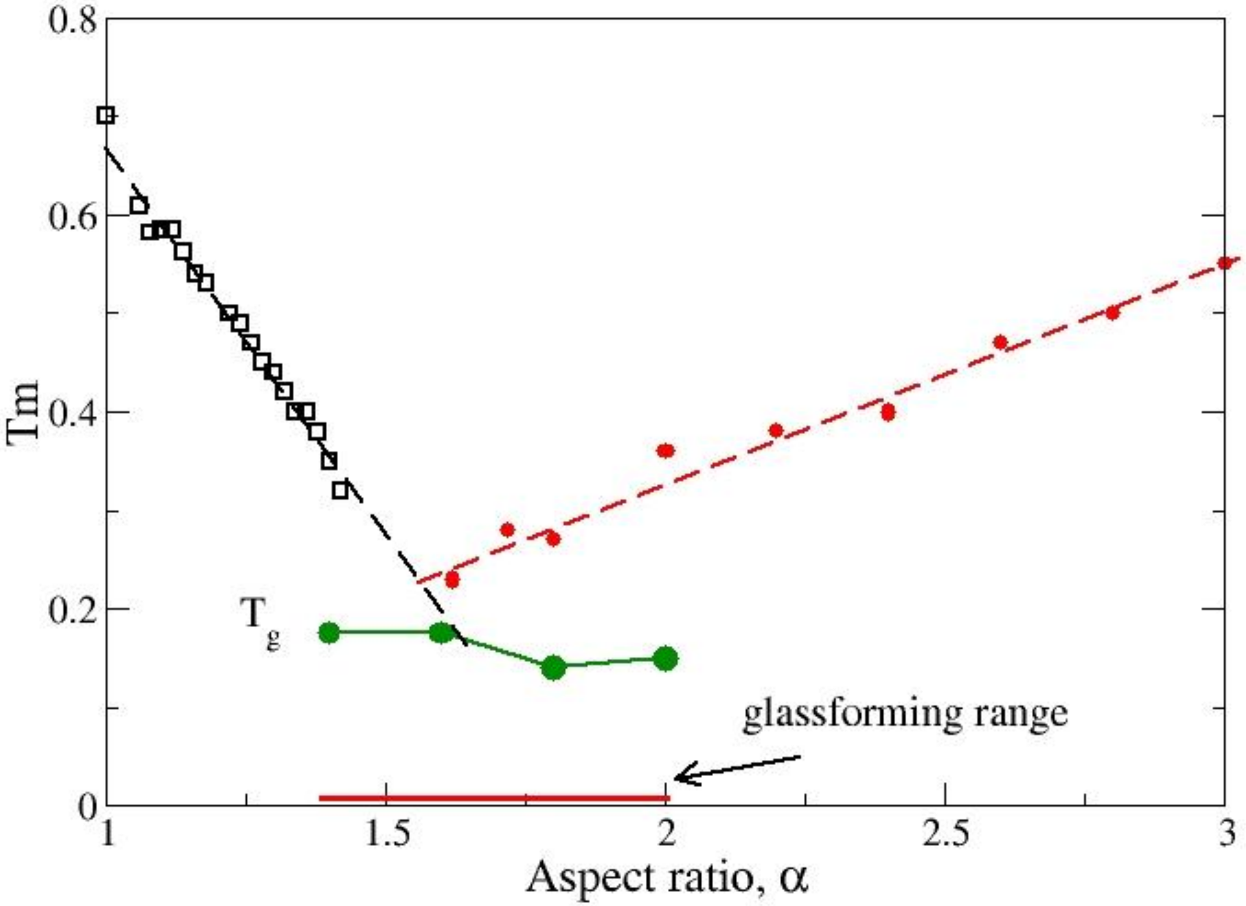
And, heats of fusion of FCT and smecticB phases

Melting points and glass temps in the Gay-Berne model

Paradox: Positive melting point with zero fusion enthalpy

Problem: determining melting points ($G_L = G_C$) when the liquid phase is near a glass transition.

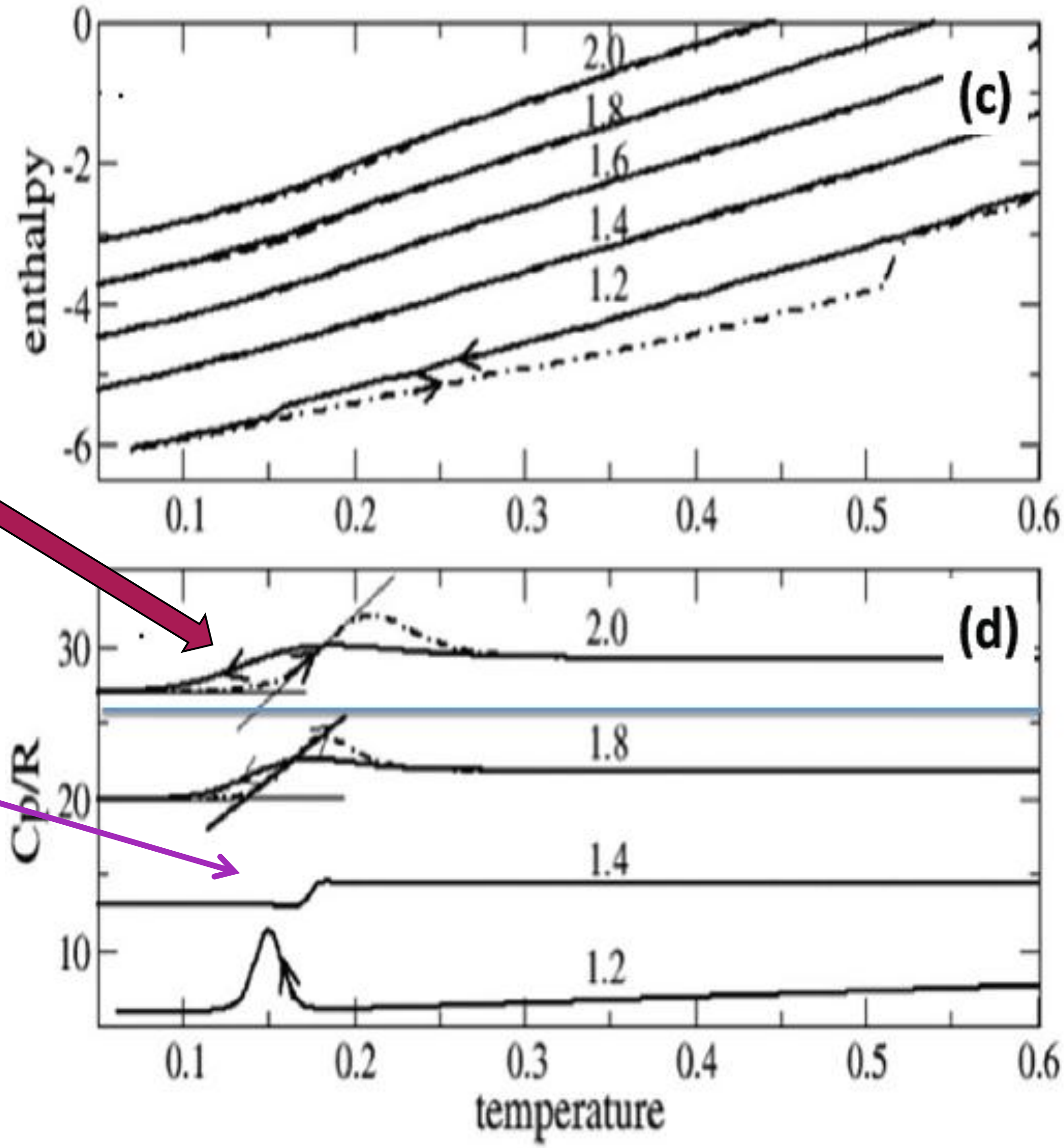
Superheating
The cases of quartz and albite



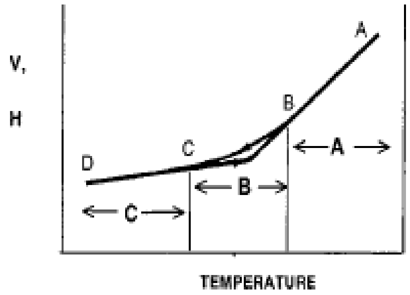
Enthalpy and heat capacity **and fragility**

Continuous cooling, followed heating at the same rate

At aspect ratio, $\alpha = 1.4 - 1.5$, the hysterisis disappears



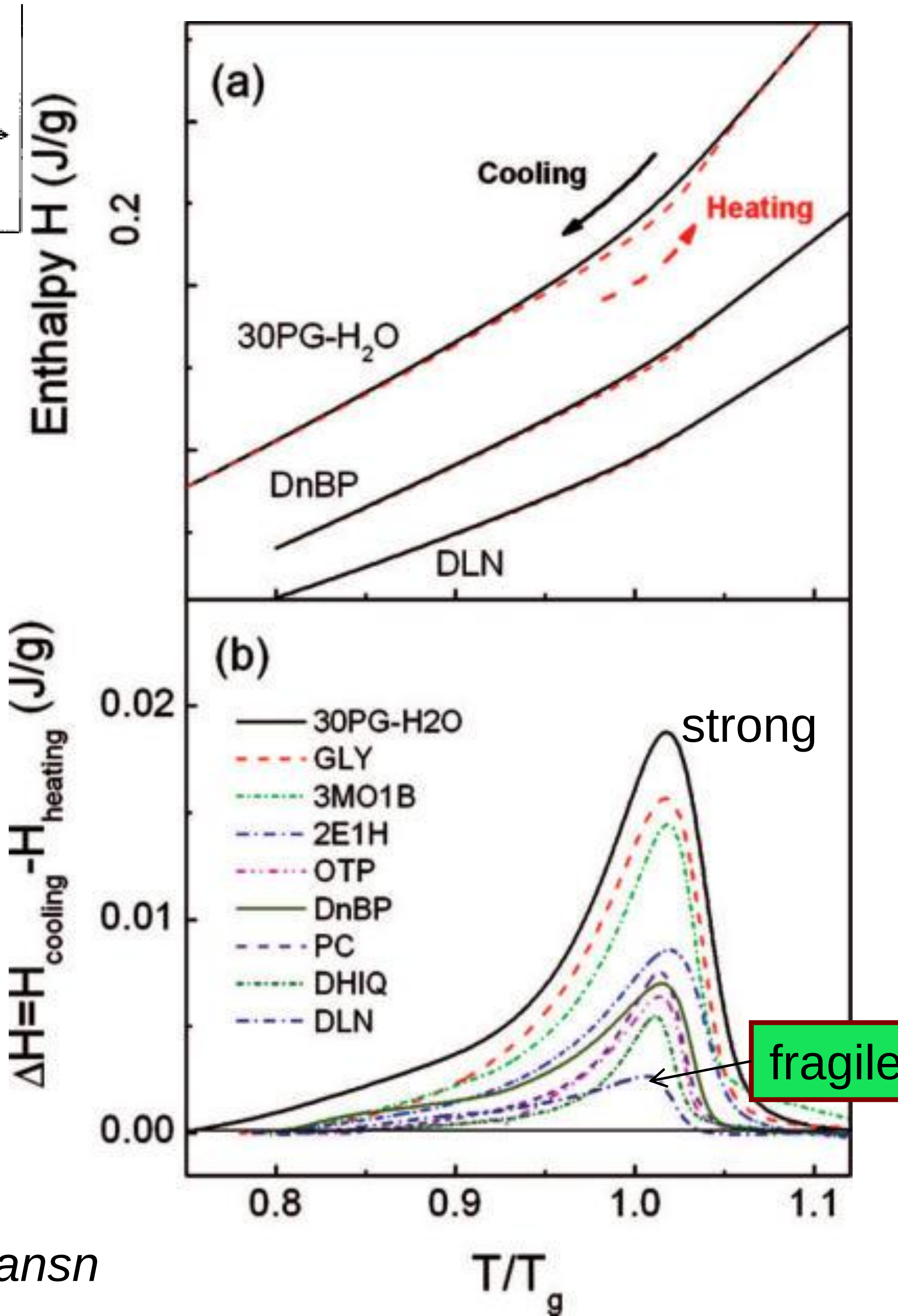
Hysterisis peaks and fragility



Work of Limin Wang
JPC 2002

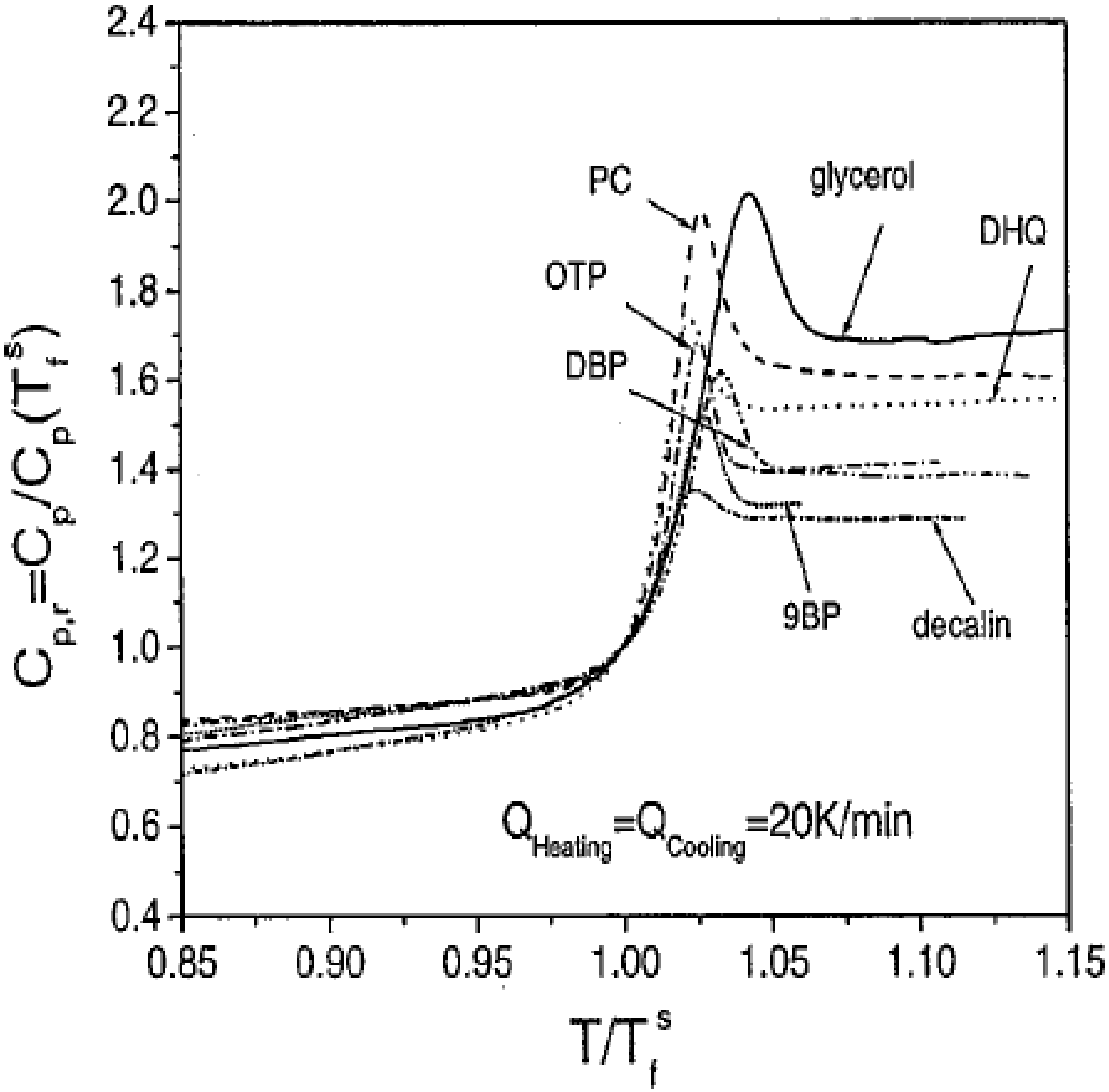
Where the hysterisis disappears is where the system is most fragile …..(α = 1.4 - 1.5 for vdW ellipsoids)

