

Serving the greater Phoenix “Valley of the Sun” (pop. > 3M)



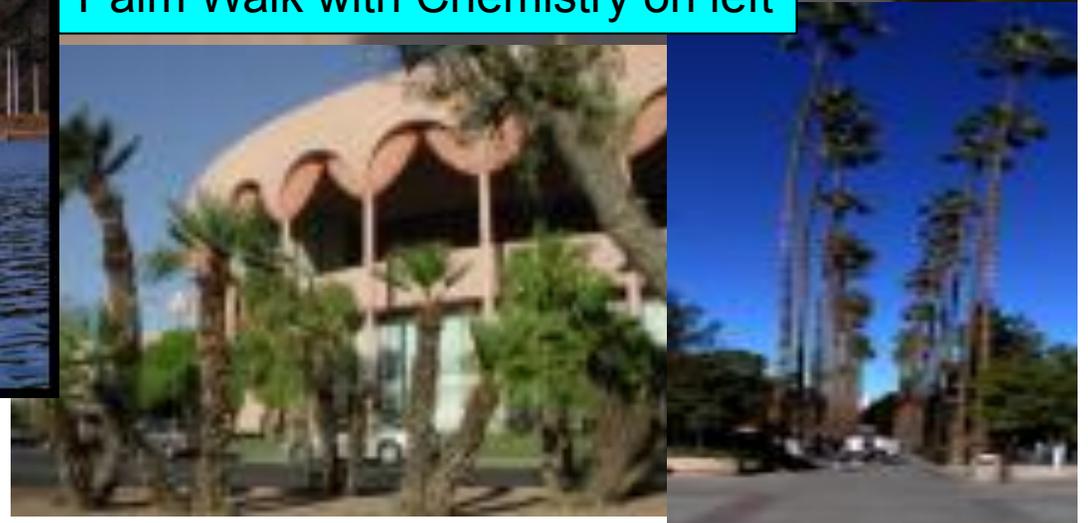
ARIZONA STATE U.



Palm Walk with Chemistry on left



Sun Devil Stadium, from
Tempe Town lake



Chemistry, At the Highest Level

Featured Analyses, September/October 2011

A world ranking

Thompson Reuters Web of Science

by Christopher King

Recognizing the international year of Chemistry

Institutions in Chemistry

(Listed by citations and citation impact) Cites per paper

Institution	Citations 2001-11	Institution (>= 1,000 papers)	Impact 2001-2011
Chinese Academy of Sciences	357,682	1 Scripps Research Institute	41.70
Max Planck Society	213,801	2 Harvard University	36.76
University California, Berkeley	158,308	3 Rice University	34.44
Kyoto University	136,840	4 Caltech	34.02
University of Tokyo	128,672	5 Northwestern University	32.47
MIT	118,935	6 Arizona State University	31.81
CNRS (France)	117,297	MIT	31.04
Russian Academy of Sciences	109,256	University California, Berkeley	30.84
Harvard University	106,946	Stanford University	29.35
Northwestern University	100,676	Lawrence Berkeley National Lab	29.26
University of Illinois	94,037	Yale University	29.05
Japan Science & Technology Agency	91,870	University California, Los Angeles	27.08
Osaka University	90,188	Georgia Tech	26.94
AIST (Japan)	90,063	University of Washington	26.78
CSIC (Spain)	87,538	University California, Santa Barbara	26.65
		University of Michigan	26.47
		Carnegie Mellon University	26.27
		Columbia University	25.75
		University of Pennsylvania	23.94
		University of Utrecht	23.93
University of Cambridge	83,672		
Tohoku University	77,036		

<http://archive.sciencewatch.com/ana/fea/11sepoctFea/>



Fragility concept (and origin) and the glass transition.



Austen Angell
Dept. of Chemistry and Biochemistry
Now, the School of Molecular Sciences, Arizona State University, AZ

Connie
Moynihan



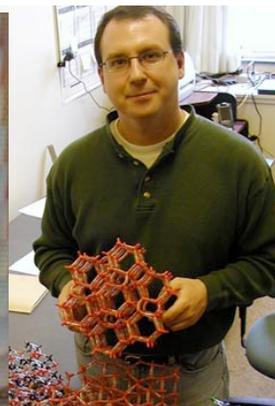
Robin Speedy



Masaharu
Oguni



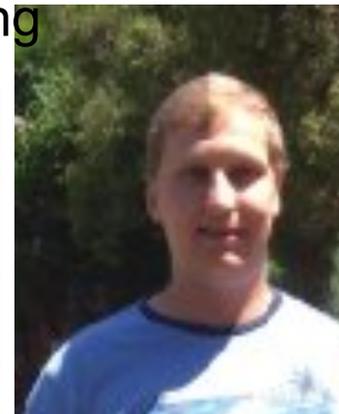
Peter Poole



Limin Wang



Vitaliy Kapko



Outline

- A. **STARTING UP**: What is meant by “glass”. How formed? Degrees of freedom. The “entropy problem”, the three “nons”, and the glass transition. Are there “perfect glasses?” glassy water
- B. (a) fragile vs strong liquids. Fragility from thermodynamics. Two state thermodynamics and entropic origin of fragility. Soft spots, defects, configurons, and phase transitions .
(b) Origin of fragility (shocker: it’ s probably in the vibrations)
- C. Details on fragility .(a) The shear modulus, its temperature dependence and the origin of this temperature dependence.
(b) Shear and bulk moduli, infinite and low fequency,
(c) confusion on Poisson ratio of glasses and other materials, **MECHANICAL PROPERTIES OF GLASS-FORMERS** (brittle and ductile glasses)

The many routes to the structural glassy state

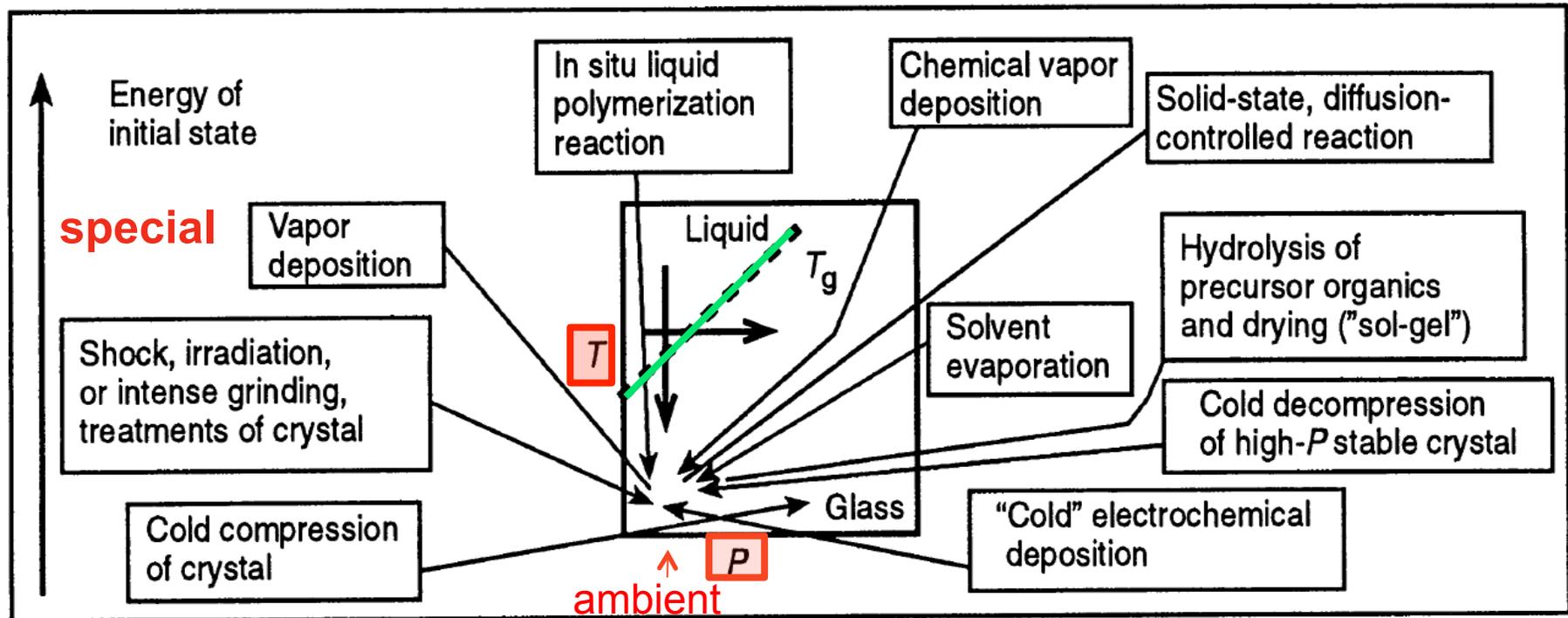
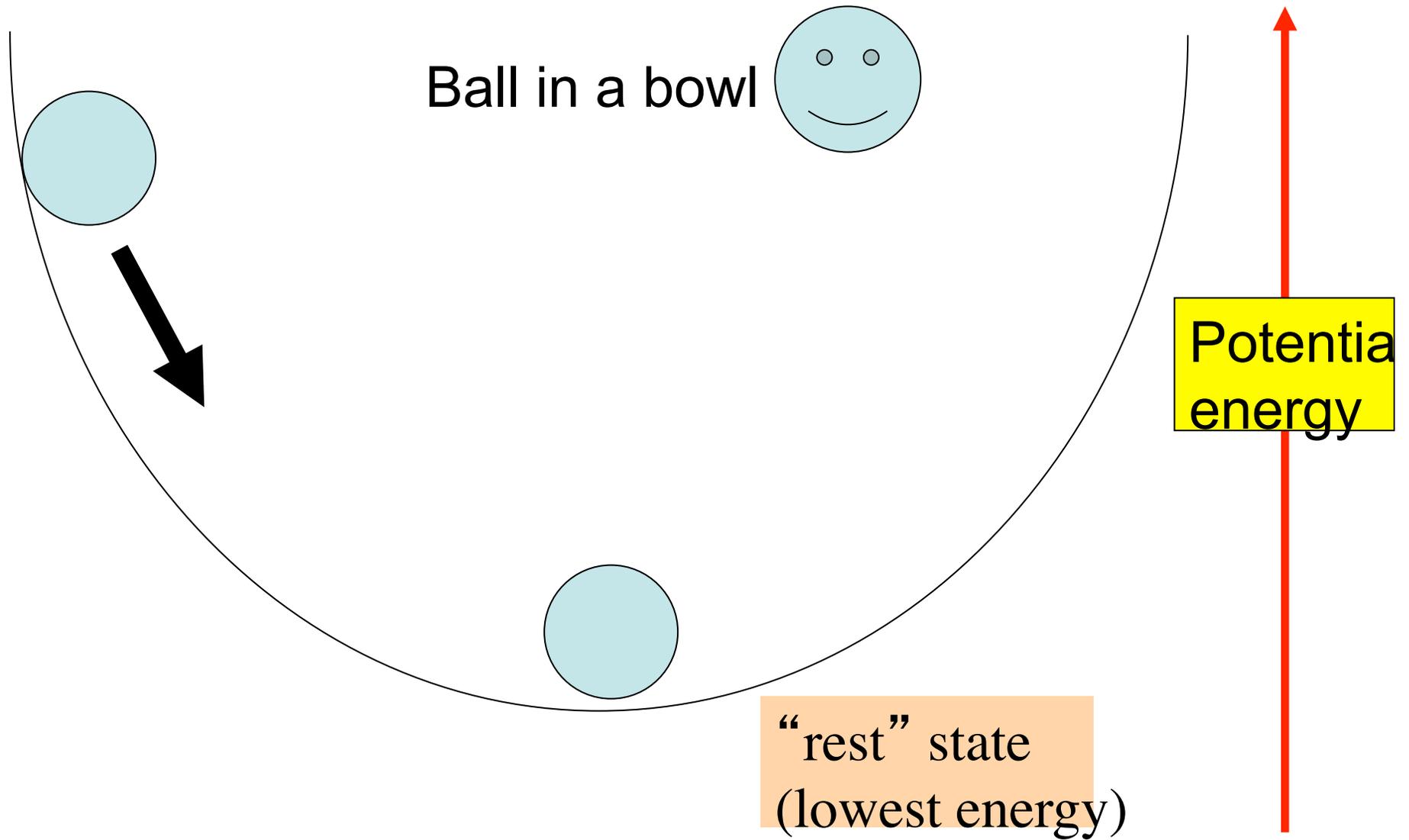
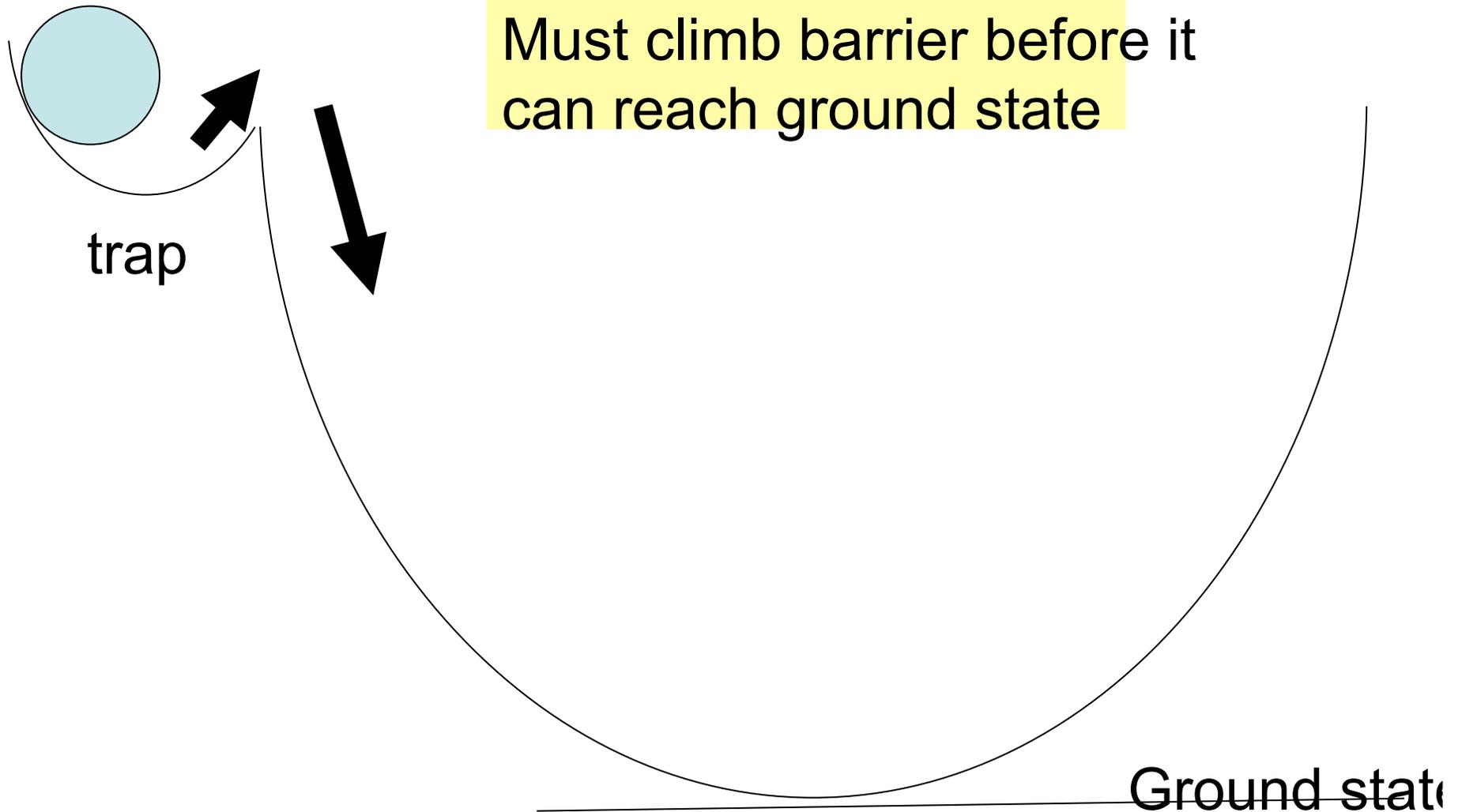


Fig. 1. Various routes to the glassy state, roughly indicating the energies of the initial states relative to the final glassy states. The route of crystal compression below T_g may yield glasses that are thermodynamically distinct from those obtained by the other routes but which may transform to them by way of nonequilibrium first-order transitions.

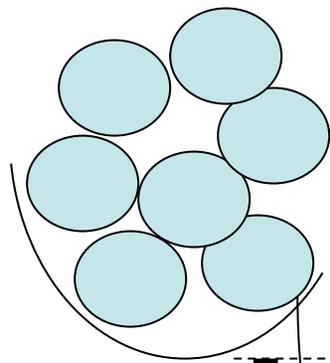
Quick introduction: Energy landscape for glassformers:



Overlapping bowls



GLASS RELATIVE TO CRYSTAL

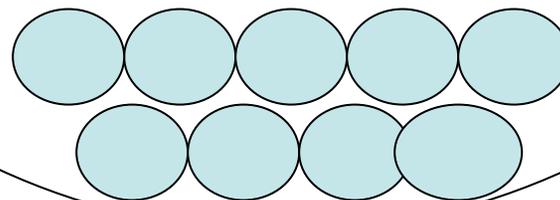


Glass
(disordered packing)

Yes, it's too simple, because.

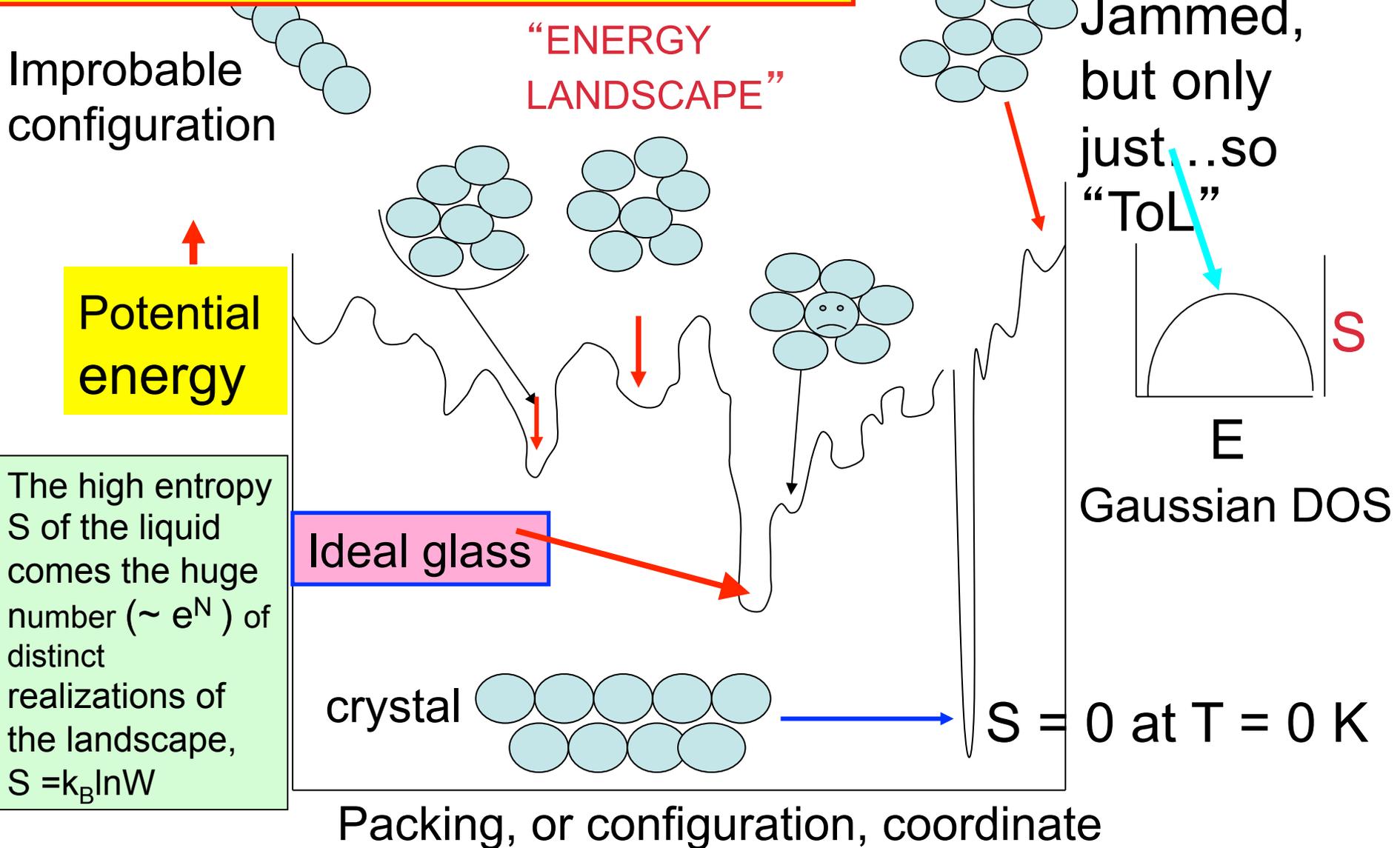
energy of
crystallization

crystal



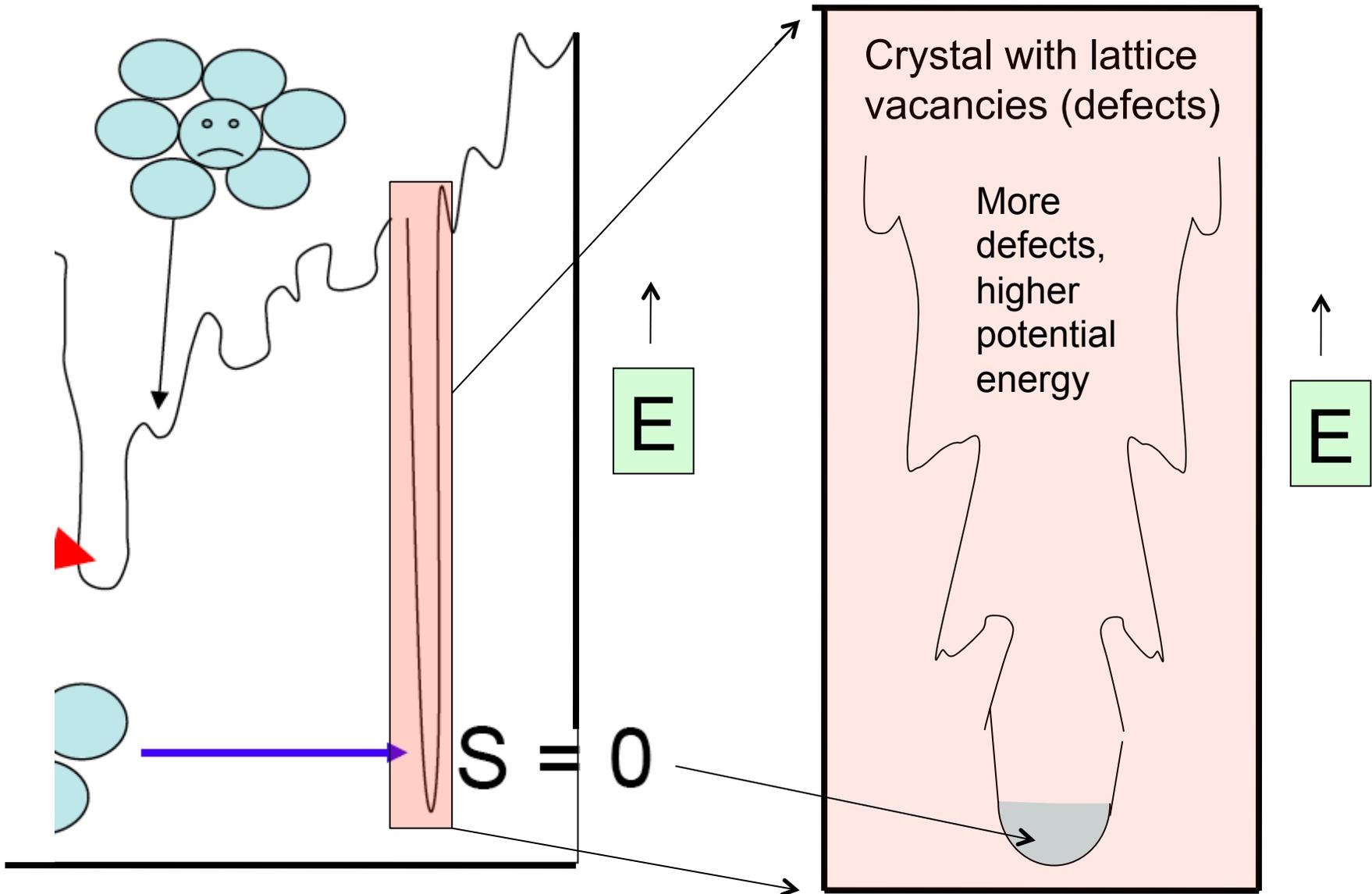
there are... TRILLIONS OF GLASSES,
all of different packing energies,