Infinite fragility = Ehrenfest 2nd order transn



Smallest ΔC_p has largest fragility

Work of Limin Wang
JCP 2002



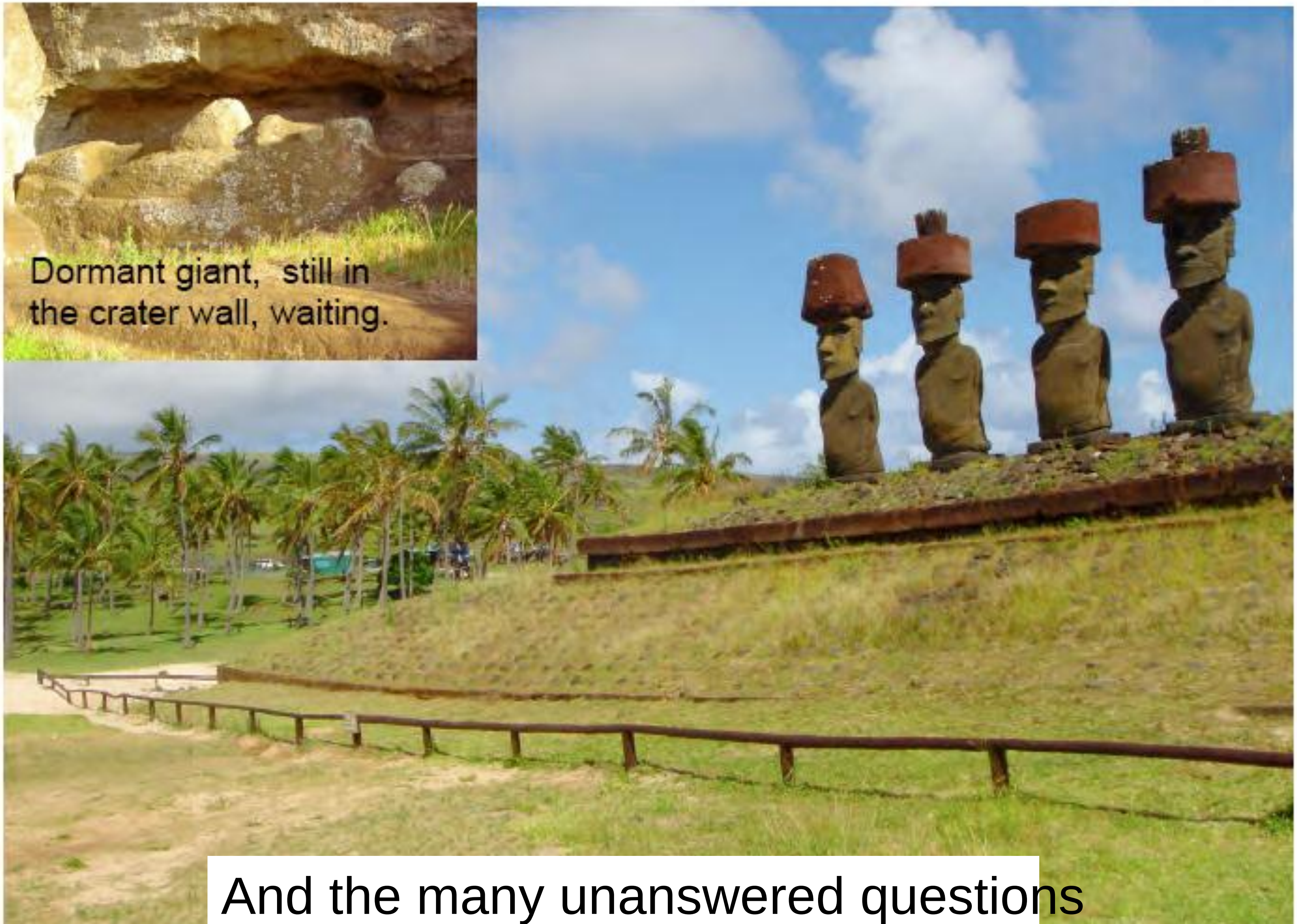
Paradoxical ?

resolved by S_{ex} scaling, as $S_{ex}(T_g)$ is also smallest for the most fragile case

Can it really be that, for ellipsoids at least, the best glassformer is the most fragile? Runs counter to what Lindsay showed us yesterday for chalcogenides.

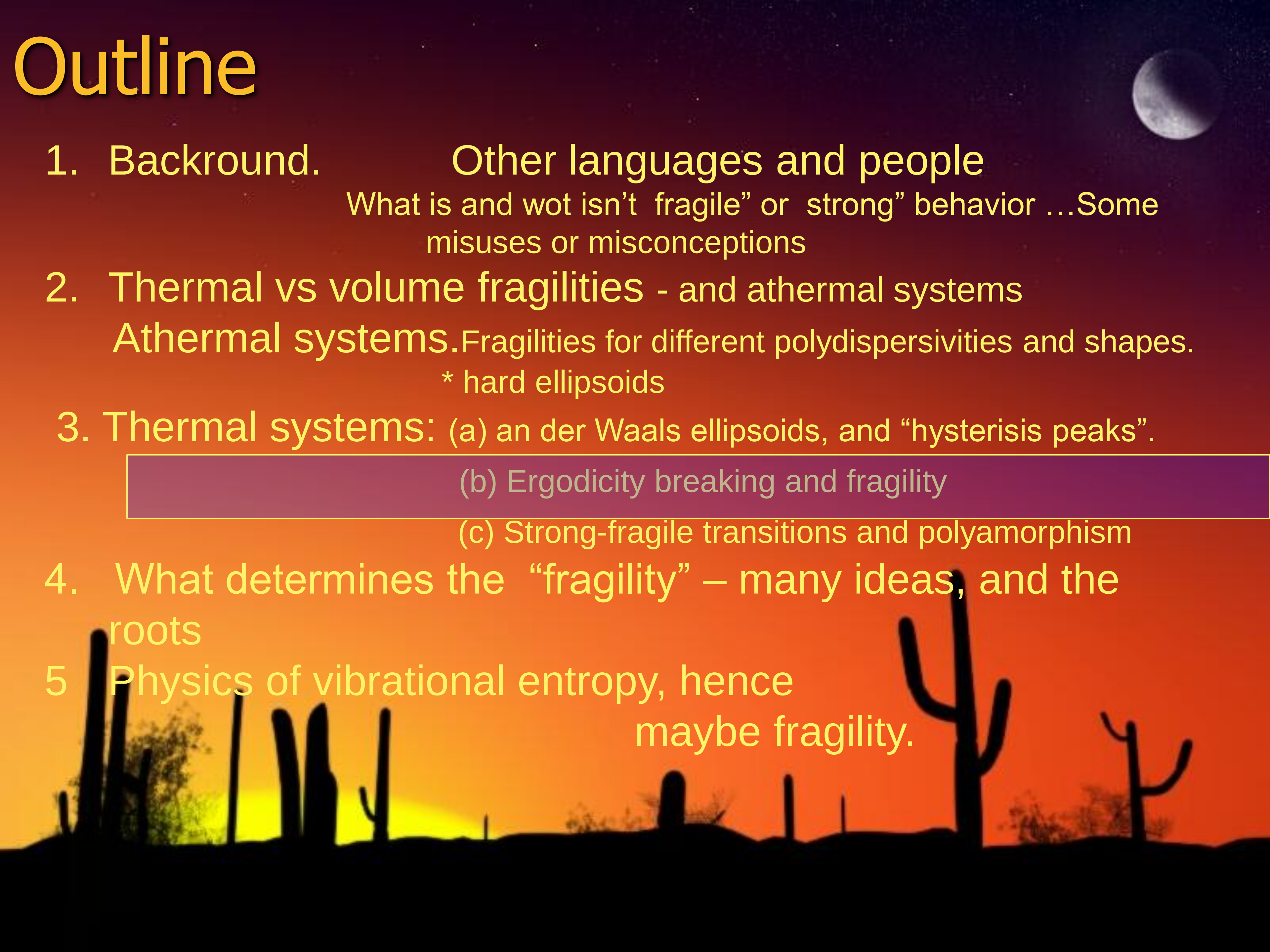
(More in Hyderabad)

Silent watch over Easter Island



Dormant giant, still in the crater wall, waiting.

And the many unanswered questions



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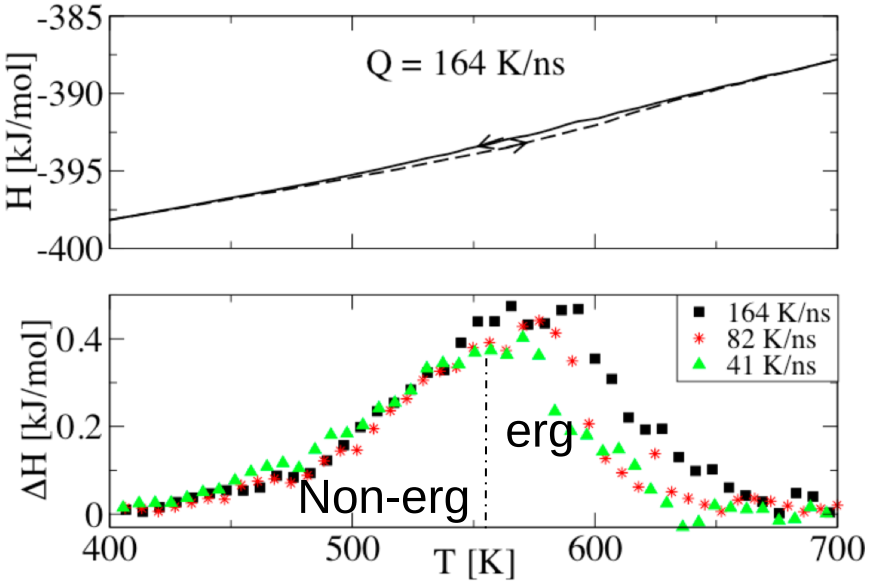
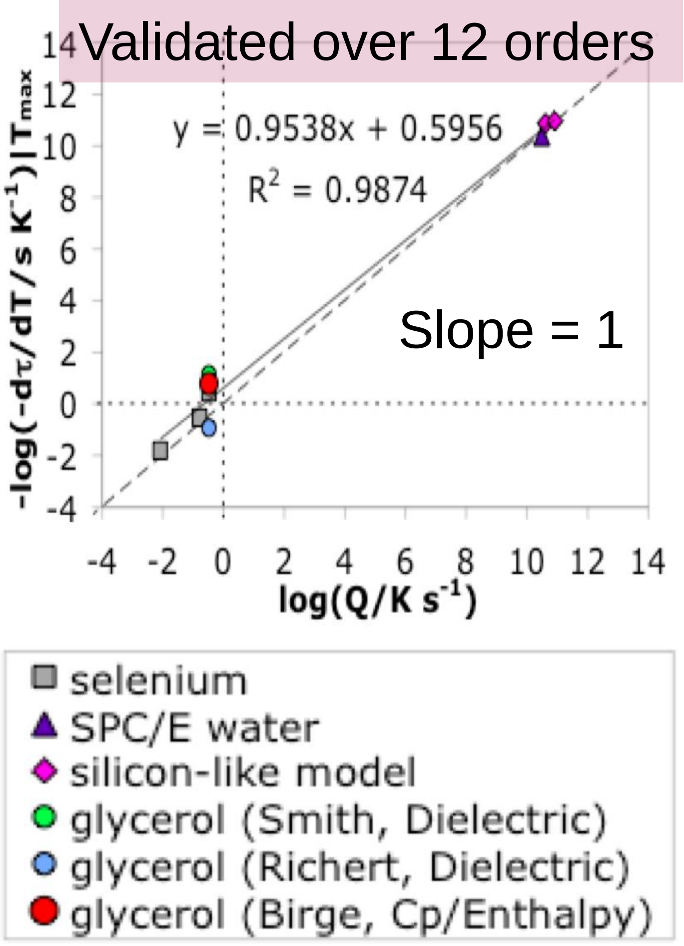
Ergodicity-breaking and the hysterisis peak

At hysterisis peak temperature (for Q- = Q+) we have the condition

$$dT/dt \cdot d(tau)/dT \approx 1.0$$




Validated over 12 orders

Slope = 1

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Water and silicon are most investigated cases, phosphorus (white --> red) is least controversial.