😊 Unjammed molecule

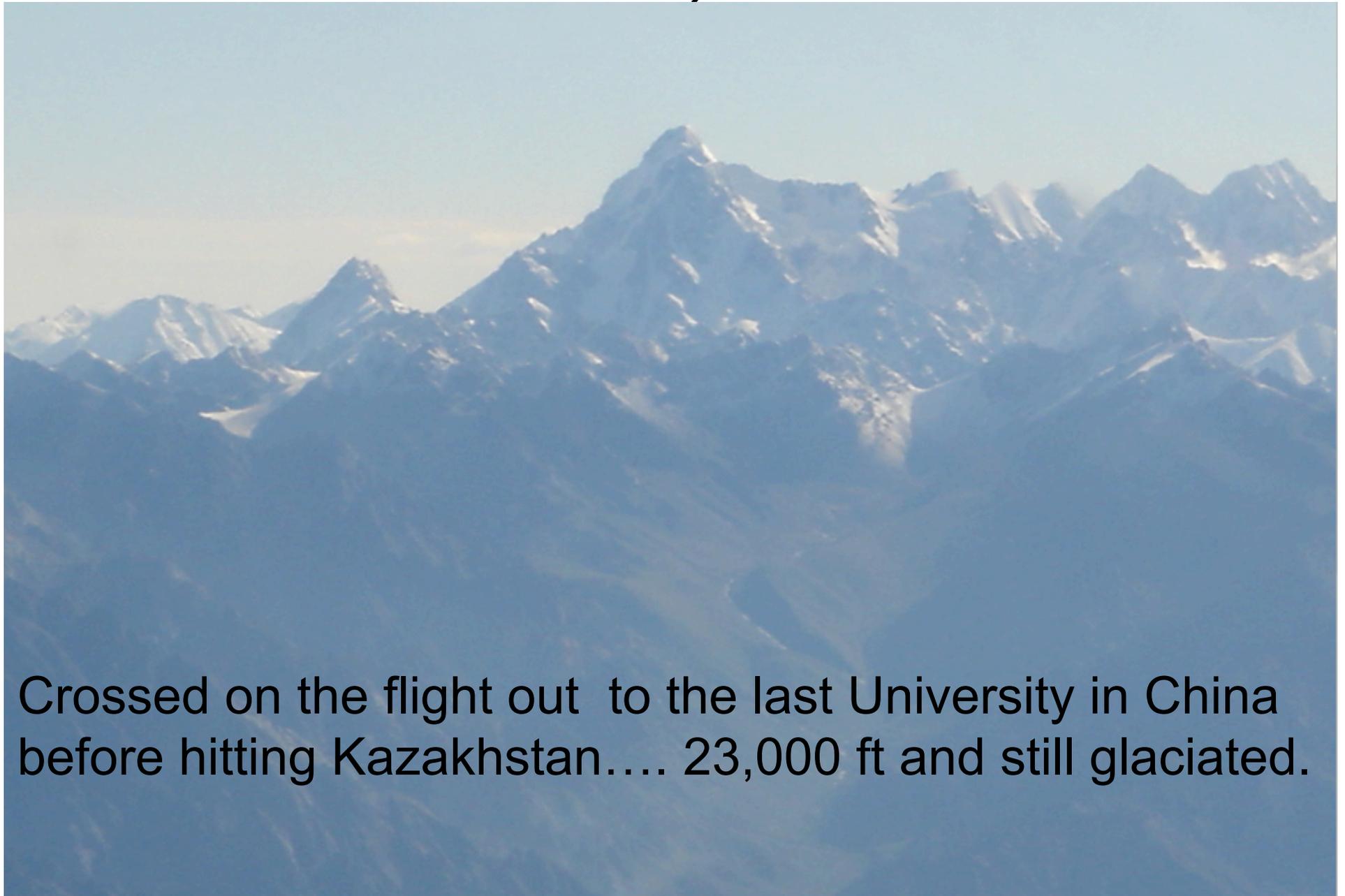


We call it the “energy landscape”

Can do similar for crystals



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.

Solid-like vs liquid-like “degrees of freedom”

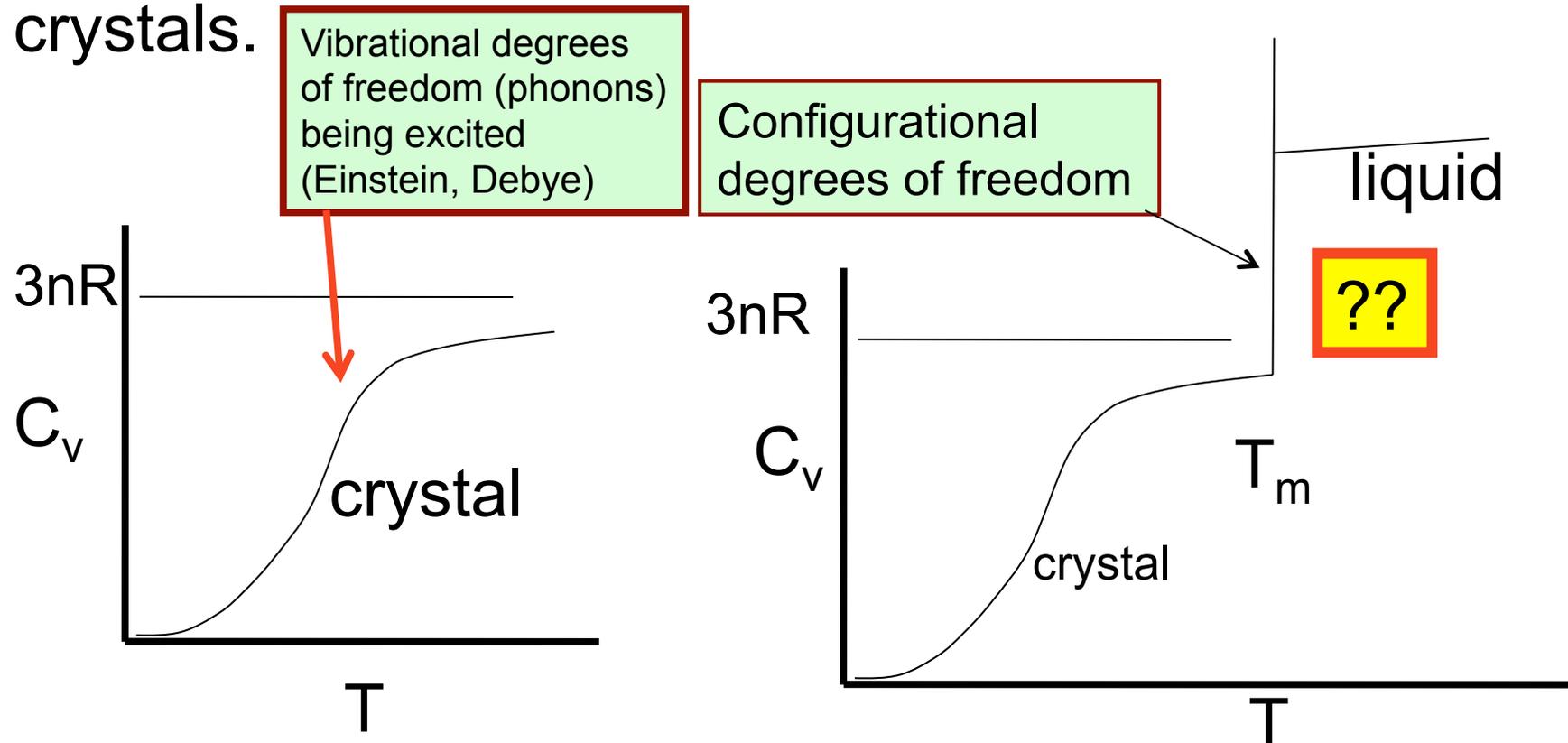
A collection of molecules confined to a single one of these basins is a “glassy” system. It can have solid-like properties but cannot flow. The crystal is a special basin characterized by *ordered* structure.

When temperature rises it can explore the other basins. It has become a liquid.

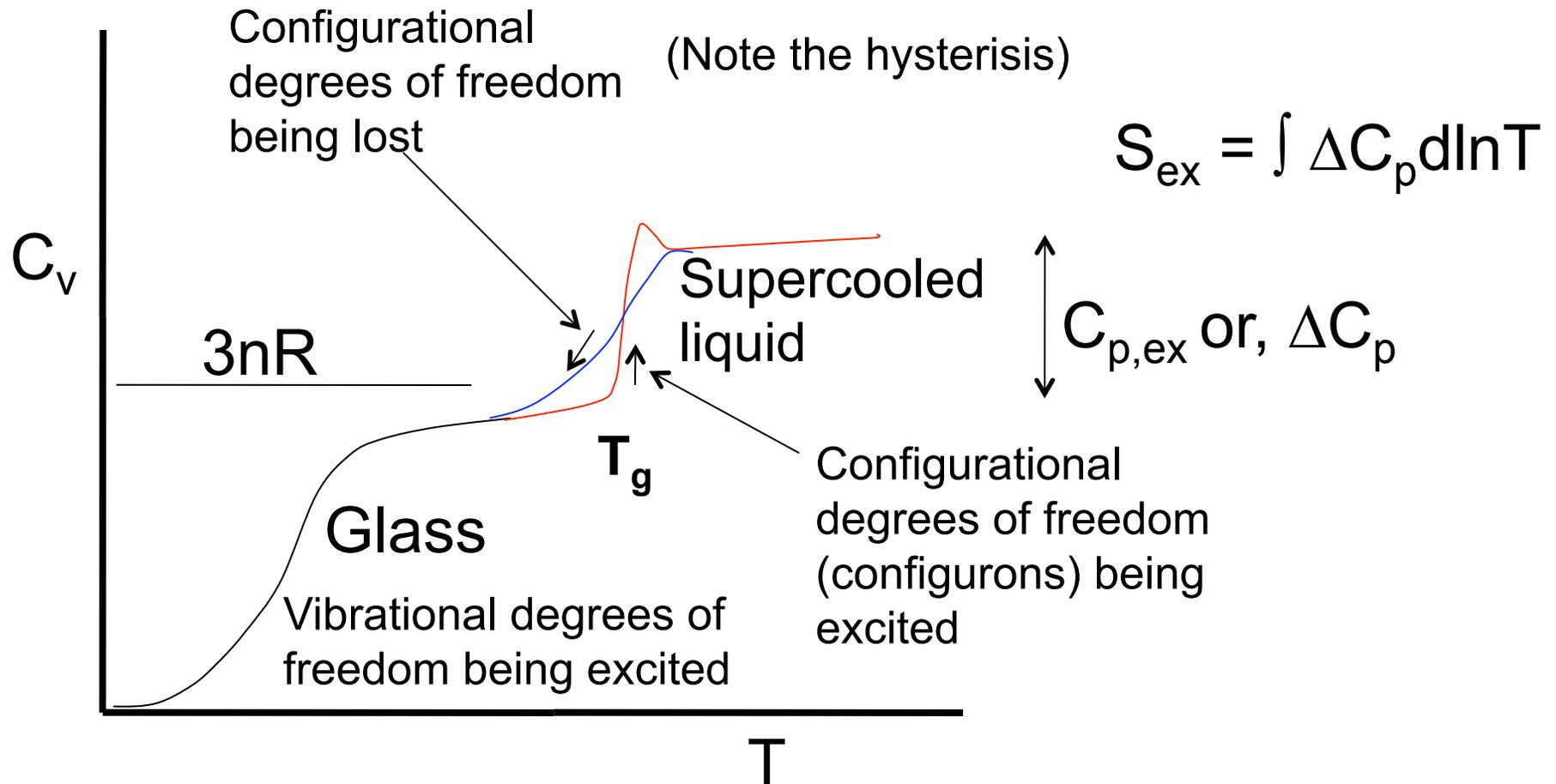
Degrees of freedom are manifested in thermodynamic property called ***heat capacity***

The “energy landscape” in the understanding of glass physics

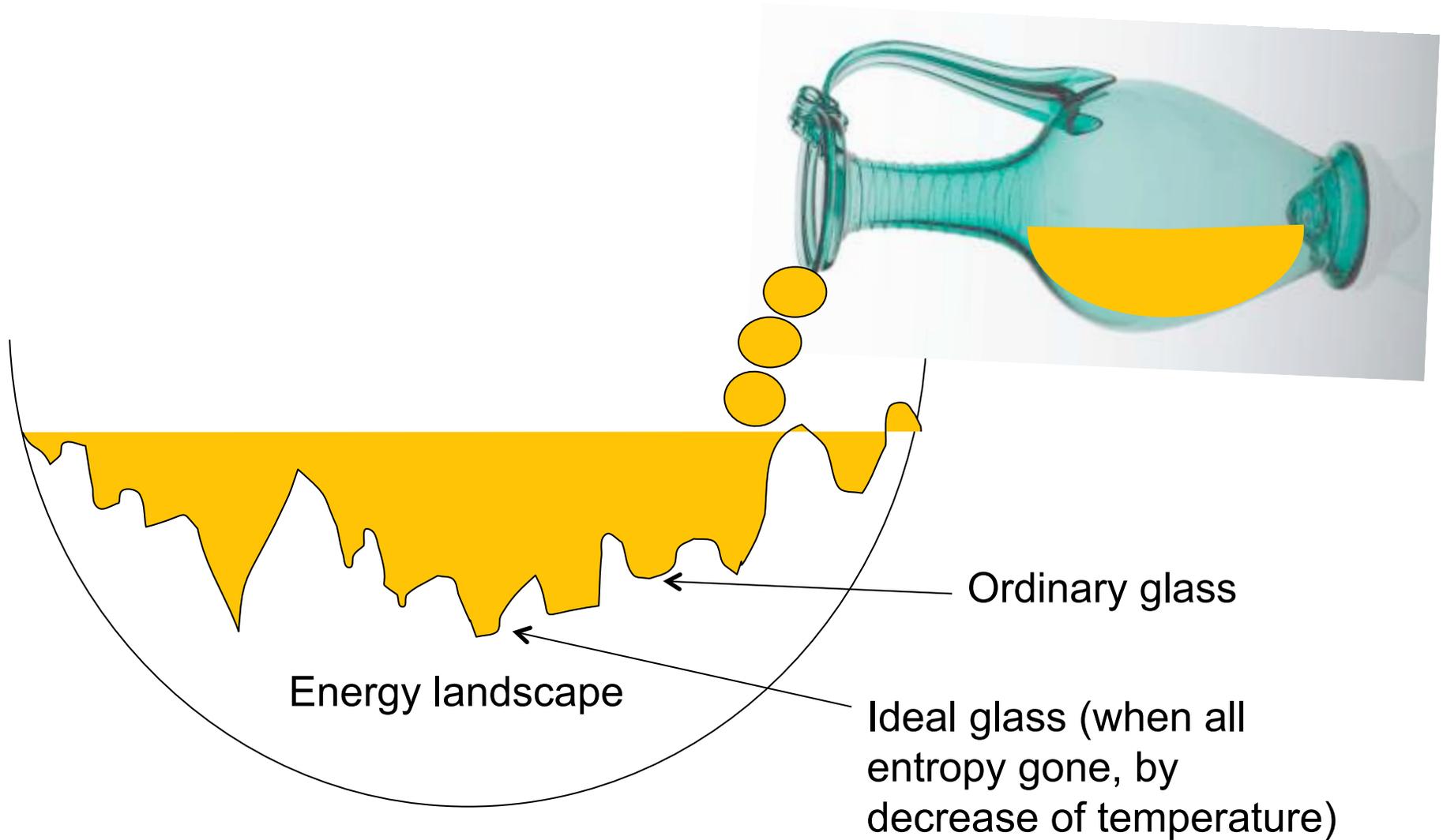
It is an attempt to develop a collective coordinates system, to do for the configurational degrees of freedom of liquids what phonons did for the physics of crystals.



Complete heat capacity function for GF liquid, and the *glass transition*

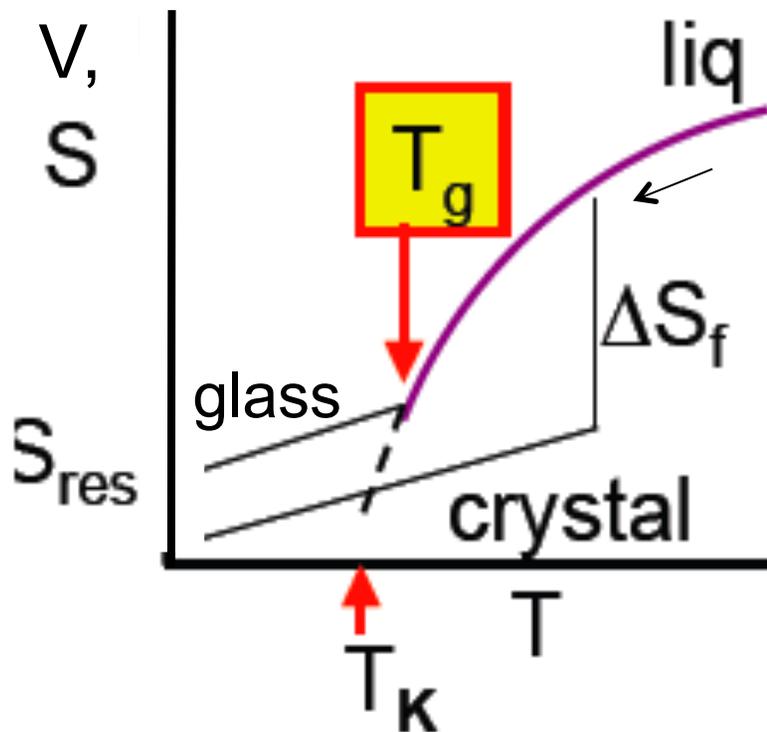


“pouring in” the entropy by raising the temperature



Liquid-solid relations: entropy, residual entropy, and the ideal glass

Normal



Major change in $\partial S / \partial \ln T)_p$
i.e. ΔC_p

The Kauzmann Paradox:
Supercooling liquid entropy about to become less than the entropy of the ordered state (crystal), saved by the glass transition.

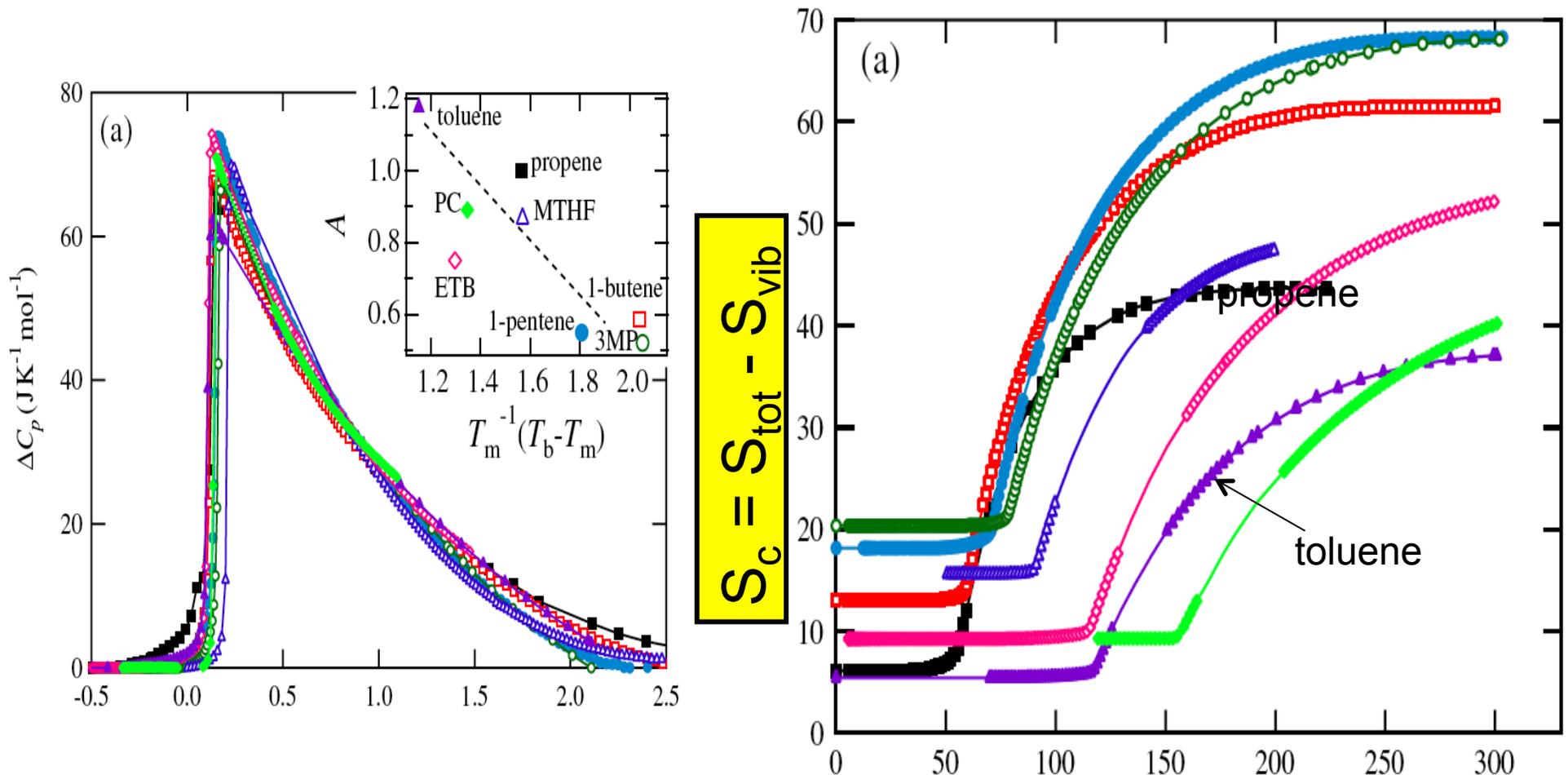
Kinetics saving thermodynamics ??????
20-30% of ΔS_f is residual.

Possible definition of the *ideal glass* would be $S_{ex}(T_g) = 0$

And then...

Approach to the Kauzmann temp. for small molecules, fragile liquids

Kawamuro and co-au. PRL **109**, 045701 (2012)

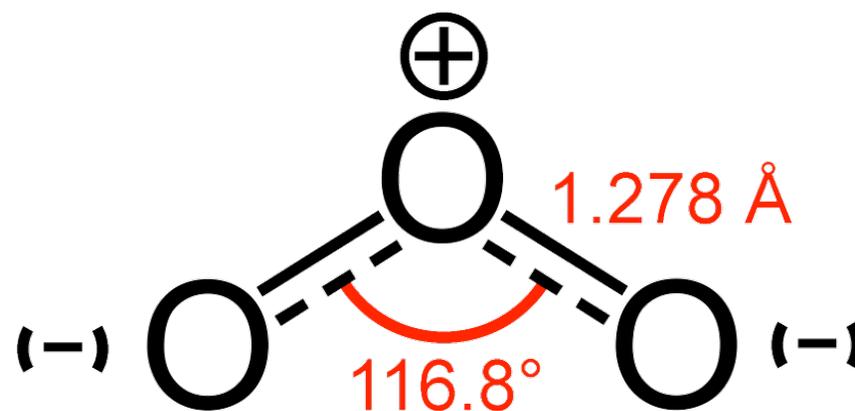
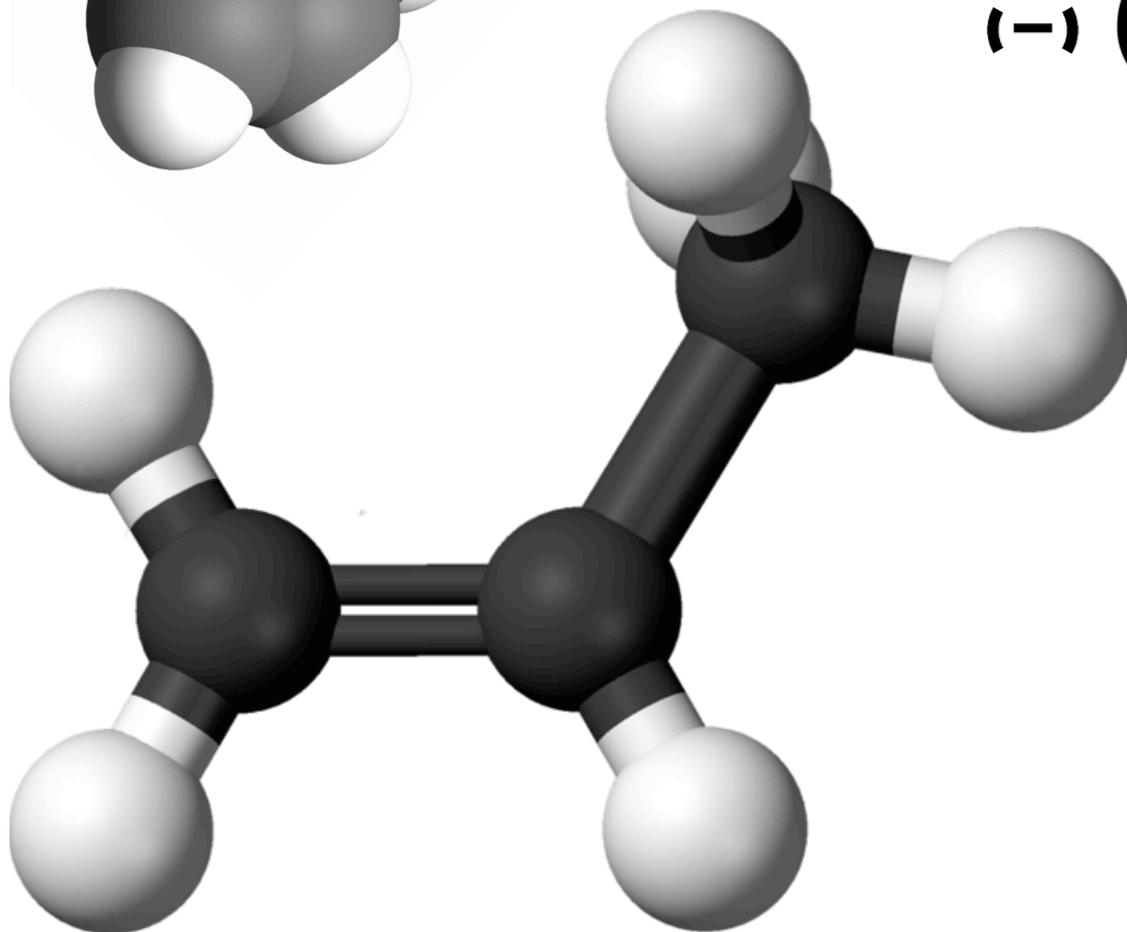
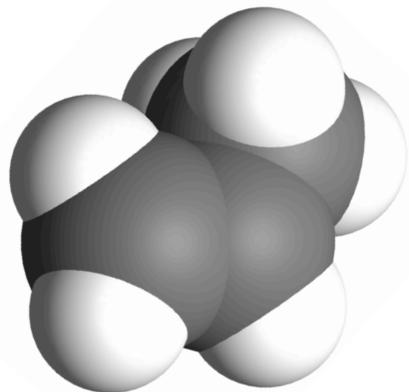


propene

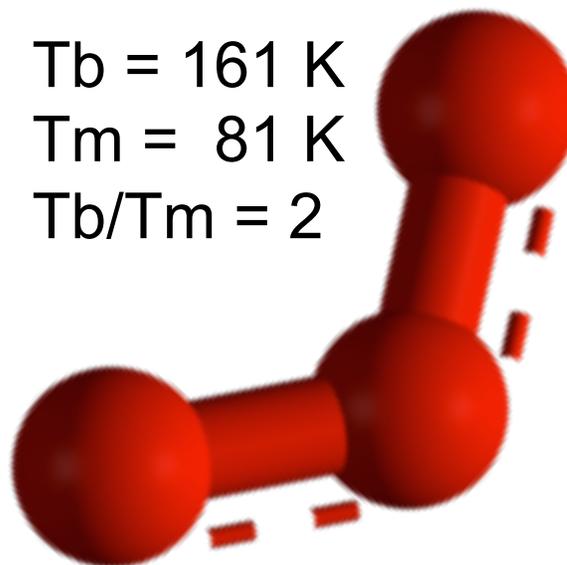
and

ozone

$T_b = 225.6$
 $T_m = 88\text{K}$
 $T_b/T_m = 2.56$



$T_b = 161\text{ K}$
 $T_m = 81\text{ K}$
 $T_b/T_m = 2$

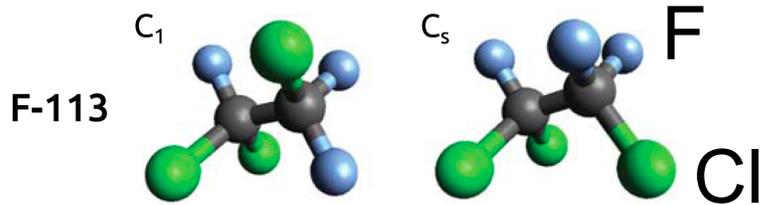


It's not just small molecule liquids near 0K, that are doing this . One of the most dramatic (later call it "fragile") is
 $\text{La}_2\text{O}_3 \cdot 3\text{B}_2\text{O}_3$