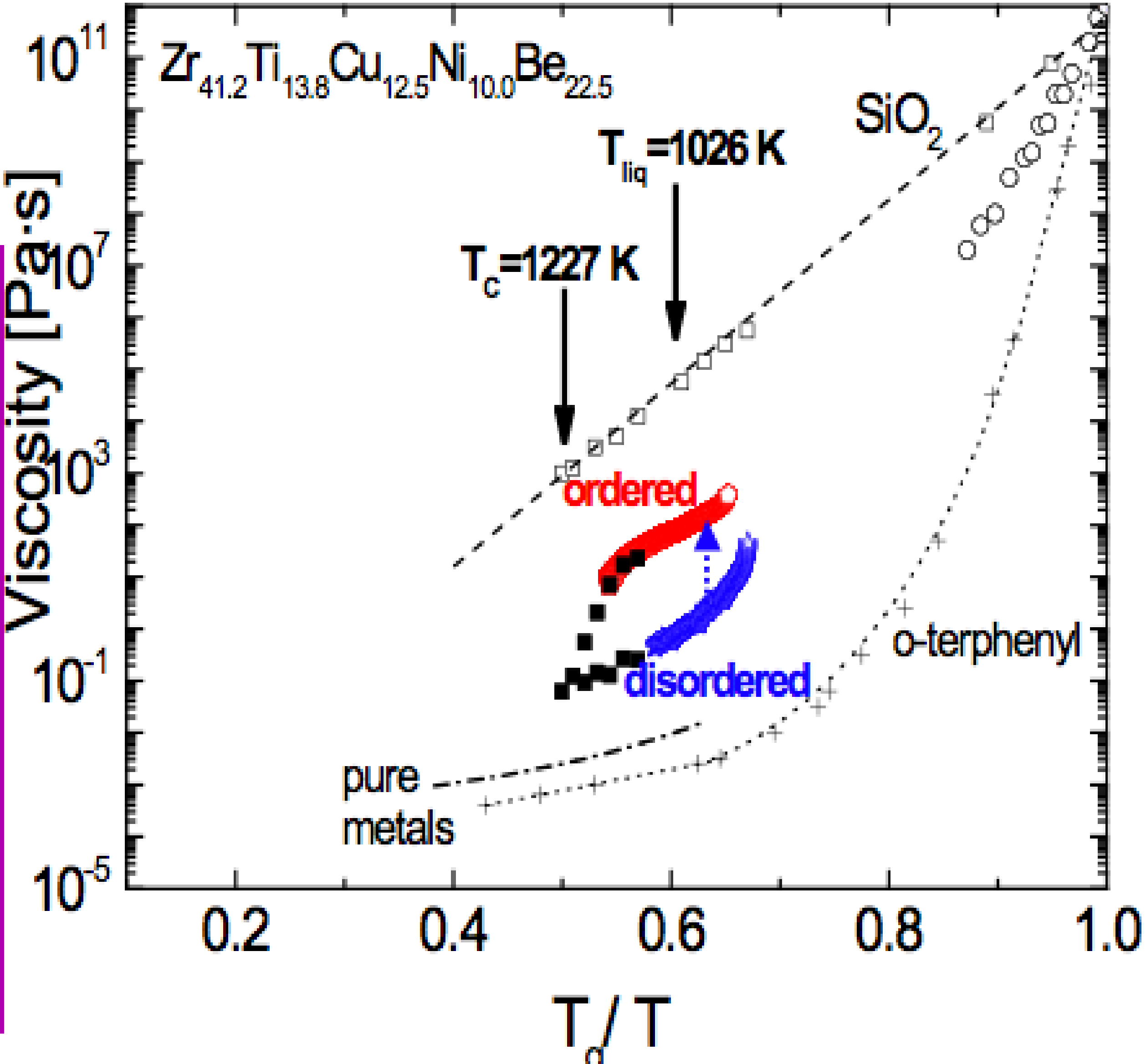
(Skip)

Real liquid metals: Reversible Complexity

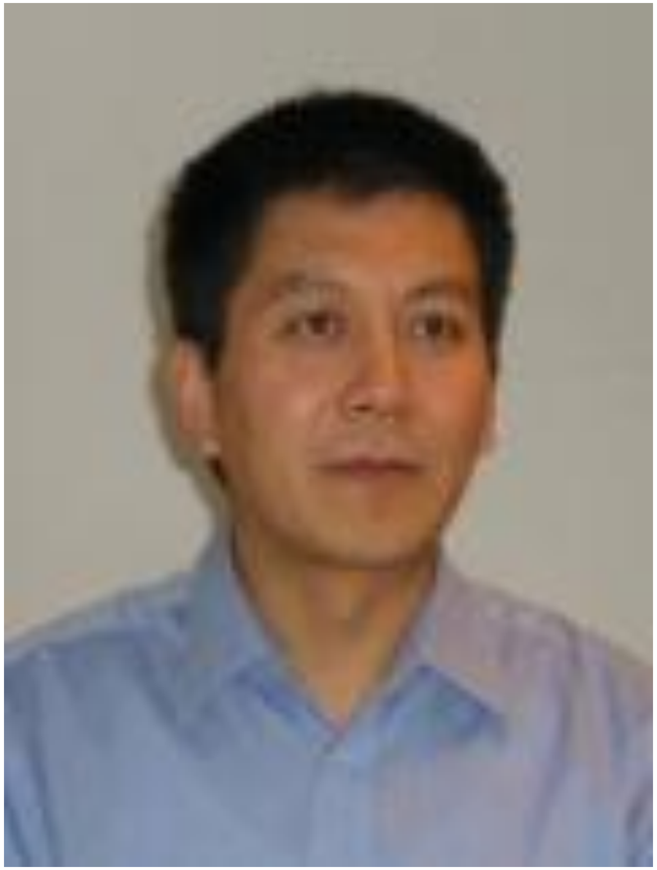
From Way et al
((Ralph Busch group)

Acta Materialia
55 (2007) 2977–

A good example of how structural complexity is revealed more sensitively in transport properties than in thermodynamic properties.. Because…
(very recent)



And then the big SURPRISE



Yuanzheng Yue

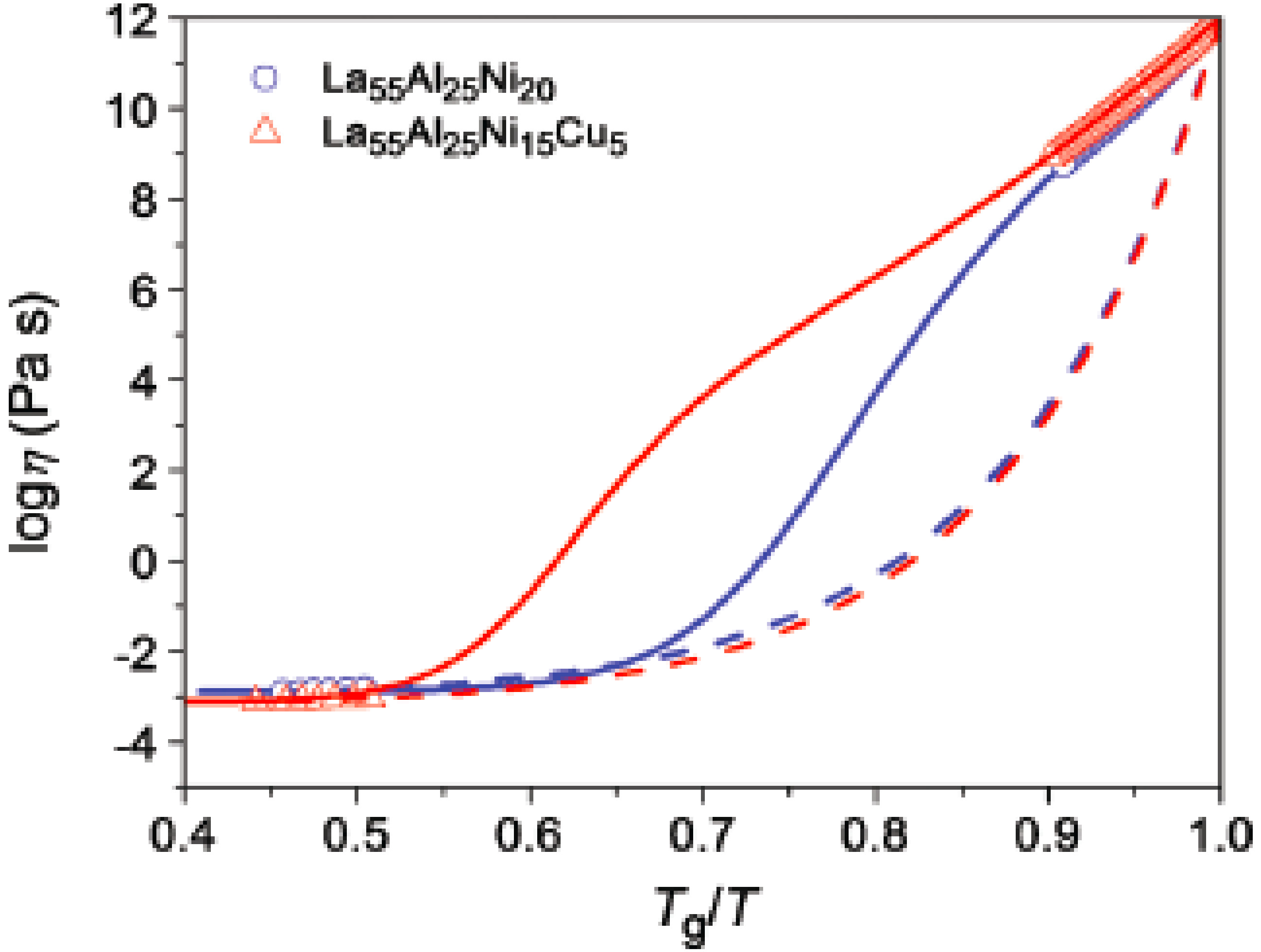
In Rome 2009,
published JCP 2010

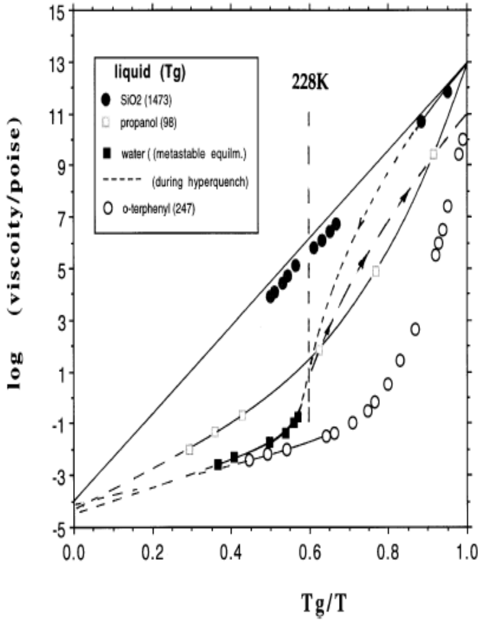
And earlier in Crete, where
he saved me a lot of time

THE JOURNAL OF CHEMICAL PHYSICS 133, 014508 (2010)

Fragile-to-strong transition in metallic glass-forming liqu

Chunzhi Zhang,[1] Lina Hu,[1] Yuanzheng Yue,[1,2,a)] and John C. Mauro[3]





The
rumor
about i-
phone

Rumor: **iPhone** 5 Will Feature "**Metallic Glass**" | Gadget News and ...

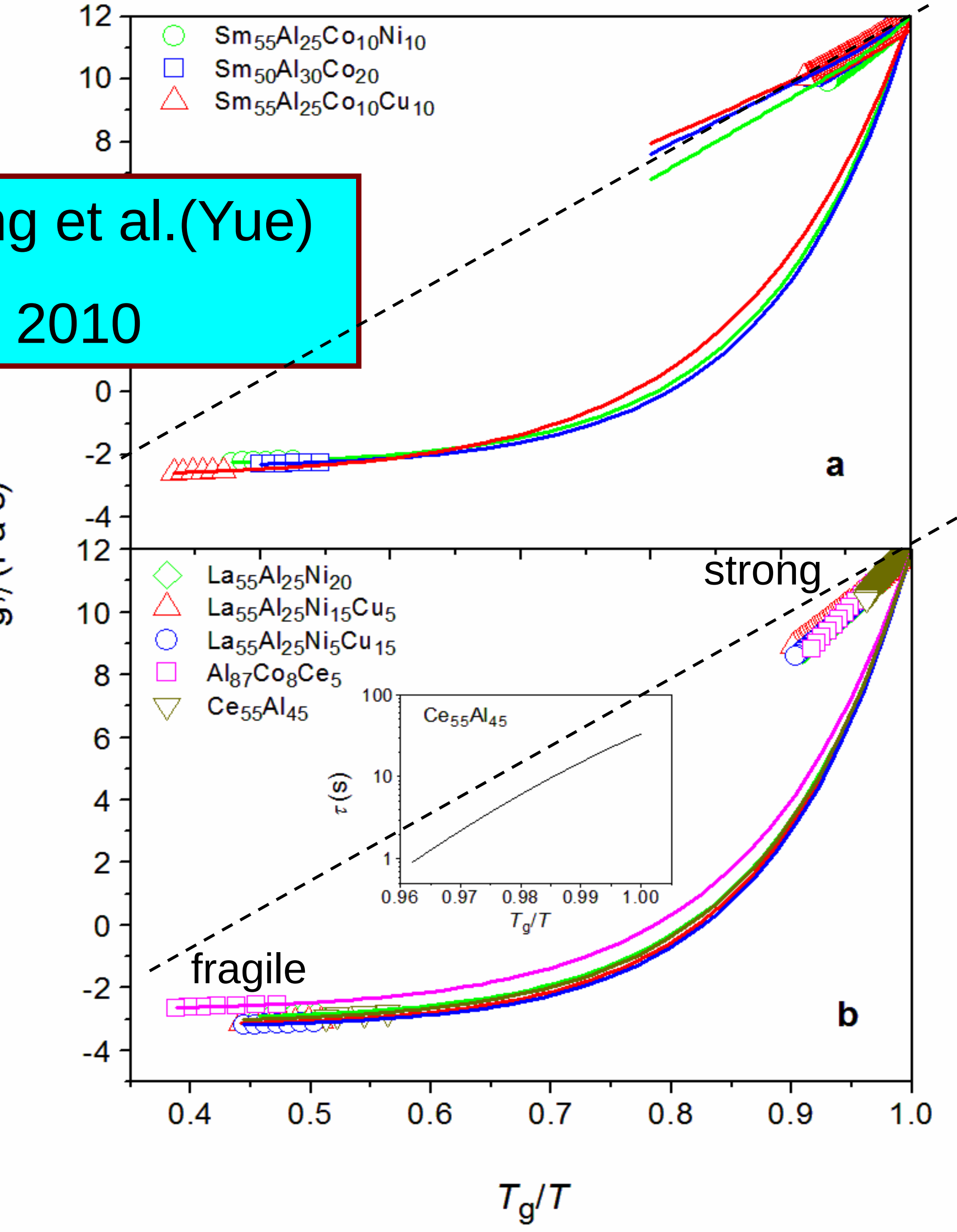
www.gadget.com/2012/.../**rumor-iphone**-5-will-feature-**metallic-glass**...

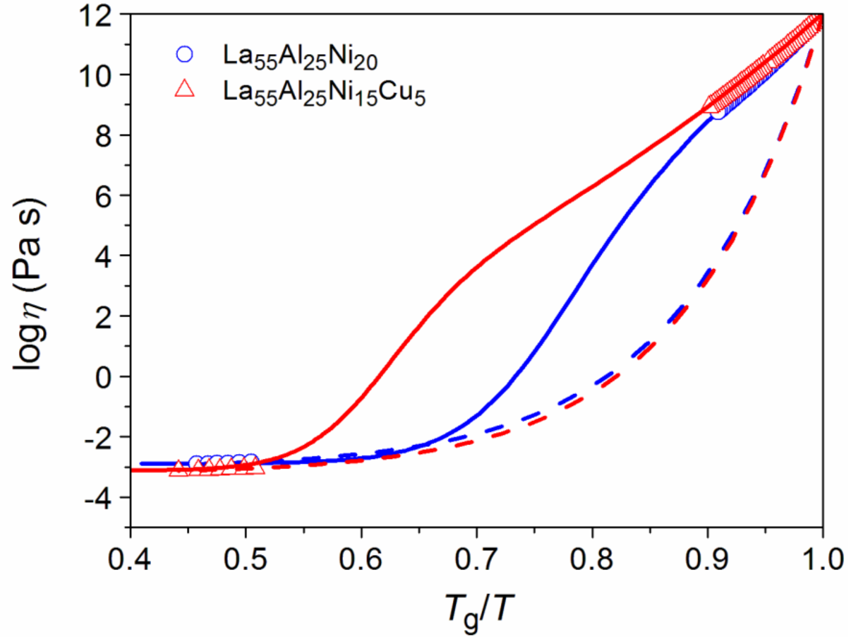
Apr 20, 2012 – Another round of **iPhone** 5 **rumors** surfaced. If talkative Korean sources are to believe, the next **iPhone** will be cased in "liquidmetal" and that it ...