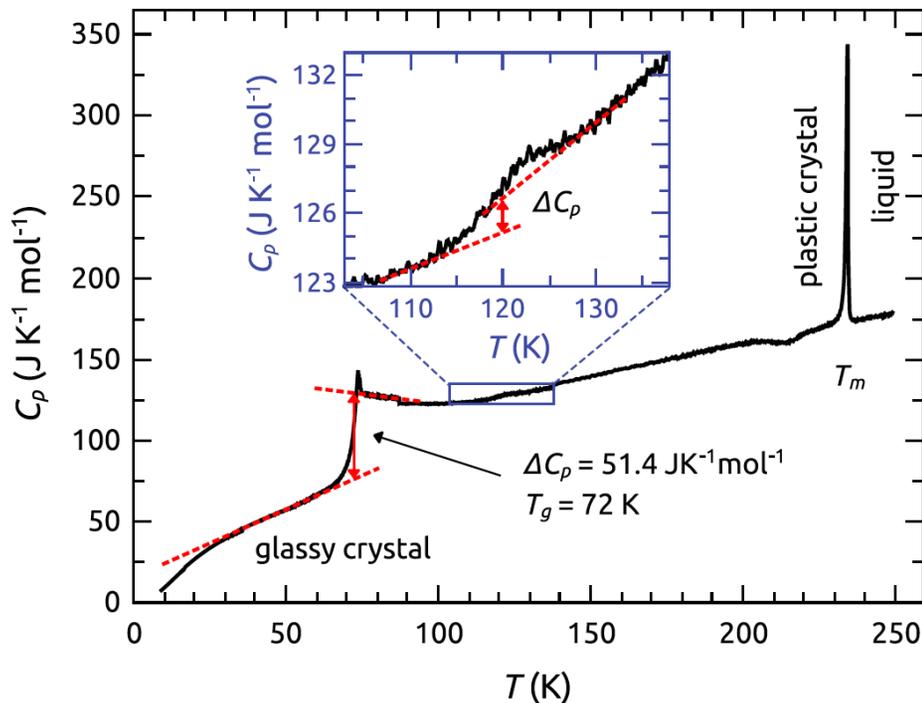
$$T_K \sim 1000\text{K}$$

Two non-liquid cases with T_g

1. Liquid --> PC--> glass.

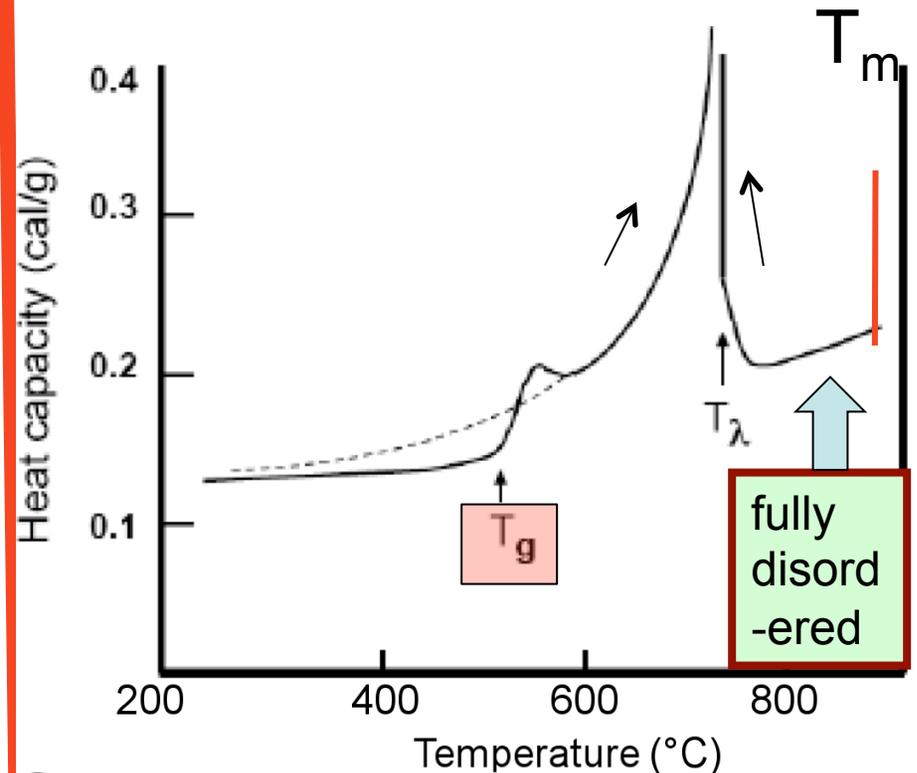


Freon-113



2. liquid --> DOC--> glass

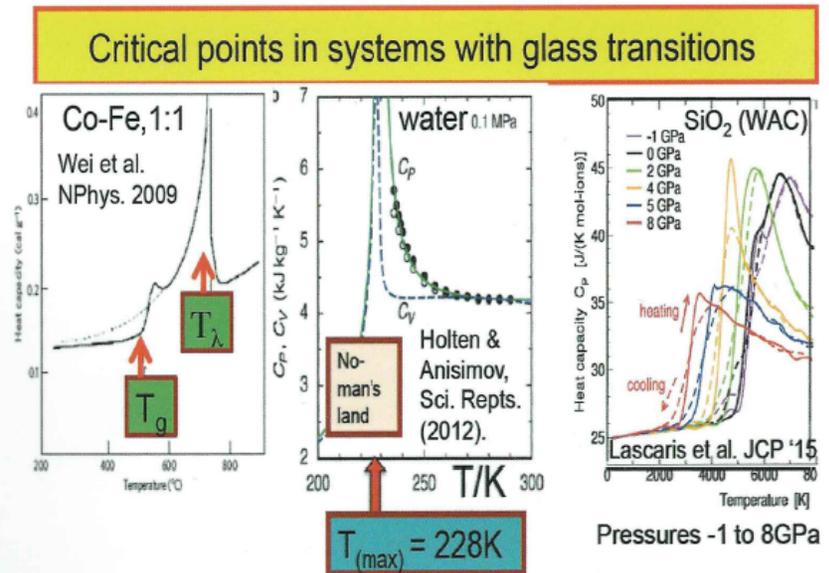
Co-Fe, 1:1 (*high T*, BCC *low T*: two interpenetrating simple cubic lattices)



Special
issue cover,
to my
surprise

PHYSICS AND CHEMISTRY OF GLASSES

European Journal of Glass Science and Technology Part B



Arizona, on the way to GC from ASU

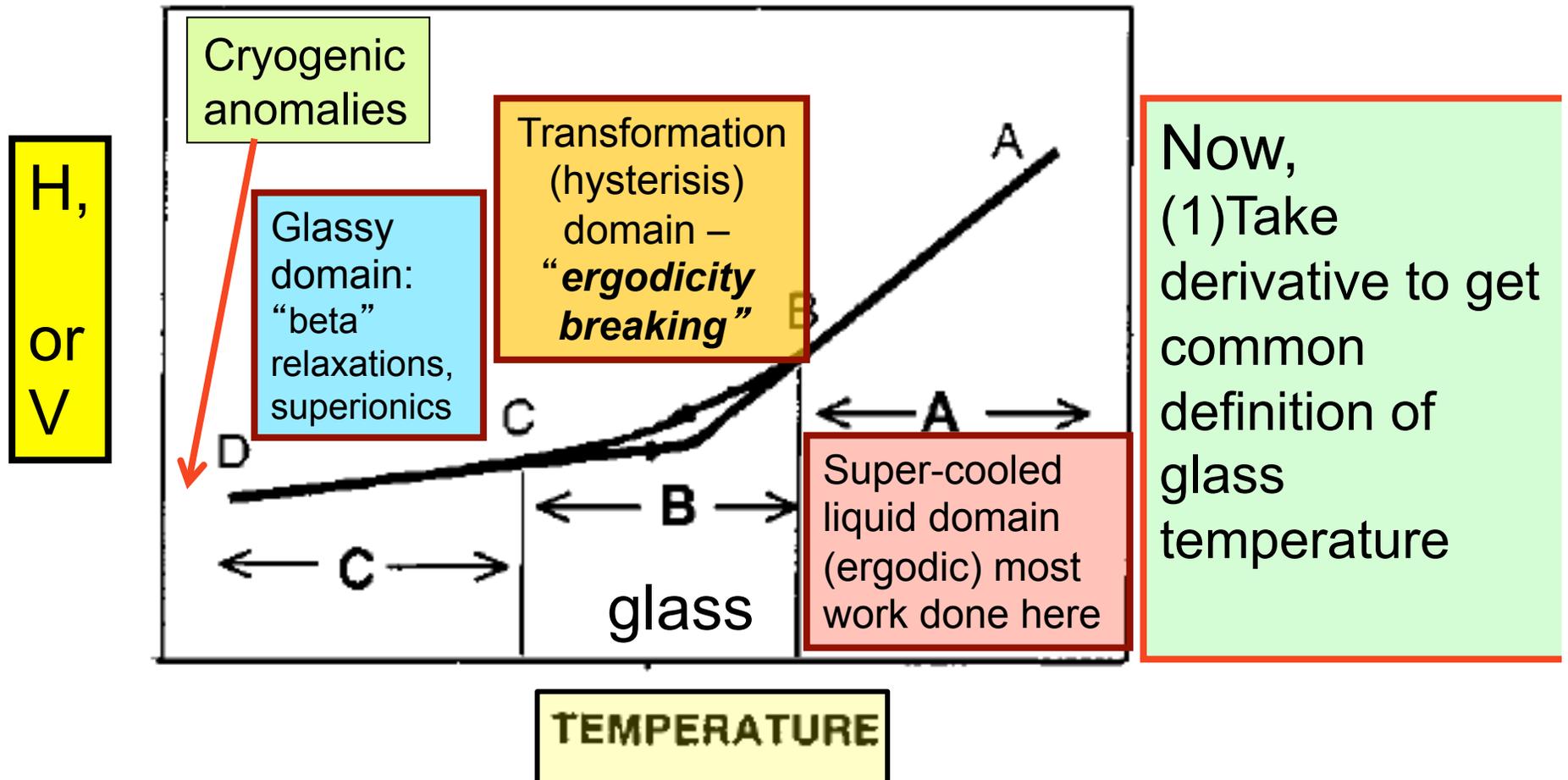


The three principal behavior domains for glassformers

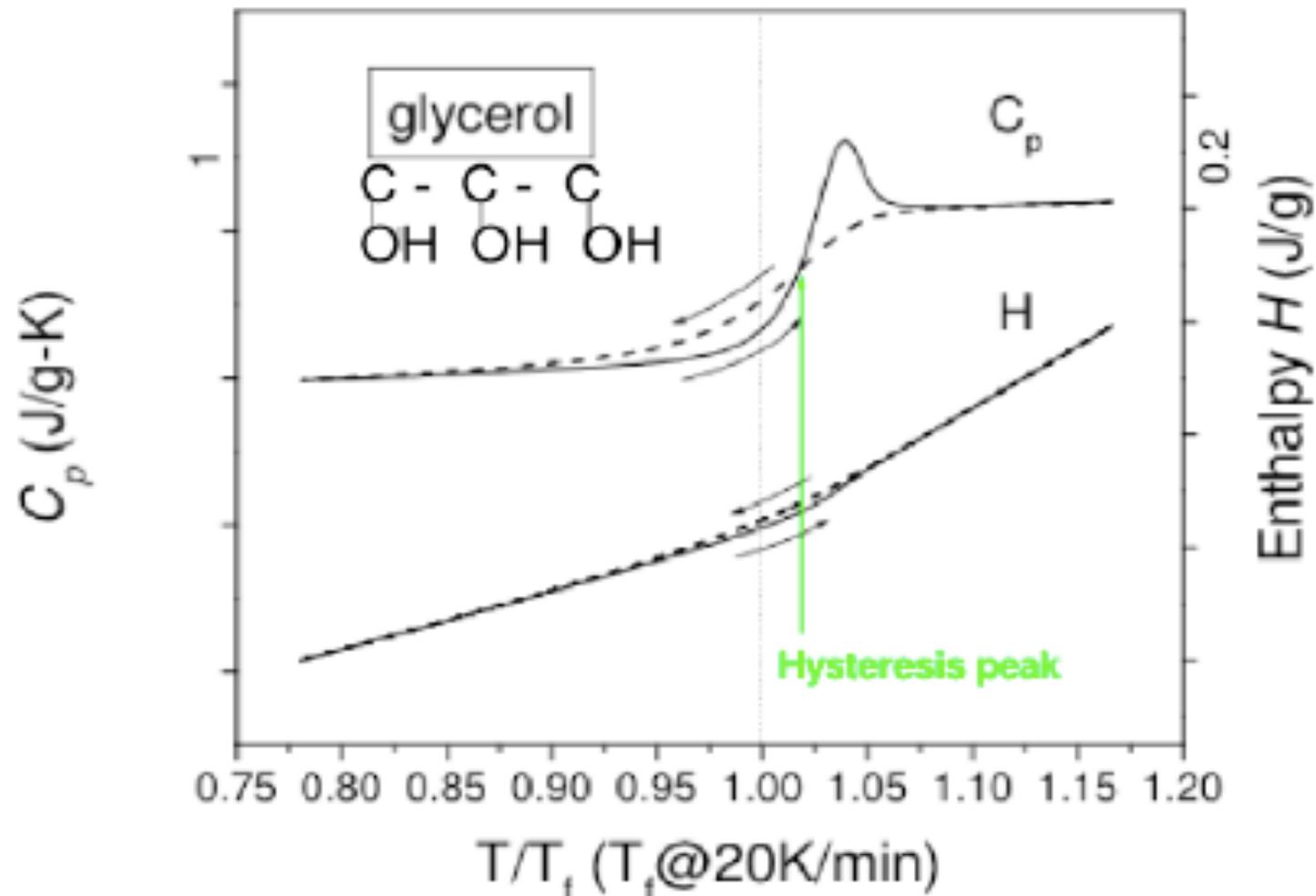
J. Appl. Phys.

Vol. 88, No. 6, 15 September 2000

Classic diagram- 3 domains



Take the derivative of the heating scan and we obtain the heat capacity usually used to define ***the glass transition (seen earlier)***

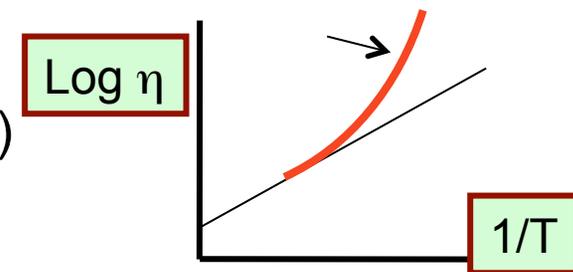


Now, the three “nons” of Domain A (all linked)

1. **Non-Arrhenius:** Except at very high temperatures, nearly all glassforming liquids (“glassformers”) fail to follow the familiar Arrhenius relations for time-dependent processes (viscosity etc).

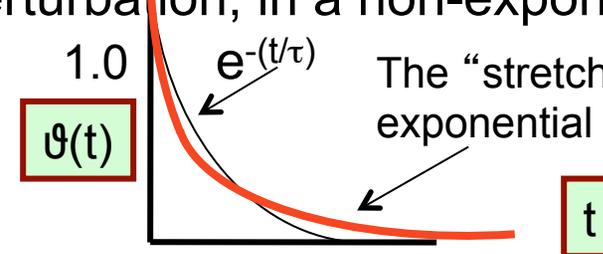
i.e. **not** $\eta = \eta_0 e^{-E/RT}$ **but** $\eta = \eta_0 e^{-B/(T-T_0)}$ with $(T_0 = T_K)$

BEST $\tau = \tau_0 \exp(-C/TS_c)$ (Adam-Gibbs equation)
(JCP 1965) and S_c varies with temperature



2. **Non-exponential:** Except at very high temperatures, nearly all glassformers relax to equilibrium, after a perturbation, in a non-exponential manner,

i.e. **not** $\vartheta(t) = e^{-(t/\tau)}$, but $\vartheta(t) = \exp[-(t/\tau)^\beta]$



3. **Non-linear** (for relaxation near T_g where S_{ex} is changing with time as $\vartheta(t)$ is being measured) (Thermo state dependence of relaxation time).

$\tau(\tau) = \tau_0 \exp(-C/TS_c(t))$ at constant T in the transformation zone (Domain B)

Iguassu (Brazil, Argentina)



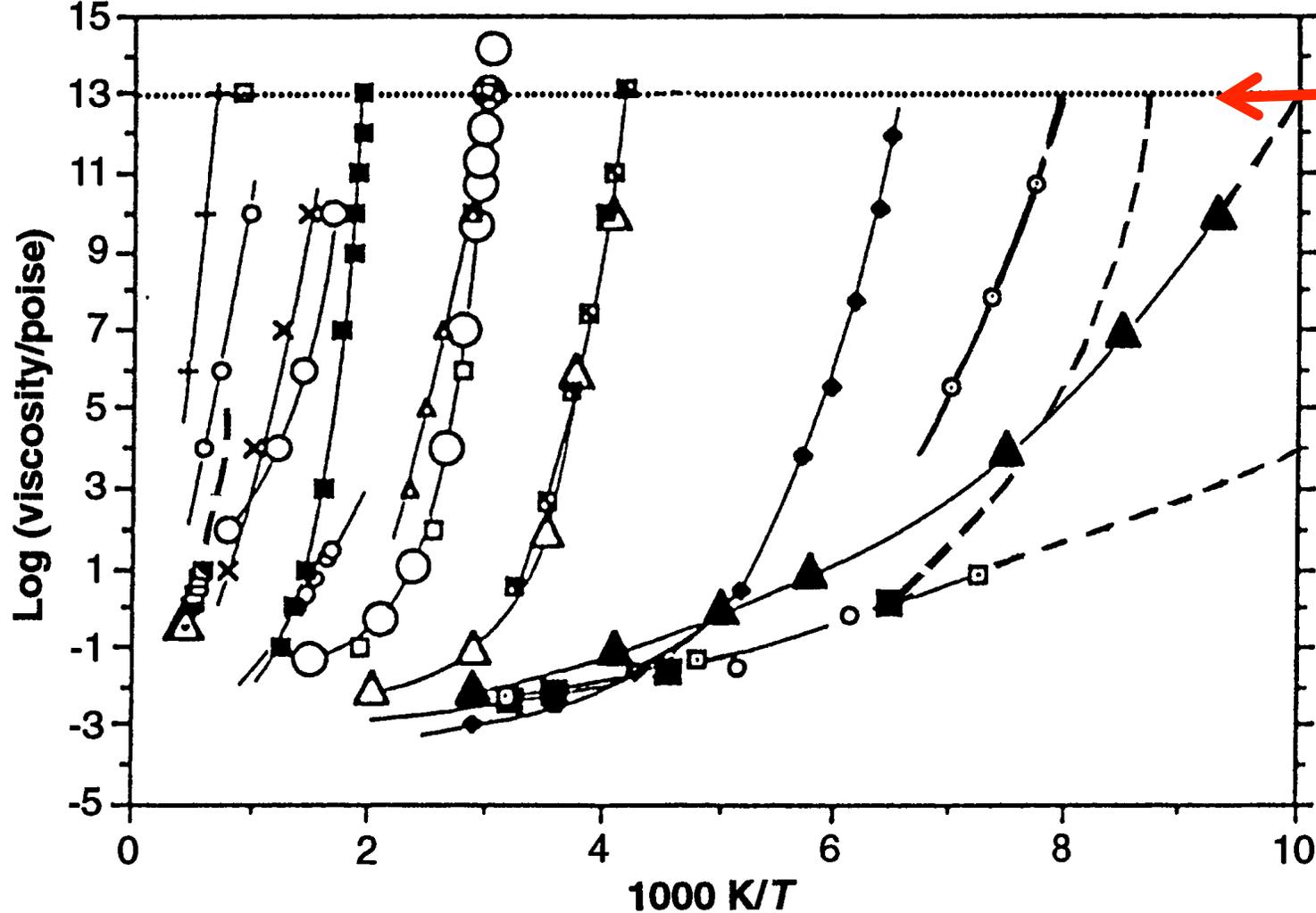
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- D. Gels: fragile and tough,

The viscosity (or relaxation time) for liquids of many types, silicates, molten salts, molec. liquids

Arrhenius, non-Arrhenius, VERY non-Arrhenius etc....

a mess. WOT to do?



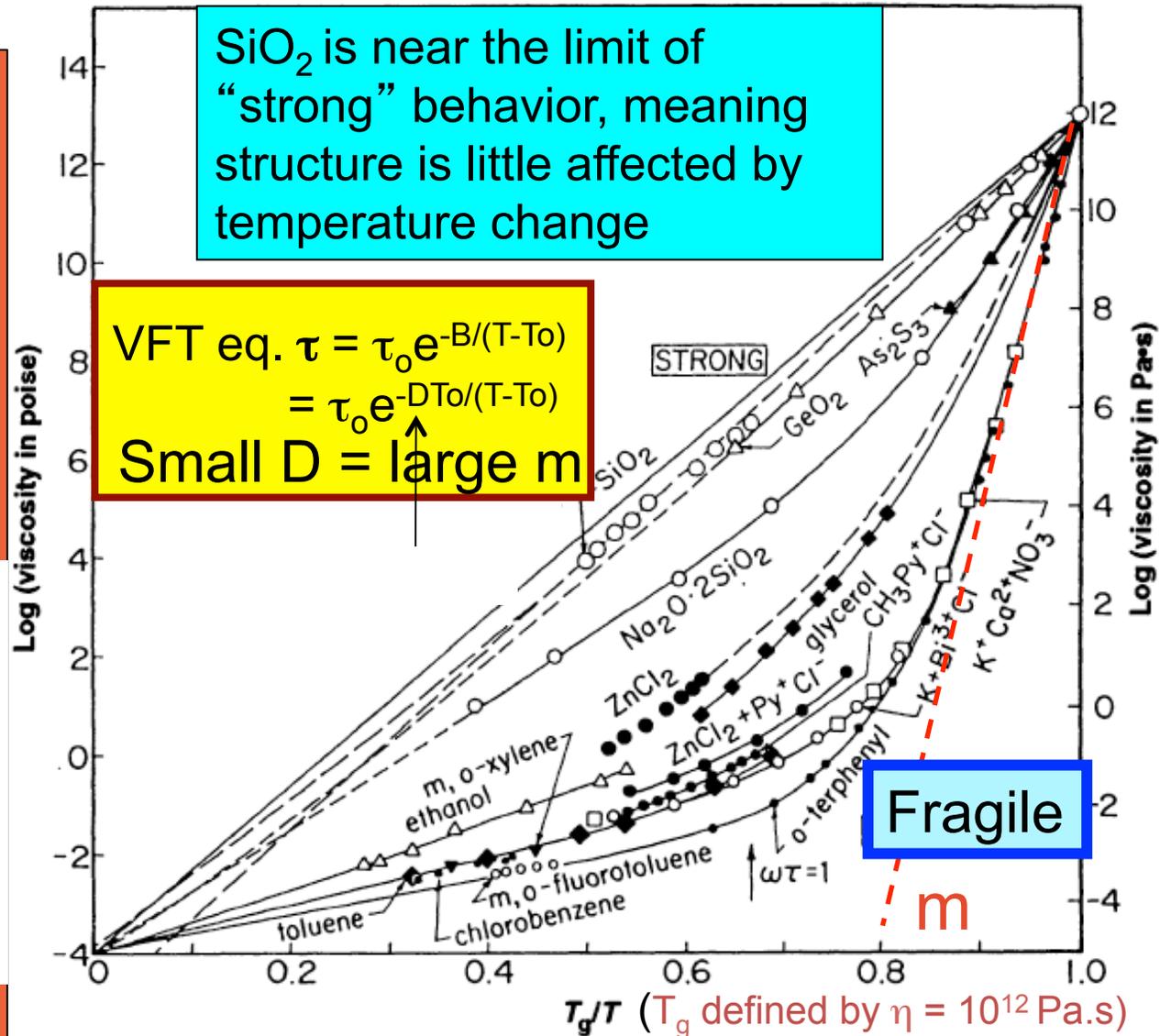
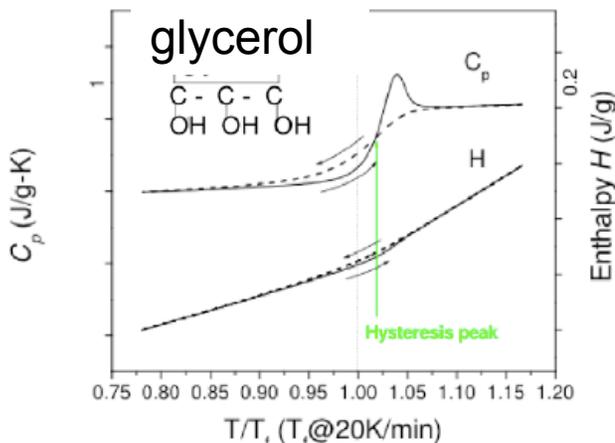
Value typical of the T_g

Now, scale $1/T$ by T_g i.e treat T_g as ref. state.