Fragile-to-strong transition in metallic glassformers

Zhang et al.(Yue)

JCP 2010





Water and Silicon: brothers

Games with the Stillinger-Weber potential

Lingering doubts removed in 2003 by

Liquid–liquid phase transition in supercooled silicon

SRIKANTH SASTRY*[1] AND C. AUSTEN ANGELL[2]

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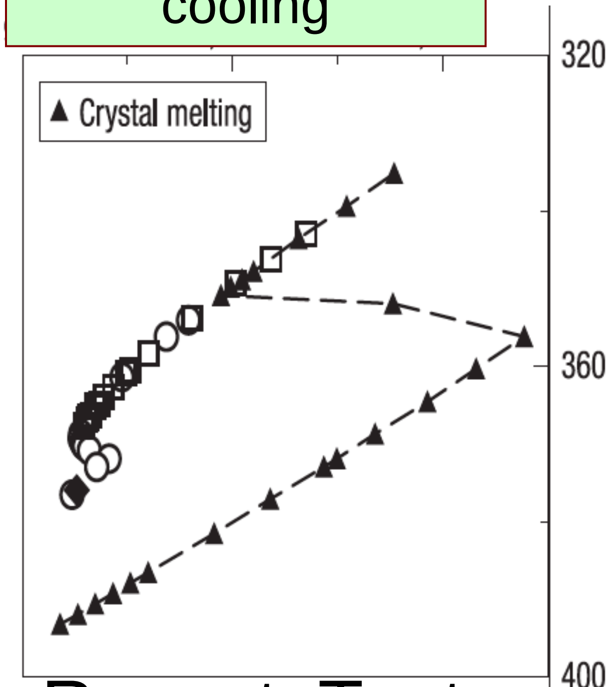
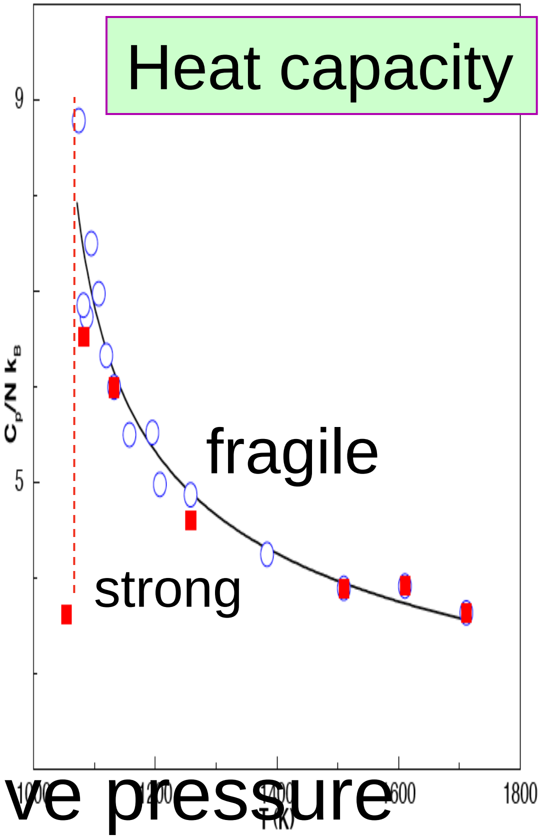
NATURE MATERIALS, November, 2003

Constant enthalpy cooling



Heat capacity

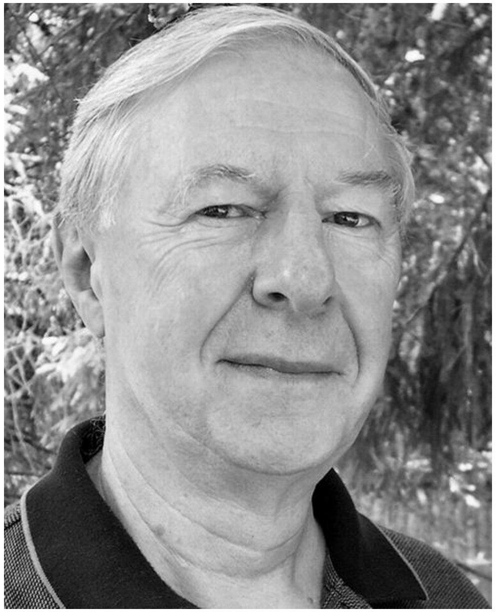


Recent: T_c at negative pressure

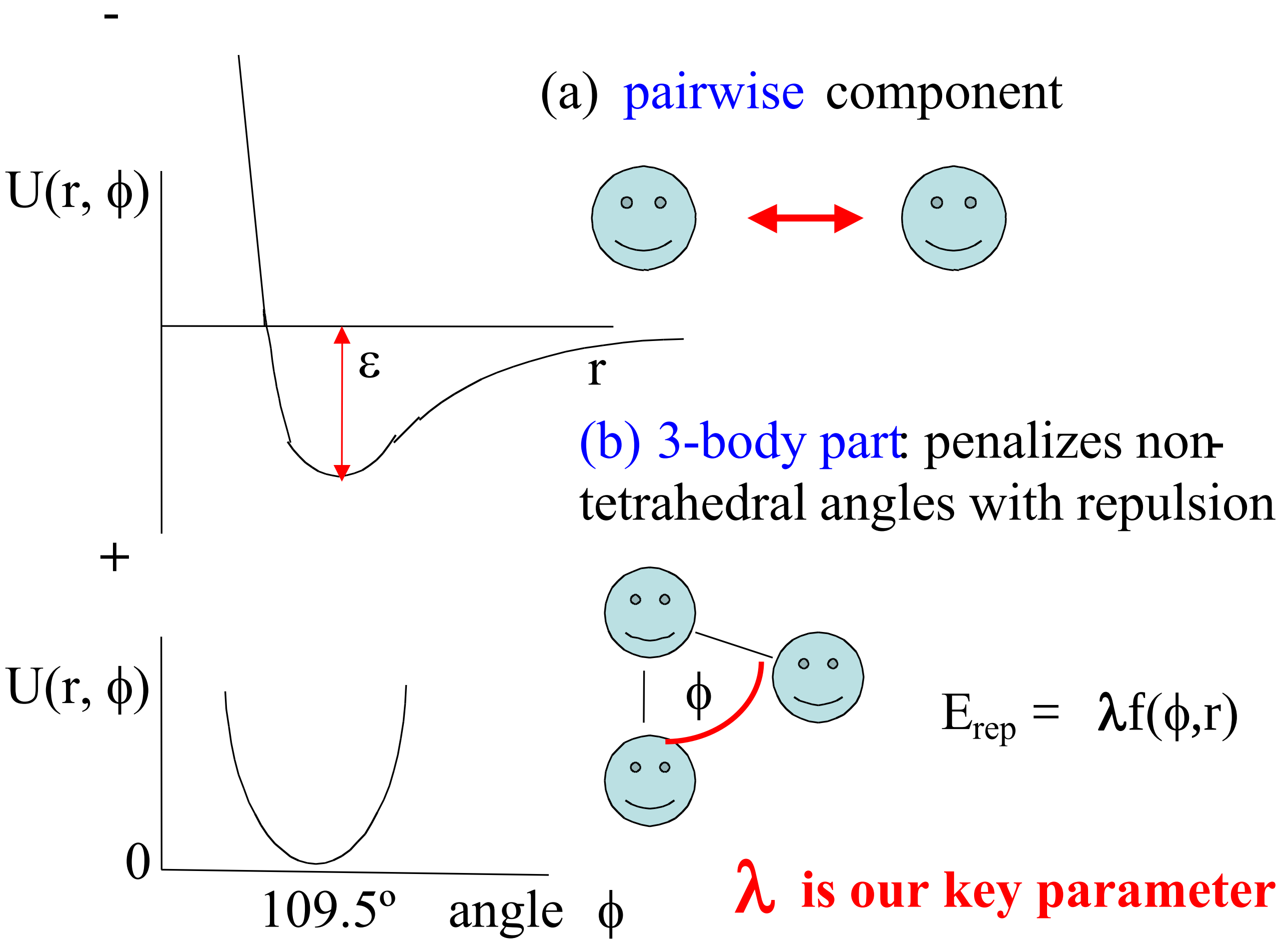
(Theoret. Physics)
J. Nehru Institute,
Bangalore, India

Stillinger-Weber potential and and potential tuning

The Stillinger Weber potential



Collaborated, with Rahman on water simulations



(a) pairwise component

(b) 3-body part: penalizes non-tetrahedral angles with repulsion

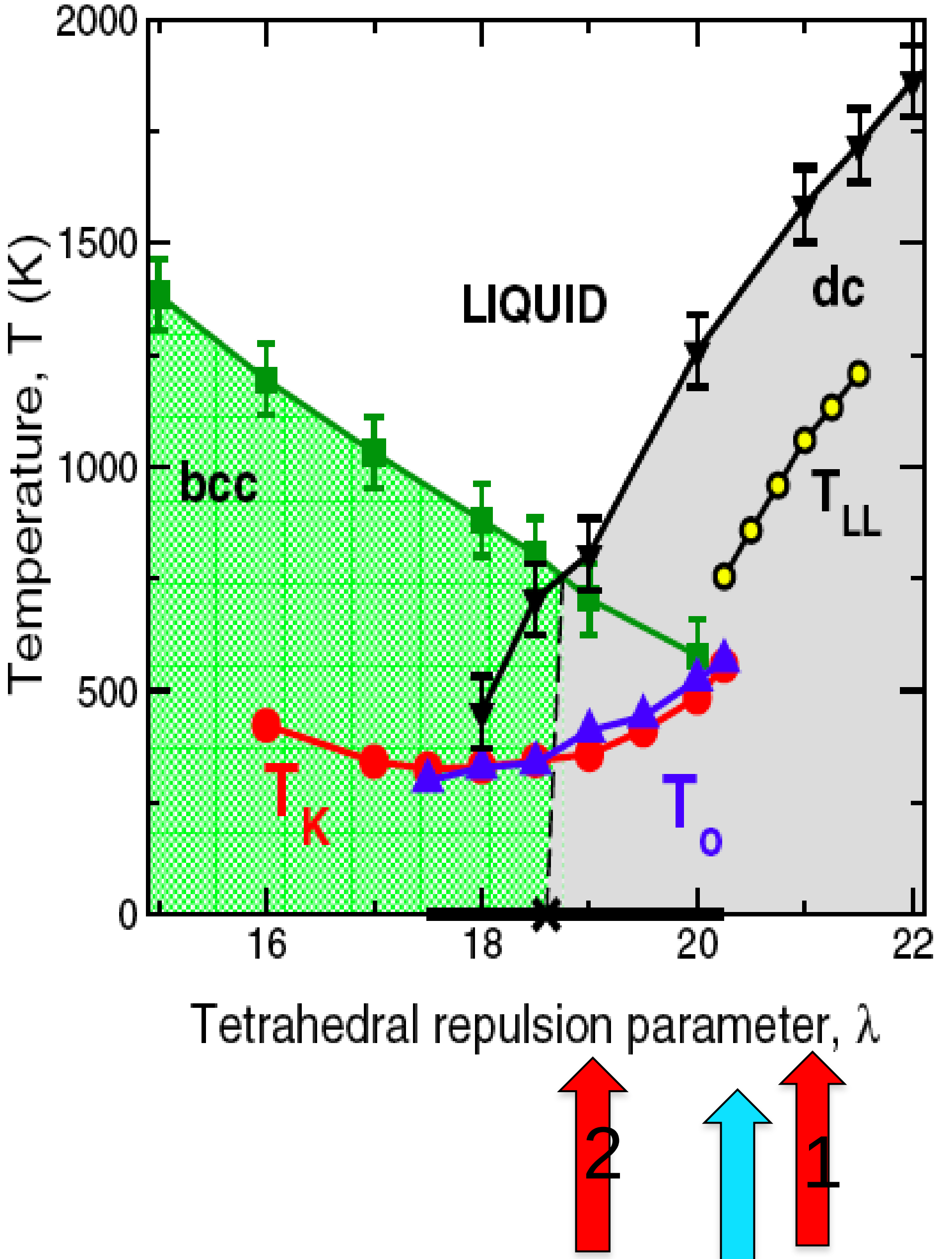
$E_{rep} = \lambda f(\phi, r)$

λ is our key parameter

EVERY λ CHOICE IS A NEW ELEMENT

N.B. So long as the angle ϕ remains the tetrahedral angle, the energy is independent of λ - so **diamond cubic crystal** lattice energy ≠ f(λ)

Potential tuning MD on mS-W with Vale, Sri



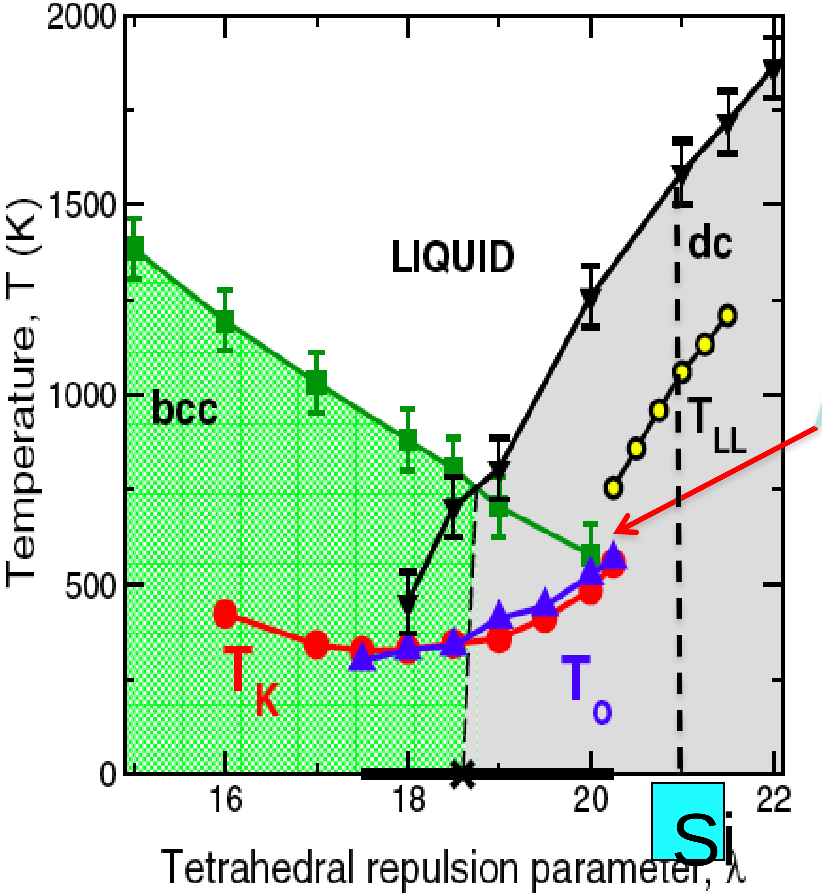
1 **Earlier,** Sastry and Angell studied mS-W at λ = 21 for phase transitions (***more recently, Vashisht & Sastry find LL critical point at -0.6 GPa***)

2. **Later,** Kapko, Matyushov and Angell studied the mS-W at λ = 19, for glassforming properties