First step, scale the viscosity data, using T_g ($\eta=10^{13}$ p) as scaling temp, to see pattern

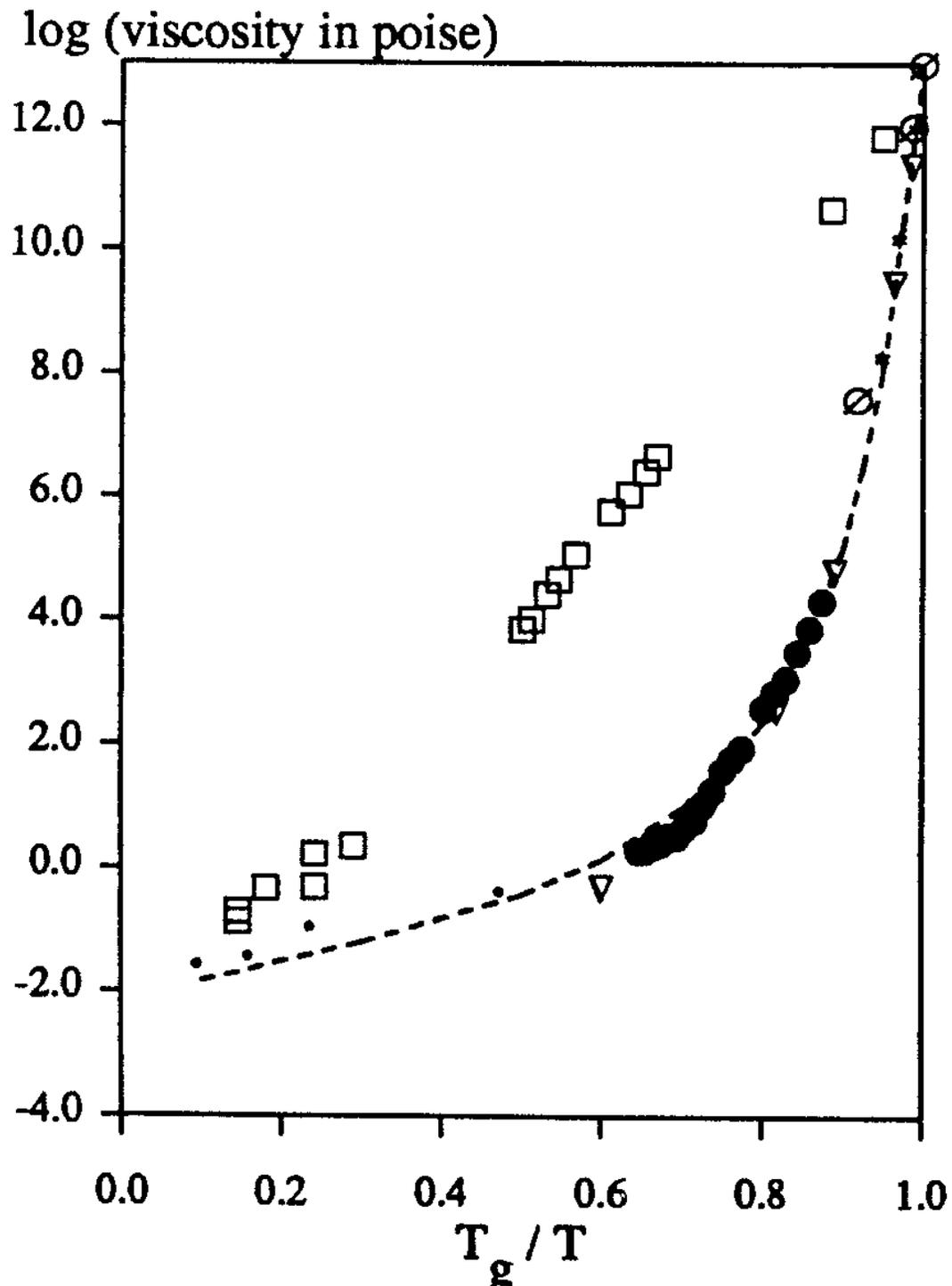
Glass transitions

At $T_g/T = 1$?
(more or less) -
the heat capacity
"jump"





Carol Scamehorn,
Don List
Purdue University



Major question: what determines the departure from Arrhenius behavior? Or, what makes a liquid fragile?

Adam-Gibbs theory for relaxation times

$$\tau = \tau_0 \exp C/TS_c$$

$$\text{where } S_c = \int \Delta C_p d \ln T$$

Suggests it's all in how the entropy is “crashing”, or probably better looked at, the way the entropy is being generated as S rises above that of some ideal glass state

Indeed, we find the same pattern for **entropy**
generation above T_g

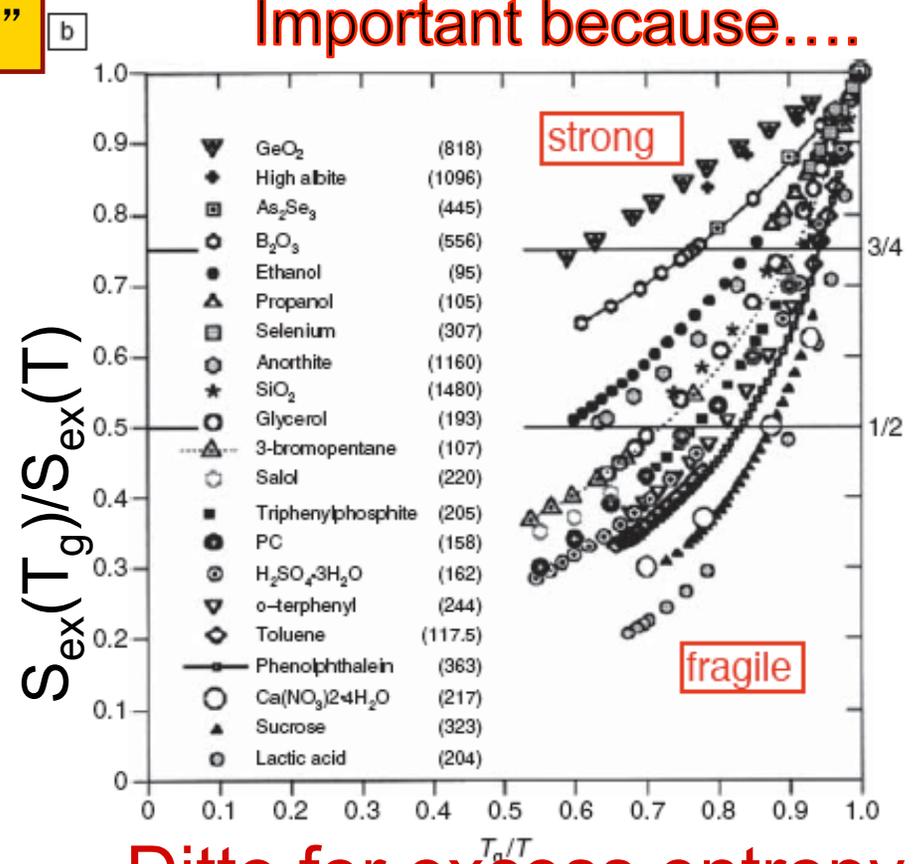
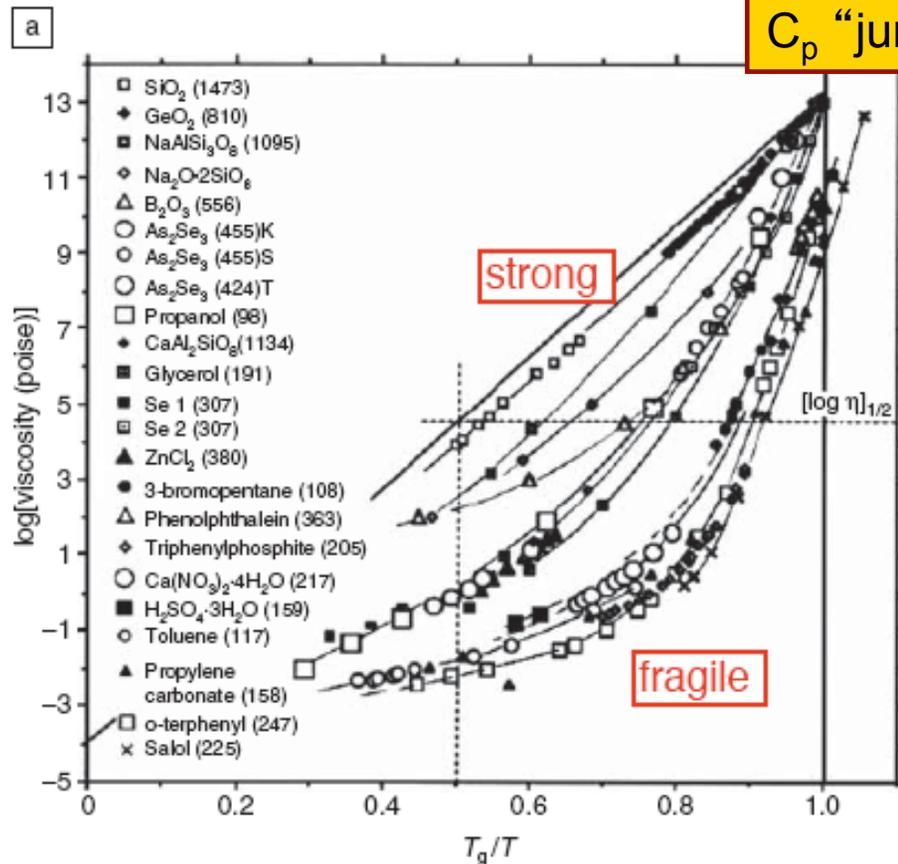
The liquids shown, and their ordering, are the same

Dynamics (viscosity)

T_g now
from T of
 C_p "jump"

Thermodynamics (entropy)

Important because....



Ditto for excess entropy

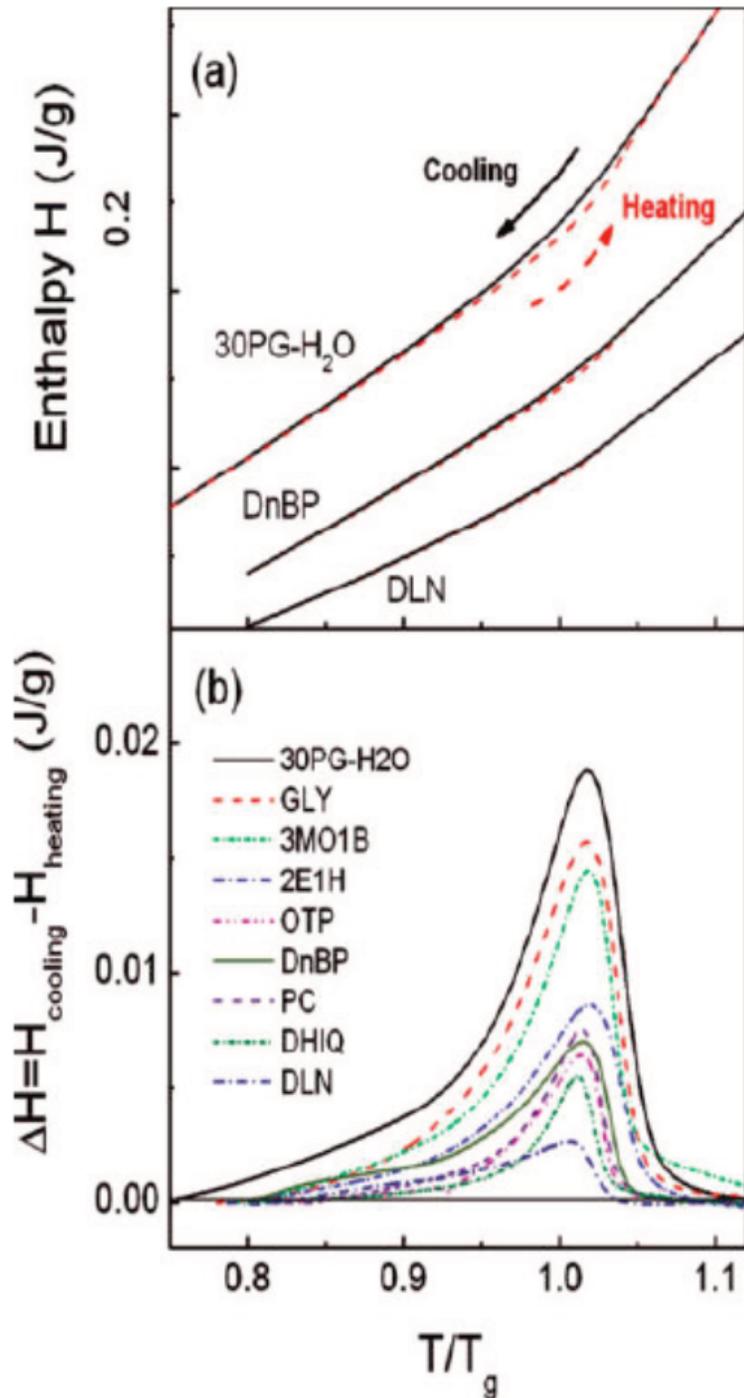
Martinez and CAA, Nature, 2001

Hysteresis peaks and fragility

(after Li-min Wang)

J. Phys Chem.

At the limit of high fragility, it thinks to a point and becomes a first order transition where all the entropy is lost at single temperature.. That is the hall-mark of a first order transition



How to understand fragility, and fragility differences ?