3. Now how about at λ = 20.5 for *critical phenomena ot ZERO pressure* ??? Look at the heat capacities vs at λ = 20.5

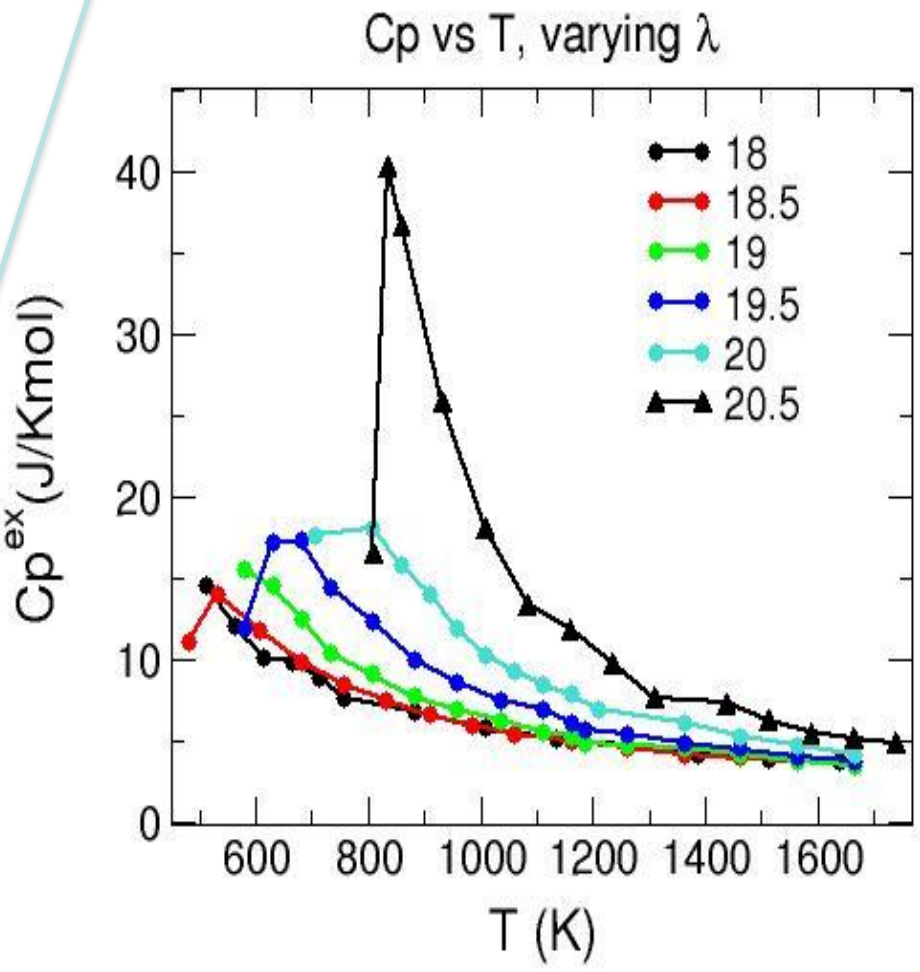
mS-W

note how the Cp spike comes just at the end of the line of first order transitions, and beginning of glassforming range



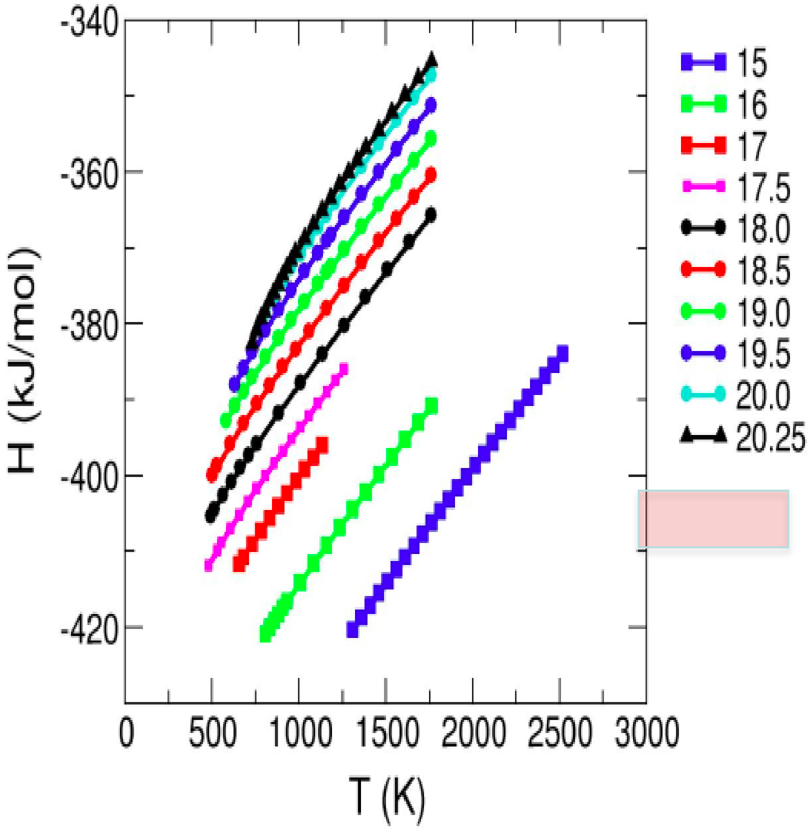
Tc?

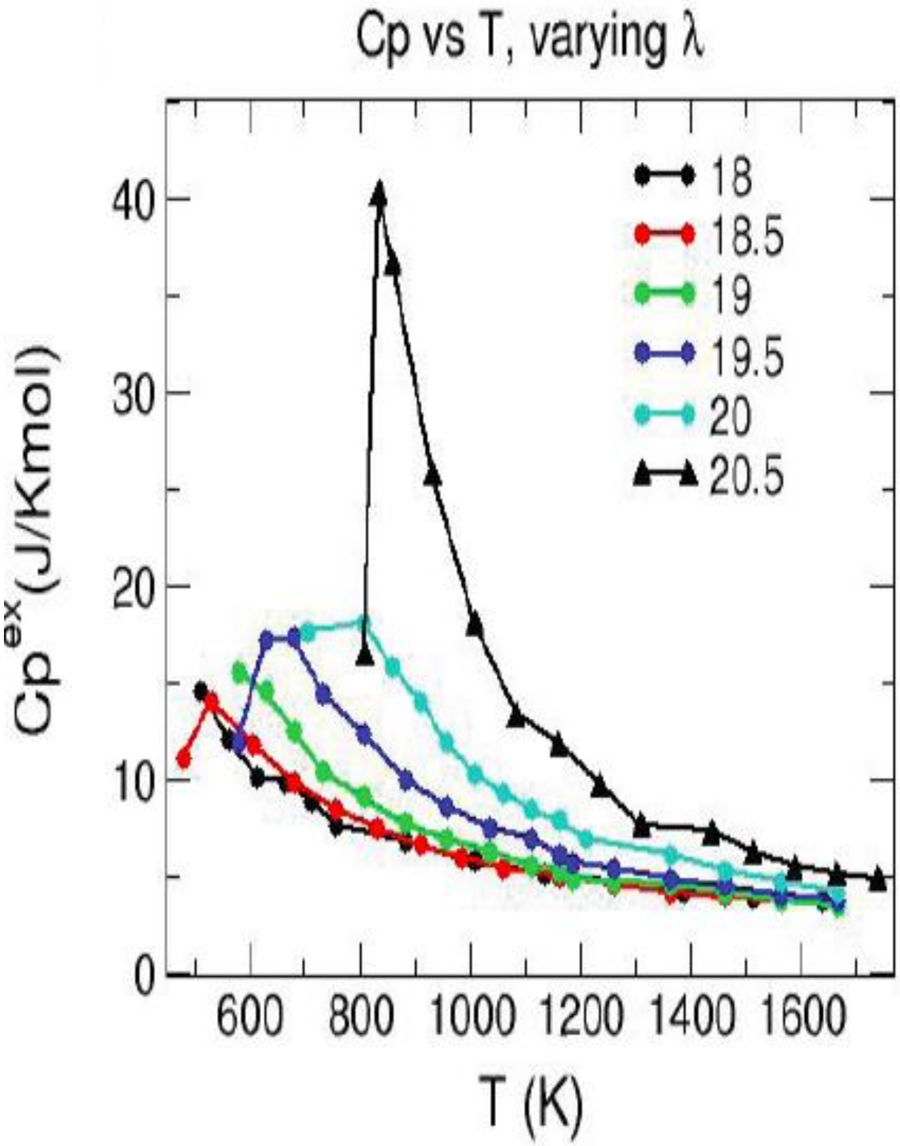
Cp vs T, varying λ



XS Heat capacity of the S-W model as $\lambda > 18 < 21$

Molinero et al PRL
(supplementary Inf)

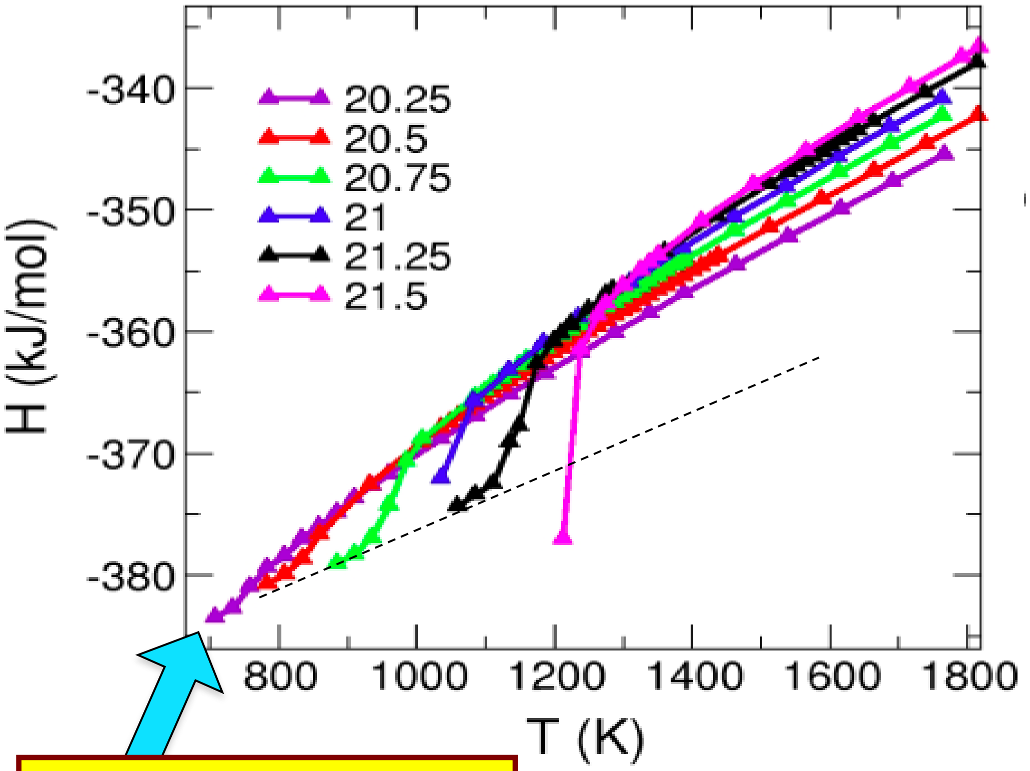




Variations of H and V with λ in the S-W model

Add Kapko point

H vs T, for $20.25 < \lambda <21.5$
from Molinero S&A PRL (SI)

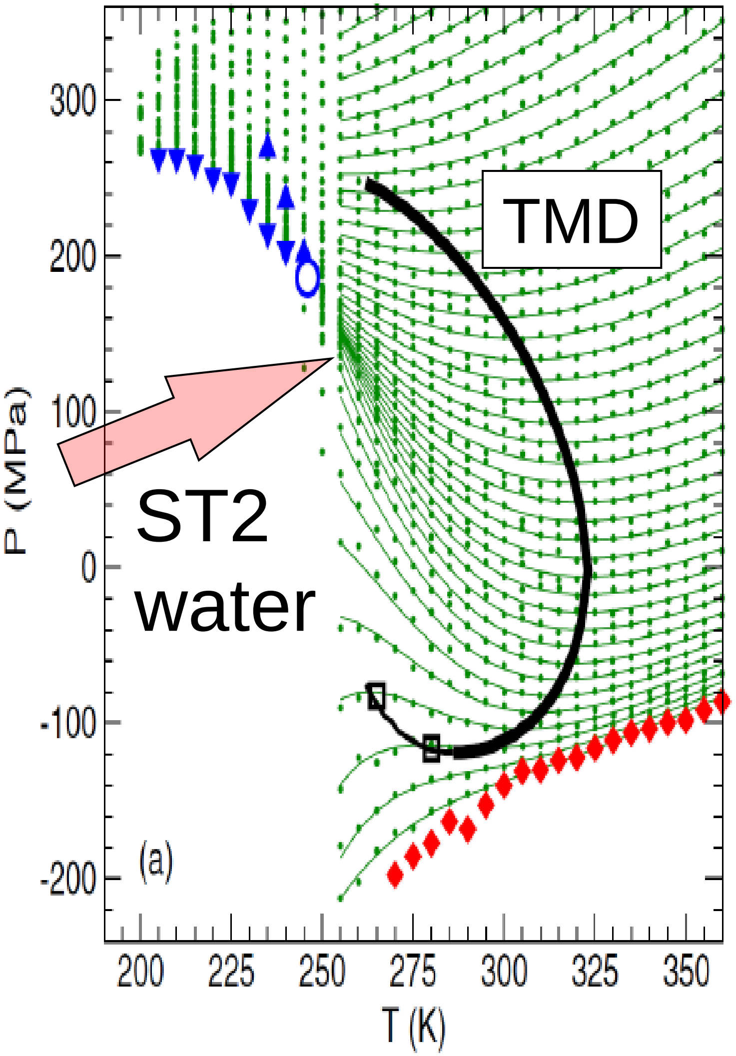


Vanishing ΔH:
Tc = **700K** for p = 0

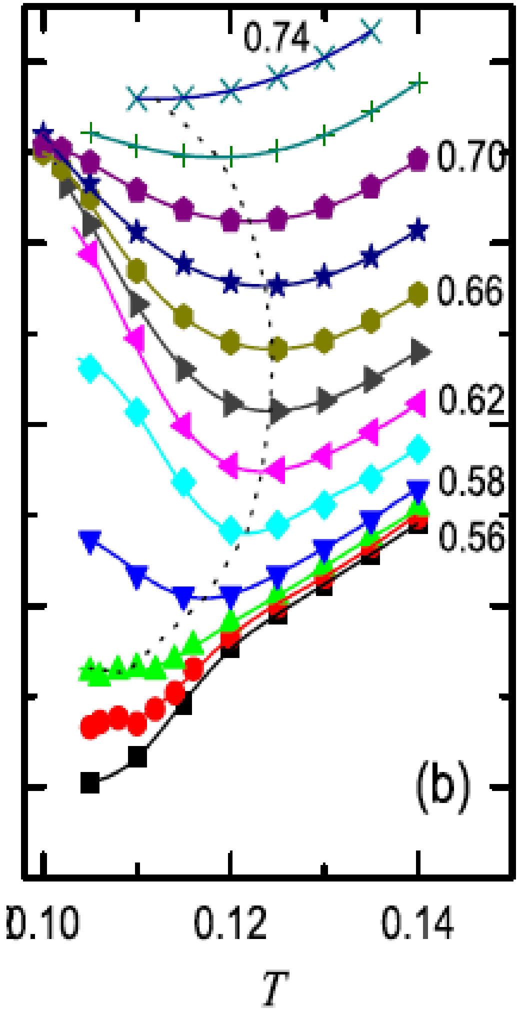
T

Isochore cross test for critical point inflection or Van der Waals loop

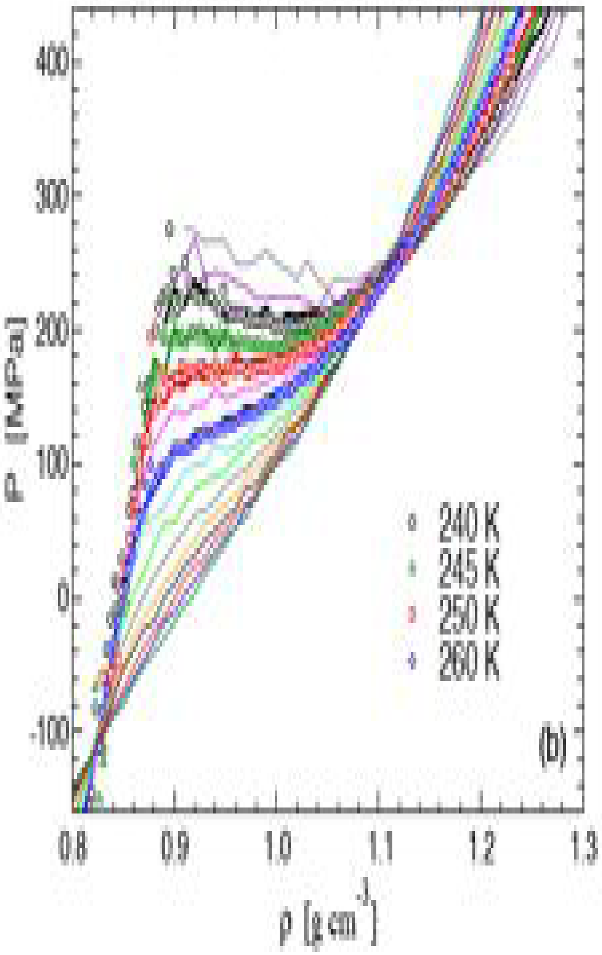
Saika-Voivod, Sciortino, Poole



Tu et al (Buldyrev)



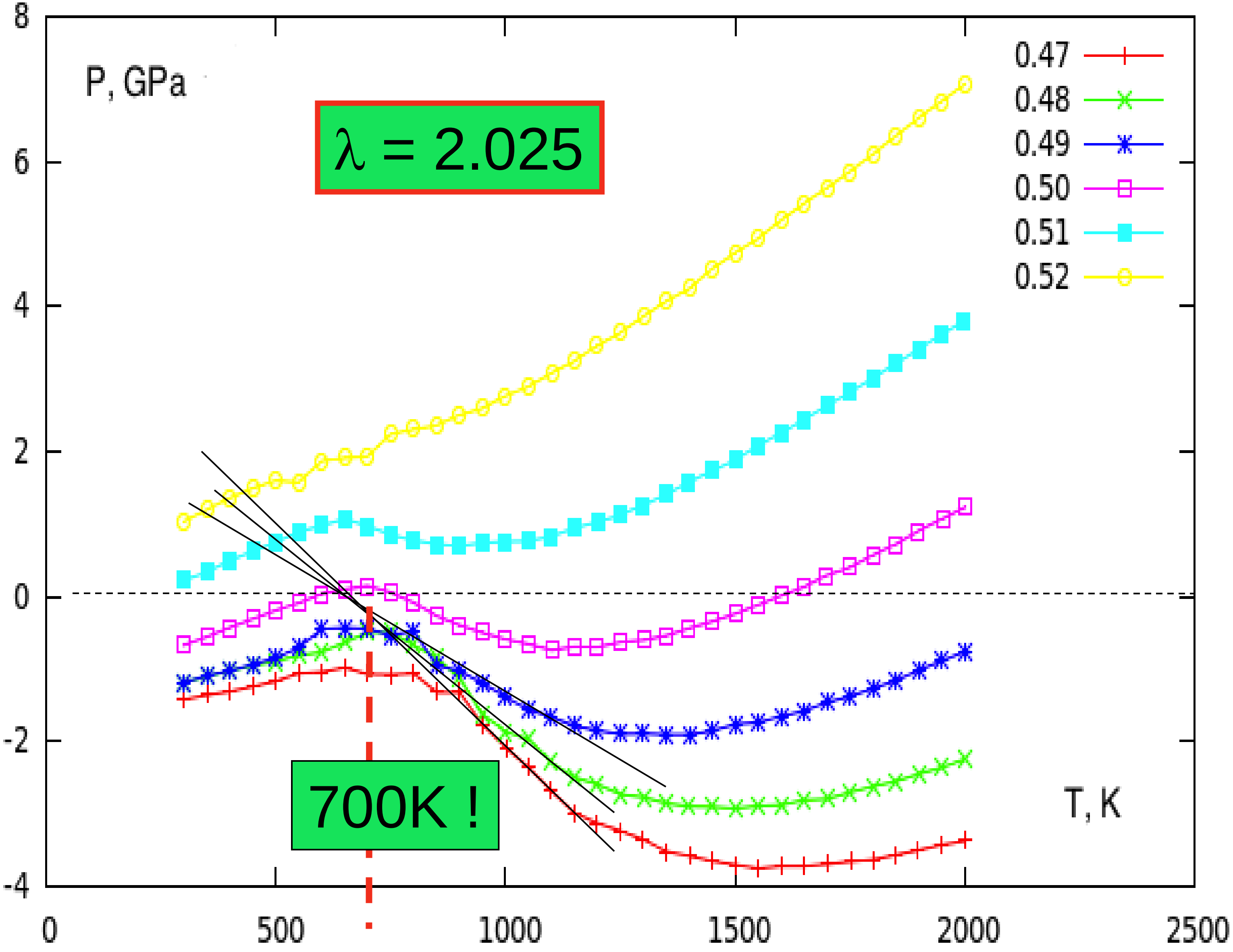
Saika-Voivod,
Sciortino, Poole



S-W Isochores

From Vitaliy, last week

There's no crystallization near this critical point !!

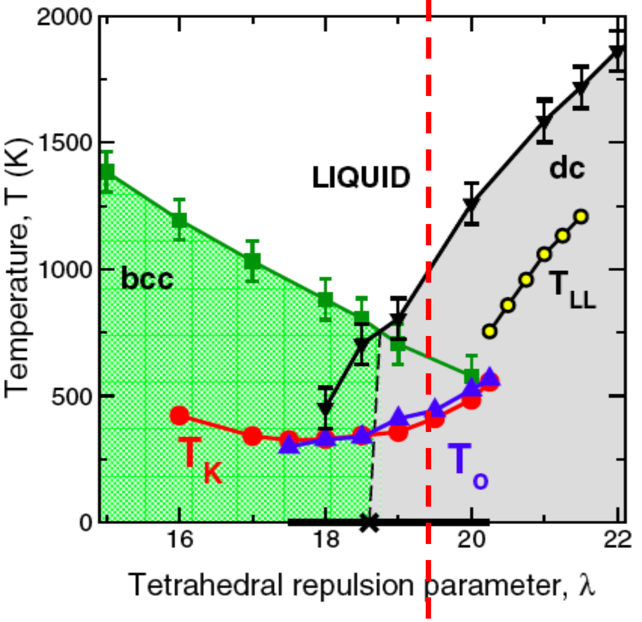


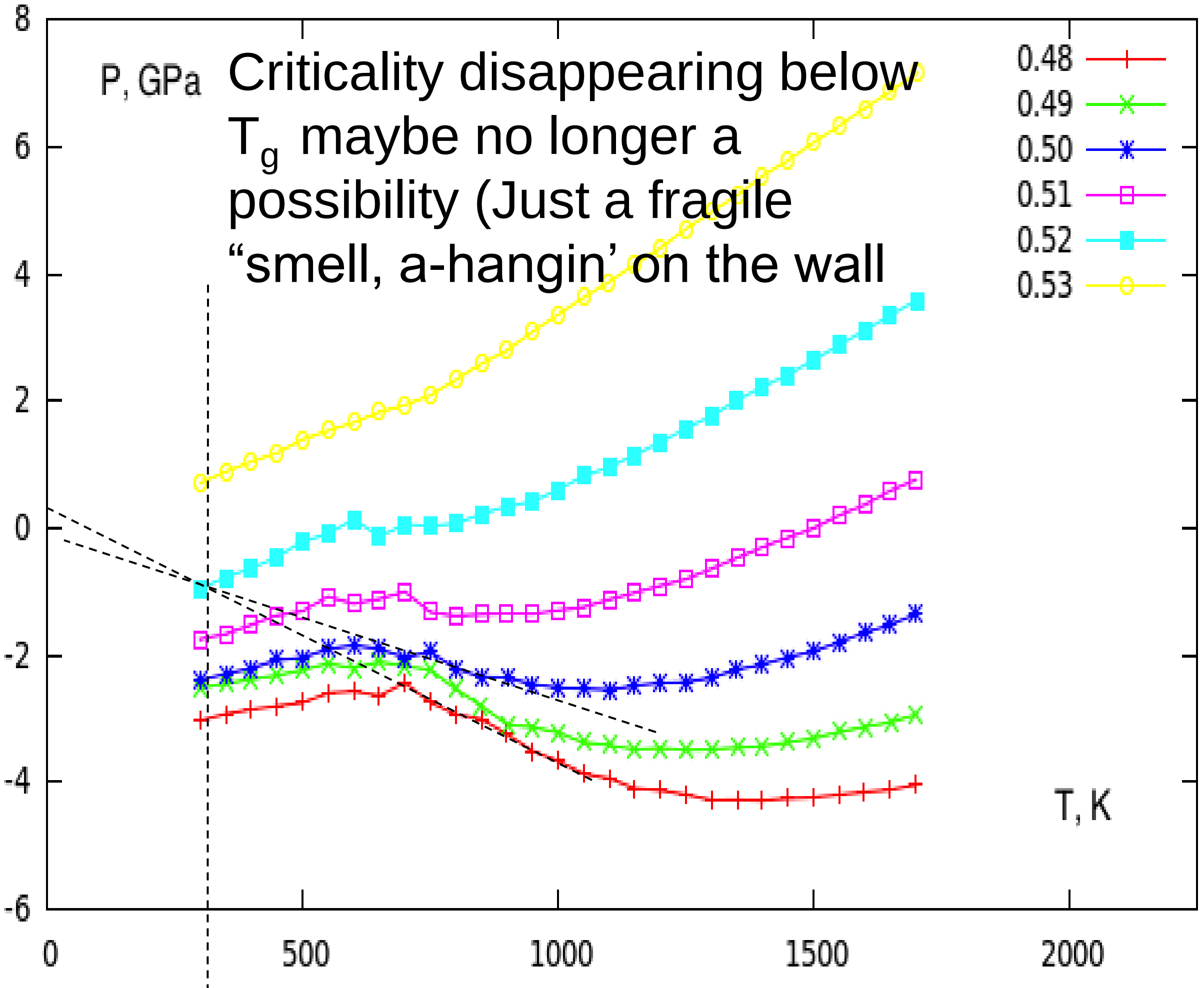
λ = 2.025

700K !

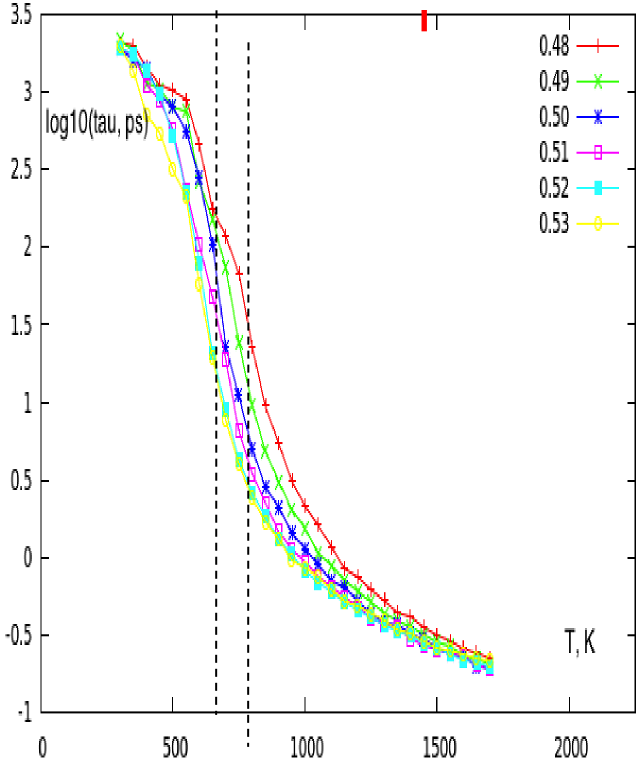
But, λ = 19.5

(work of Vitaliy Kapko, received yesterday)





Criticality disappearing below T_g maybe no longer a possibility (Just a fragile "smell, a-hangin' on the wall



Outline

1. Backround. Other languages and people
   What is and wot isn't fragile" or strong" behavior …Some misuses or misconceptions
2. Thermal vs volume fragilities - and athermal systems
   Athermal systems.Fragilities for different polydispersivities and shapes.
   * hard ellipsoids
3. Thermal systems: (a) an der Waals ellipsoids, and "hysterisis peaks".
   (b) Ergodicity breaking and fragility
   (c) Strong-fragile transitions and polyamorphism
4. What determines the "fragility" – many ideas, and the roots
5 Physics of vibrational entropy, hence maybe fragility

.

Ordinary waves? Small challenge

Riding the 100 foot wave

Brazilian Carlos Burle took on the monster wave - created by the St Jude storm - at Praia do Norte, near the fishing village of Nazare. Estimated at nearly 100ft, it is believed to be the biggest wave ever ridden.

(c) What makes some liquids fragile? The compendium of ideas and what must underlie them.

This section begs the question. It could obviously become very long. It can be addressed at many levels. It is the essential reason, and justification, for this symposium. We remain very engaged in this problem but constrain ourselves to a couple of key remarks.

Many correlations have been offered, based both on experimental, and on computer simulation observations, only a few of which can be mentioned here. From experiments, fragility is argued to be determined by:

(*) the value of the Poisson ratio[75]
(*) non-ergodicity factor[76]
(*) the anharmonicity[77] (Gruneisen constant)[78] at the boson peak frequency[79]
(*) molecular volume or more specifically the expansion coefficient (basis of free volume theory[80])
(*) the heat capacity, or the configurational heat capacity scaled in some way, e.g. by the excess entropy at Tg[25]

(*) the temperature dependence of the shear modulus[81]
(*) the degree of frustration between crystal and locally favored structures[82, 83]
(*) polymer chain stiffness and packing[84],

And from simulations

- *generation of shoulder and double well modes [85, 86],*

and, in particular,

- *temperature dependence of the configurational entropy [29]*
- where the latter is related to the width of the enumeration function, (see also S. Sastry, this volume for the relation to the high temperature activation energy, which is a variable in the Adam-Gibbs equation).

What might be behind it all?

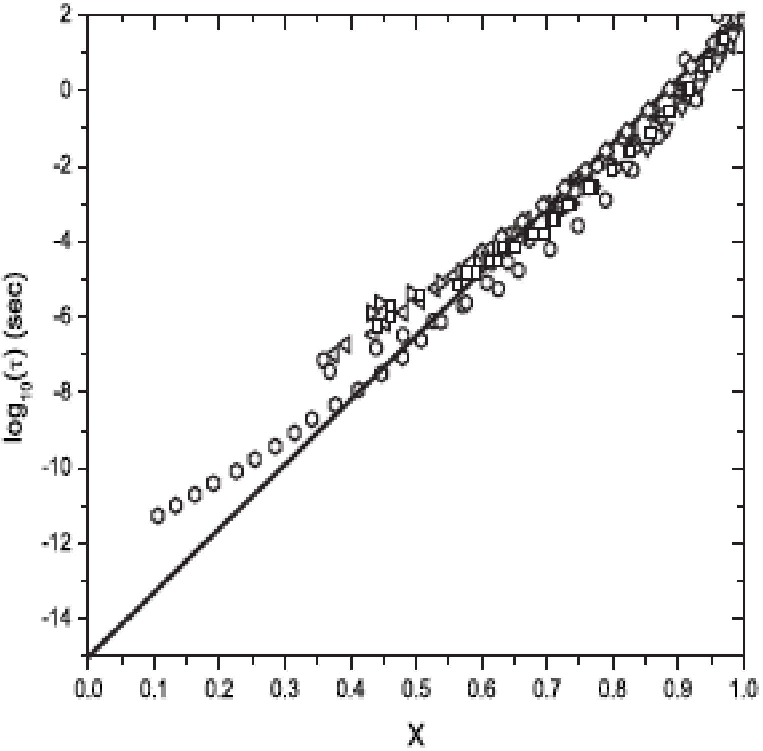
With so many correlations, each with its own merits, there must be some common factor.

e.g. **1.** key example: the **shoving model** (Dyre) and its support by wide ranging dynamic G_∞ measurements (Nelson and co.)
Strong support for the importance of a shear modulus with variable temperature dependence.. But what would control the shear modulus itself, and particularly it's T-dependence?

Or 2. in entropy models, (Adam-Gibbs) what determines the rate of entropy increase? Hence the fragility.

Surely, it's the same thing…….
Control by Quasi-lattice excitations with **different** entropy contributions to the excitation free energy increment.

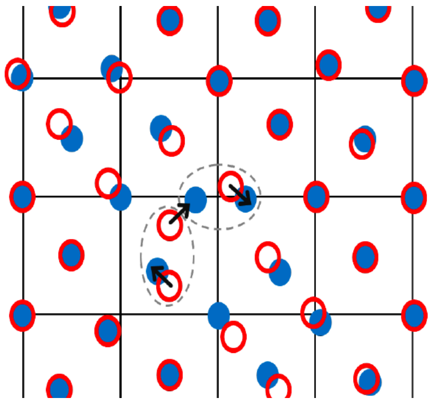
The shear modulus



Torchinsky and Nelson, testing the “shoving model”

Granato, and the interstitial defects that, in crystals, control G_∞

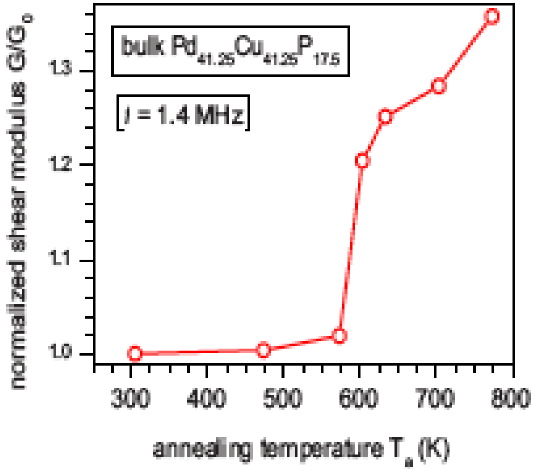
In the crystal



SO

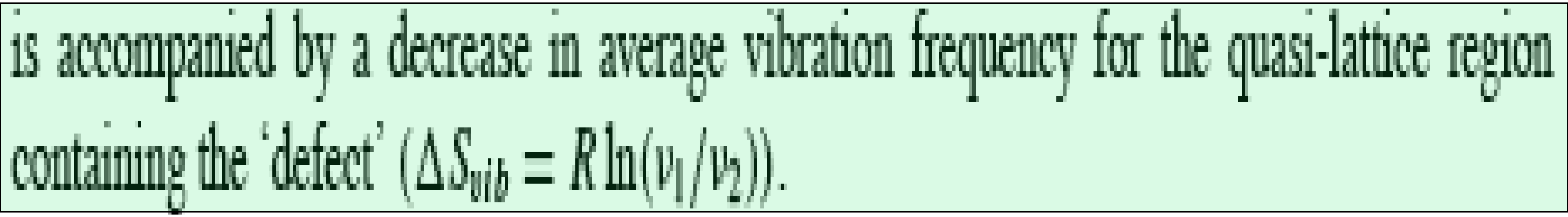
1. Is there an amorphous analog of the crystal interstitial for the glassy and liquid states?

2. If yes, what controls its dc/dT?



Two-state excitations or, better, Gaussian excitations

An excitation requires an **enthalpy** increment, but is encouraged if accompanied by a positive ΔS, i.e.



is accompanied by a decrease in average vibration frequency for the quasi-lattice region containing the ‘defect’ ($\Delta S_{vib} \equiv R\ln(\nu_1/\nu_2)$).

So it could all originate in the nature of the VDoS

And if it does….

(No time)

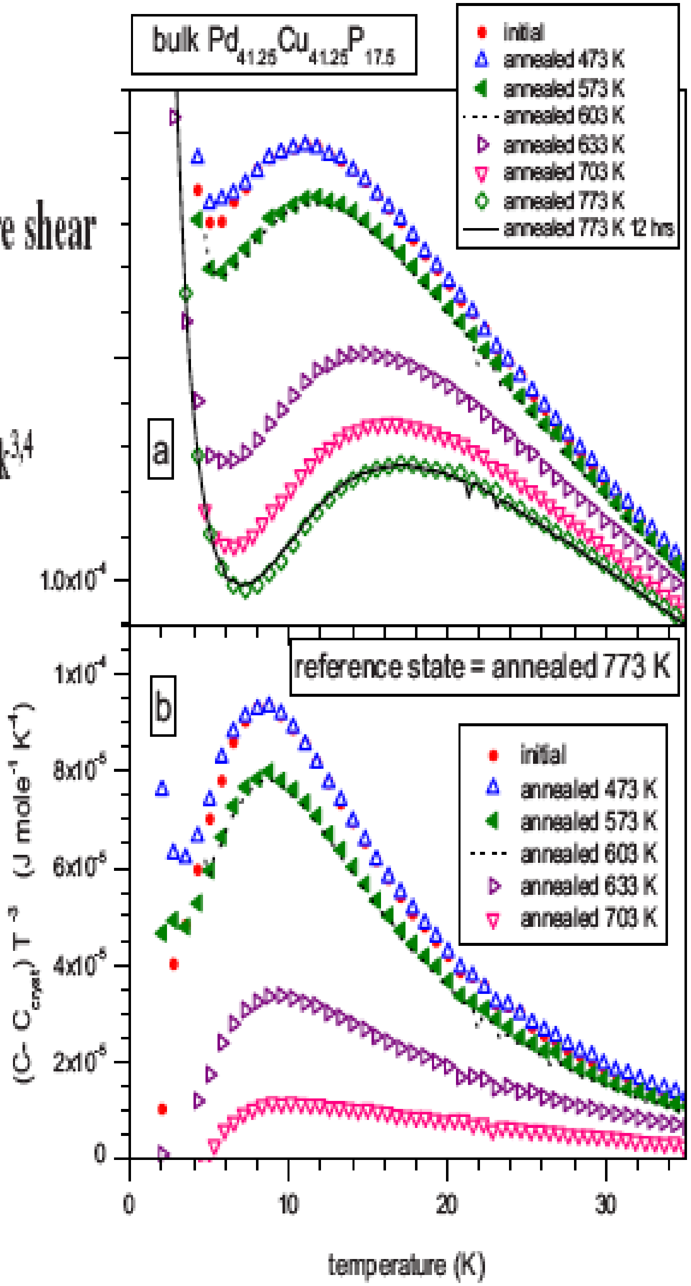
The shear modulus

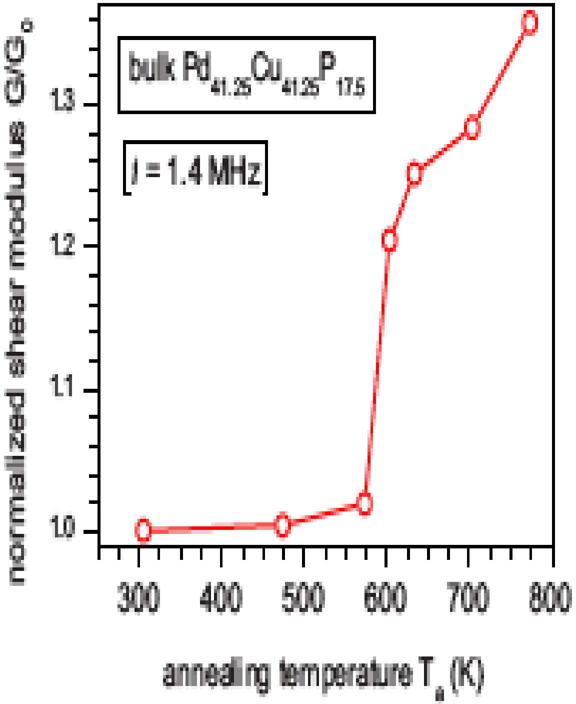
BRIEF REPORTS

PHYSICAL REVIEW B 80, 172102 (2009)

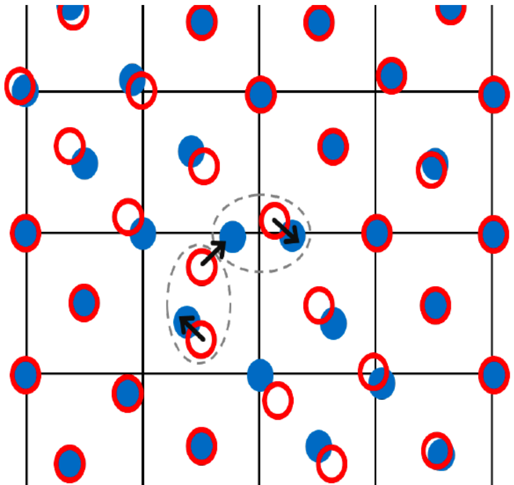
Relationship between low-temperature boson heat capacity peak and high-temperature shear modulus relaxation in a metallic glass

A. N. Vasiliev,[1] T. N. Voloshok,[1] A. V. Granato,[2] D. M. Joncich,[2] Yu. P. Mitrofanov,[3] and V. A. Khonik[3,4]



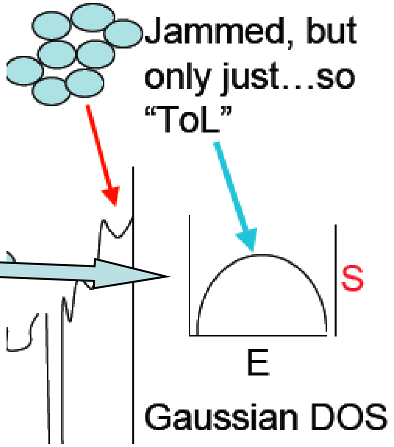


In the crystal



Grand CHALLENGE No. 1

Understanding the drive to the **ToL** (what excites some liquids more urgently than others?)



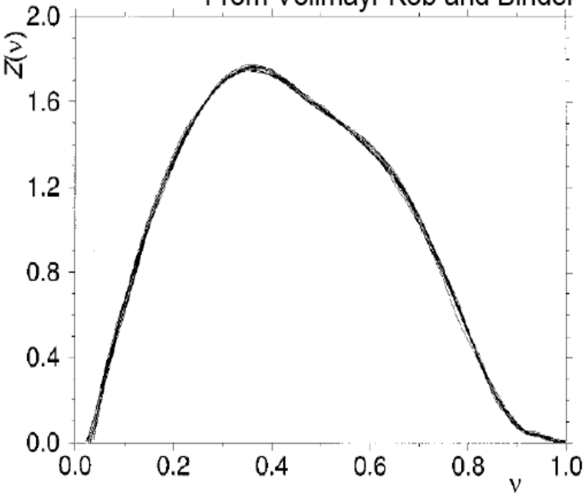
Is it to be found in the **configurational** manifold (CDoS) or the **vibrational** manifold (VDoS) ??

Vibrational density of states for KABLJ structures quenched at rates diff. by 4 OM

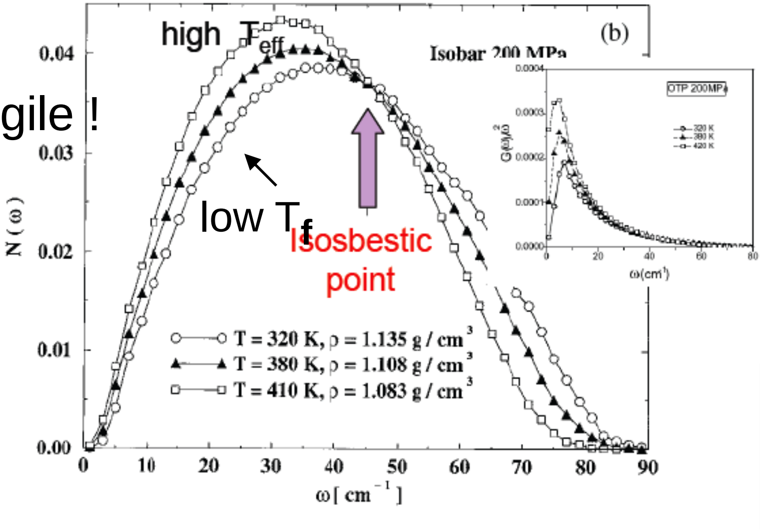
VDoS of inherent structures of the 3-bead Wahnström-Lewis model at fixed P

From Vollmayr Kob and Binder

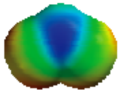
No change of shape with fictive temperature so no extra drive to TOL so ***not*** fragile



Fragile !

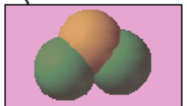


W-L "OTP"



Ozone

(Tb/Tm = 2.02



SCl_2

Tb/Tm =>2.2

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5 Physics of vibrational entropy, hence maybe fragility.

Role of Vibrational Entropy?

1. Vibrational entropy and fictive temperature:

Does vibrational density of states change with fictive temperature?

NO, if it is a ***strong*** glassformer,

YES, if it ***is fragile*** glassformer

Vibrational density of states for KABLJ structures quenched at rates diff. by 4 OM

From Vollmayr Kob and Binder

NO !

fictive temperature dependence of vibrational entropy

But…

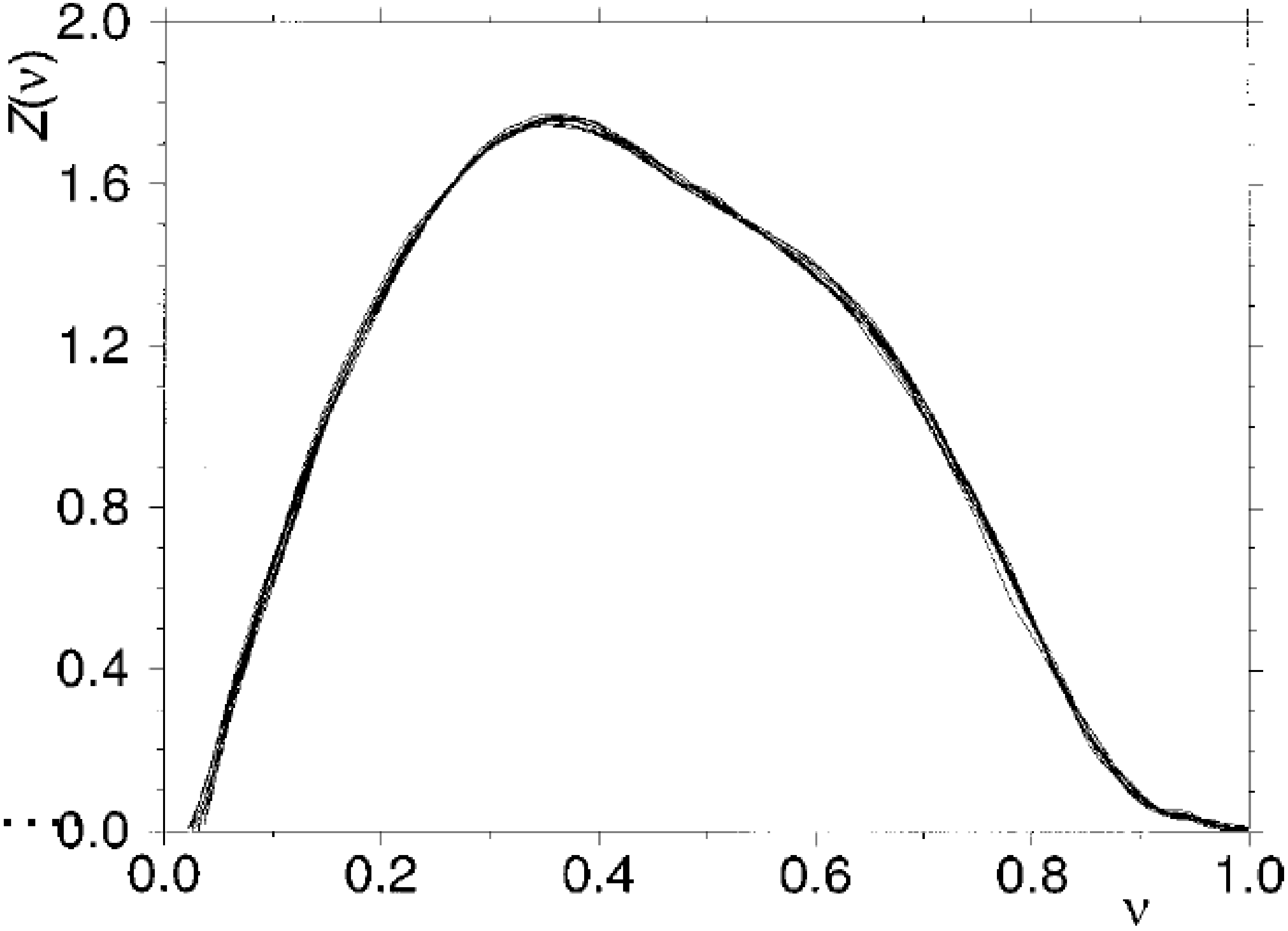
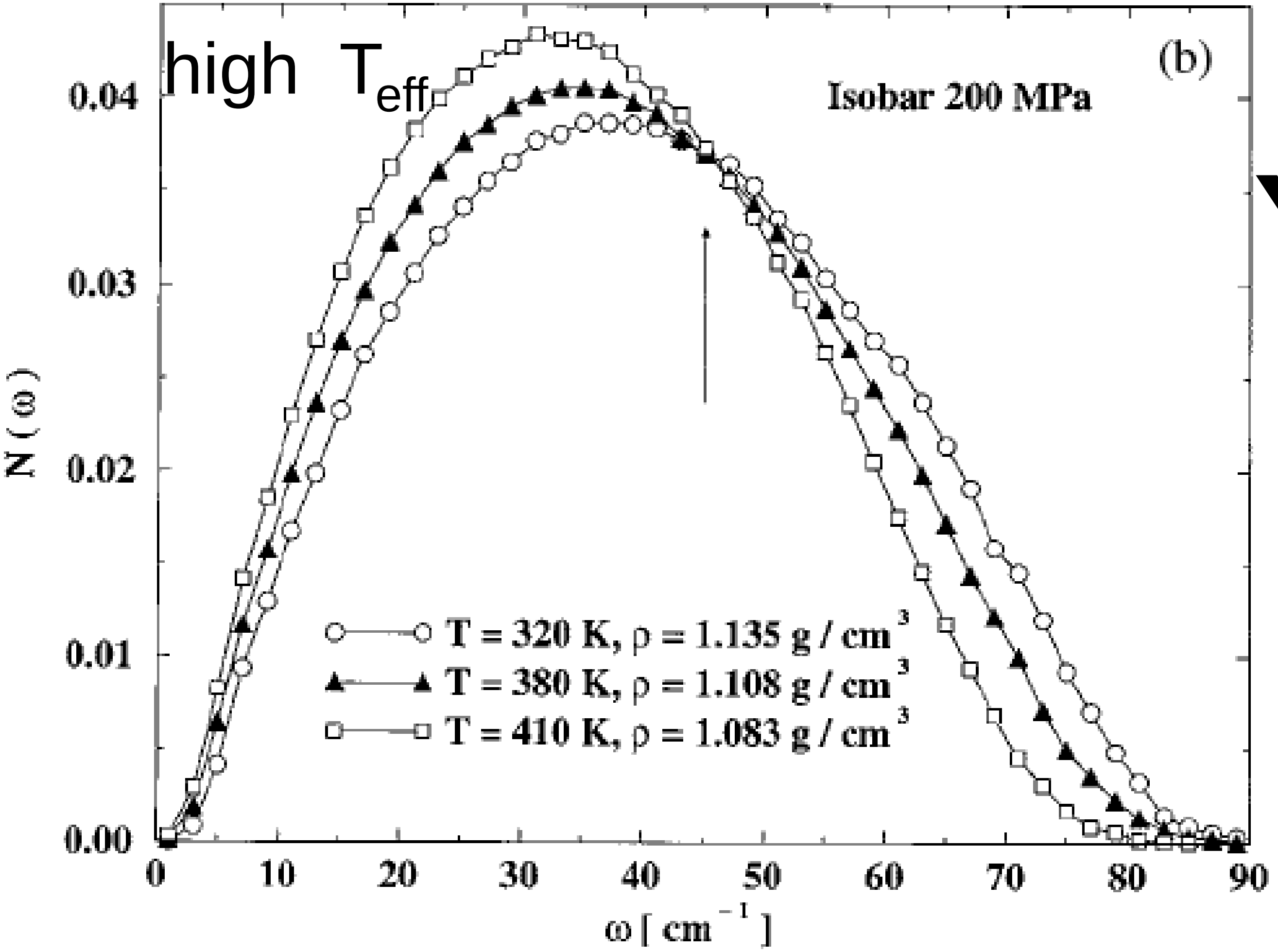


FIG. 15. $Z(\nu)$, the spectrum of the system at $T=0$ for all cooling rates investigated.

VDoS of inherent structures of the 3-bead Wahnström Lewis model **at constant pressure**



high T_{eff}

YES

See Reduced VDoS (divide by ω^2)

Figure 6. The VDOS for the inherent structures of OTP, in the Lewis–Wahnstrom model, obtained by steepest descent quenching of structures equilibrated at the designated temperatures (a) at

Next step:
divide by ω^2

↓

boson peak

(shifts to lower T with increasing fictive T)

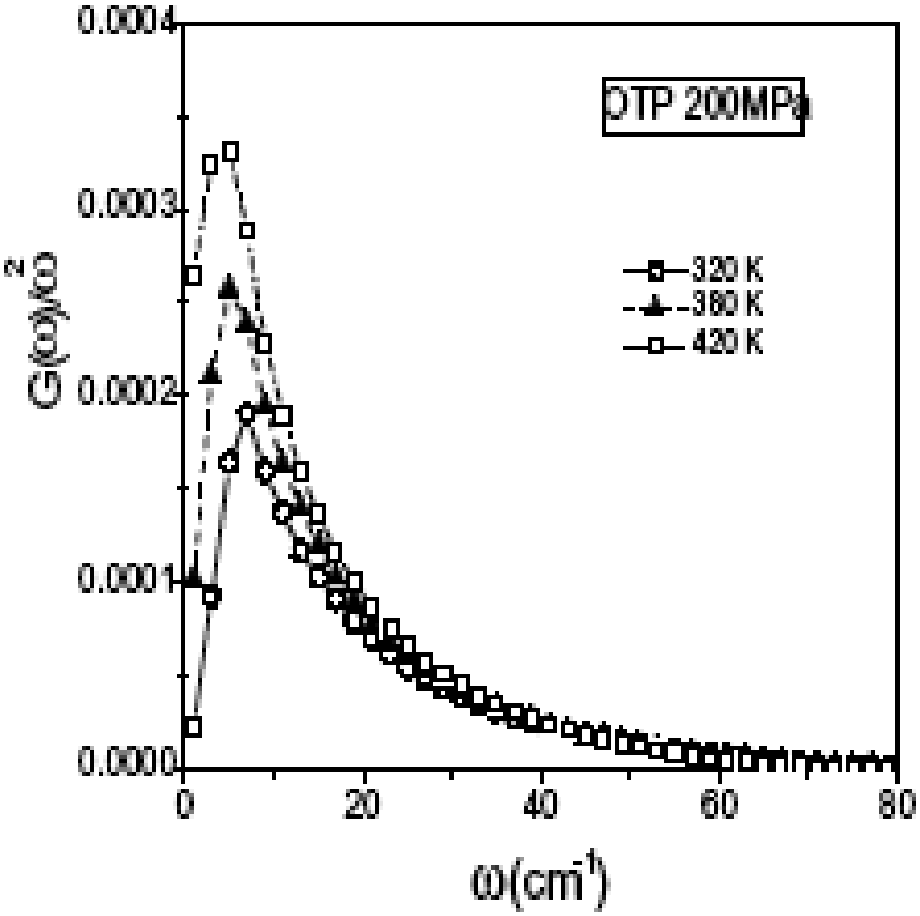
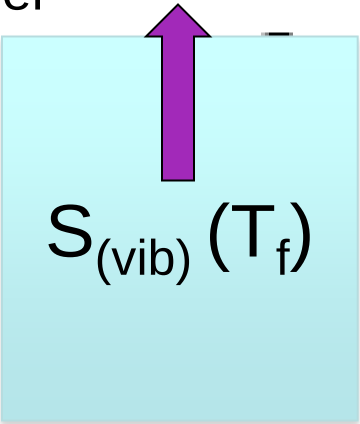


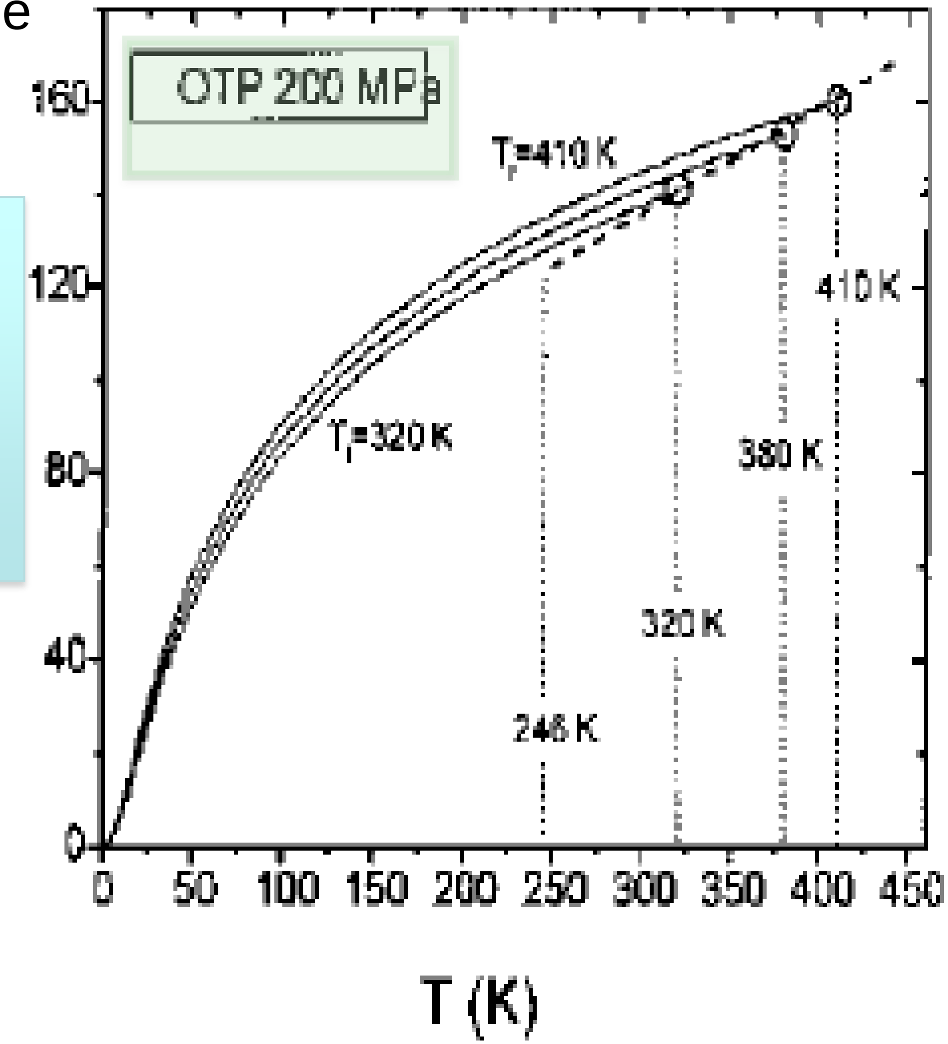
FIGURE 3. Data of Fig. 2 shown in the Boson peak representation (G(_)/_ ^{2}). The boson peak is seen to increase in intensity and move to lower frequencies as fictive temperature is increased.

Next step: assess S(vib) vs T (***using the standard expressions***) for each of the different densities of states i.e. different fictive T's (Tf's). This will be unique up to Tf

Above Tf, structure will change and **both** S_c and S_{vib} will increase together



$S_{(vib)}\,(T_f)$



Thus the entropic drive to the top of the energy landscape will increase as the fictive temperature dependence of the vibrational DoS increases, as noted by Goldstein 40 years ago, for two state systems. Thus this entropy source, that traces back to vibrational changes on excitation of quasi-lattice defects, can influence, or even control, the fragility.

M. Goldstein, J. Chem. Phys. **64, 4767 (1976).**