How is entropy generated? By excitations: "populating the landscape"
Excitations of what?

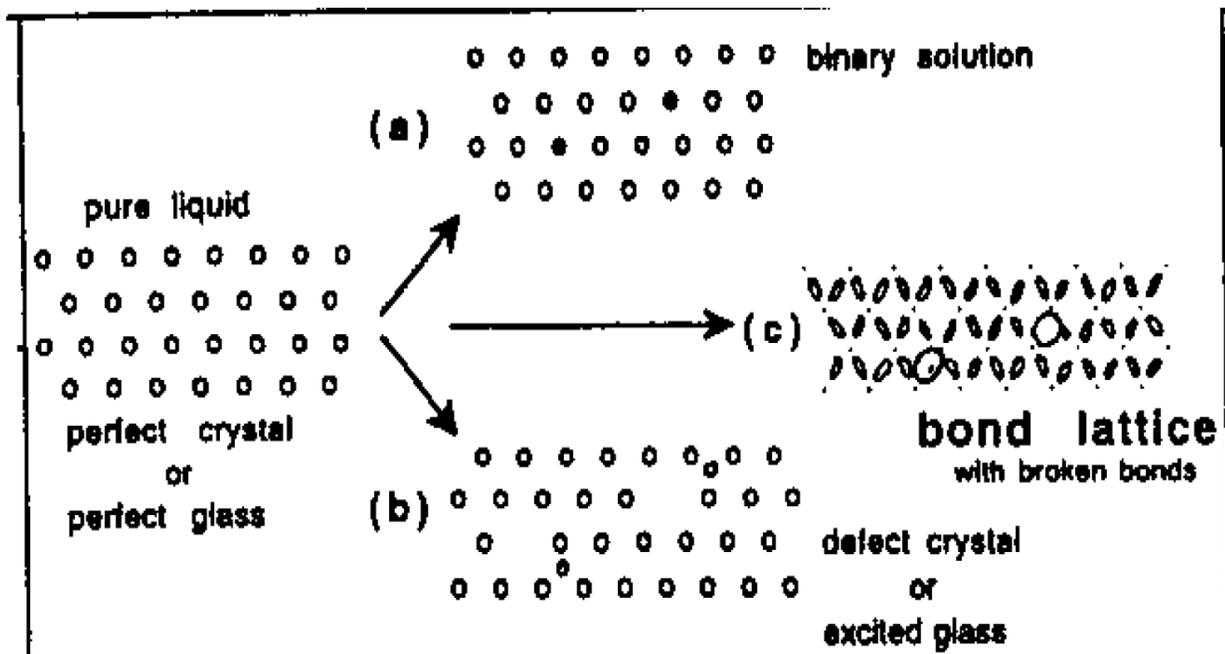
*Crystals or glassy **solids** we know – "phonons"*

*Liquids we don't know – let's say "**configurons**" (Michael O. uses it,*

plastic crystals, we sort-of know "collective orientons"

Co:Fe –like solids, we know –atomic site exchanges

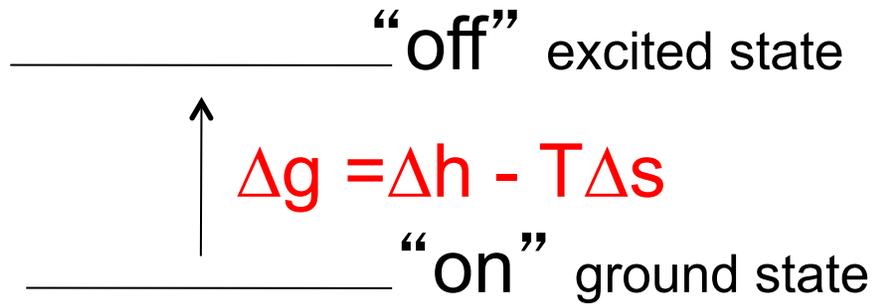
Transform particle lattice to "bond lattice"



"bonds"
have two
states, "on"
or "off".

"Two state"
models are
very simple

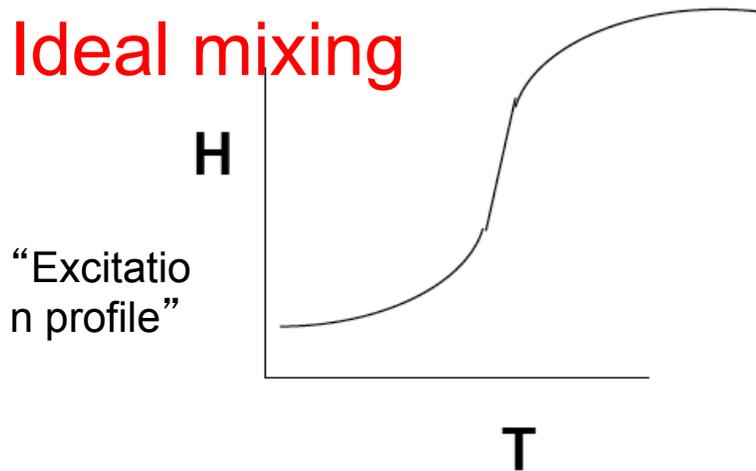
two state model “excitation profiles”



With strong **clustering**, profile develops a van der Waals loop, and the instability is relieved by a first order liquid- to-liquid transition. Since the entropy then changes discontinuously by a large amount, the diffusion coefficient will change by orders of magnitude and the transition will actually be a liquid-to-glass

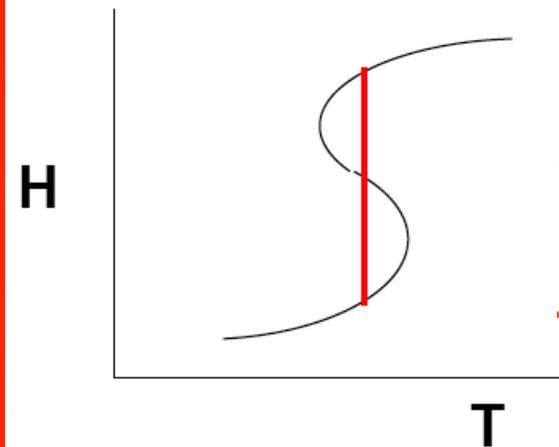
Analogous to Mauro constraint-breaking

Ideal mixing



- (a) **Simple “sparse” (Chandler) i.e.**
- (b) **Ideal mixing of normal sites and excitations (trivial thermo) 2-state**

Non-ideal mixing



Also seen in simple defect models with non-ideal (regular solution) mixing

Liquid-liquid transition

- (a) **Cooperative excitations (excitations cluster), or**
- (b) **Gaussian excitations, stabilized by disorder**

Major question: what determines the departure from Arrhenius behavior? Or, what makes a liquid fragile?

Adam-Gibbs theory for relaxation times

$$\tau = \tau_0 \exp C/TS_c$$

where $S_c = \int \Delta C_p d \ln T$

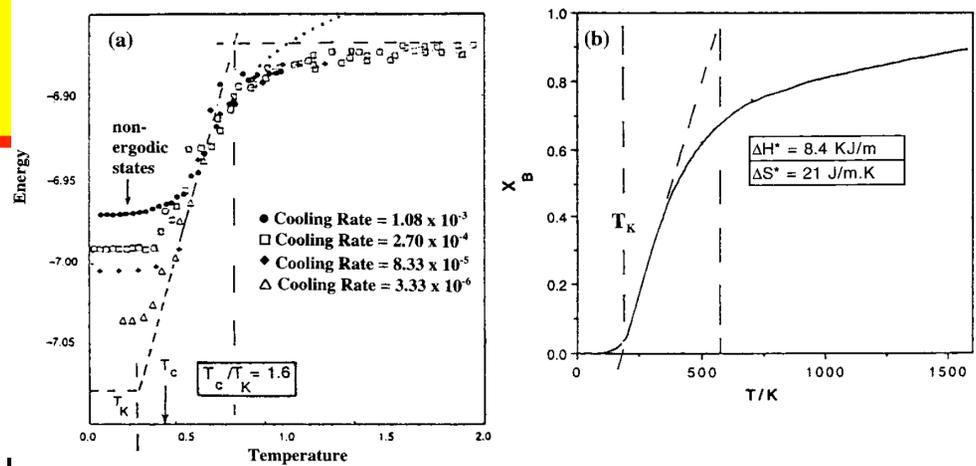
Suggests it's all in how the entropy is “crashing”, or probably better looked at, the way the entropy is being generated as S rises above that of some ideal glass state

, now, also, CAA & K.J. Rao (1972)

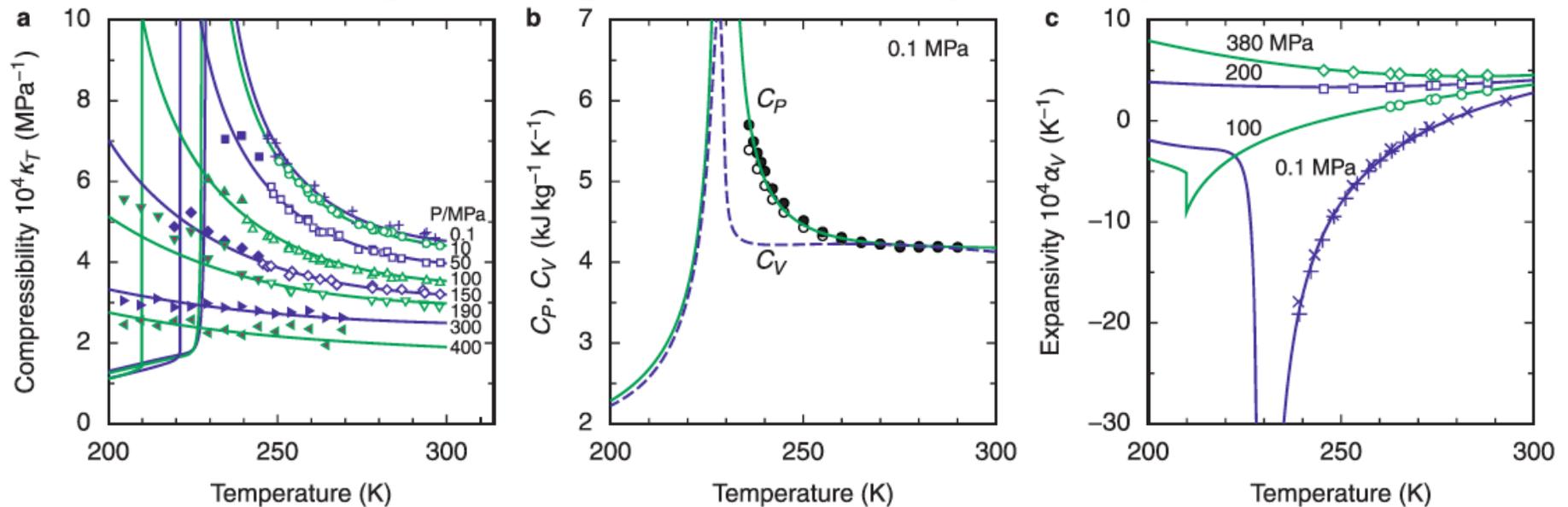
$$\eta \sim W(T) = A_W \exp\{1 + \exp[(\Delta H - T\Delta S)/RT]\}, \quad (12)$$

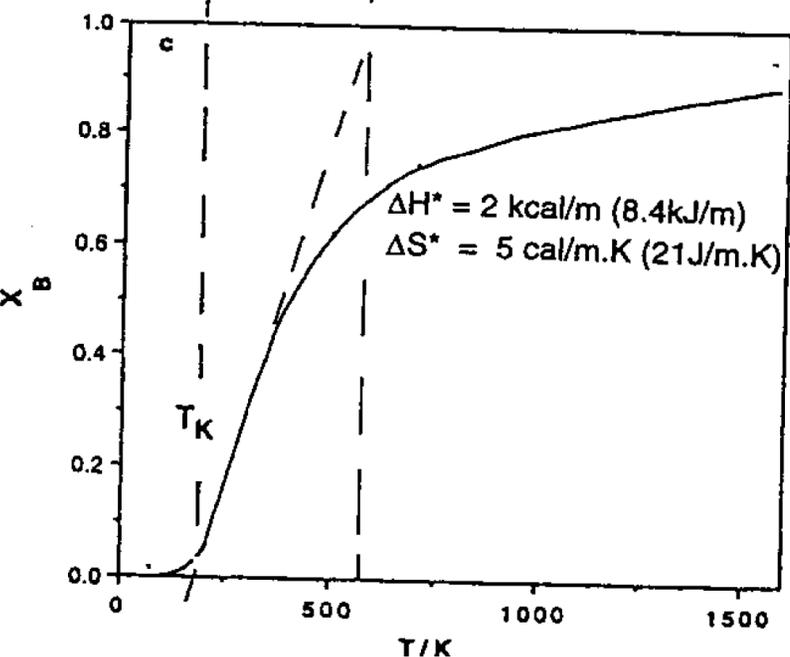
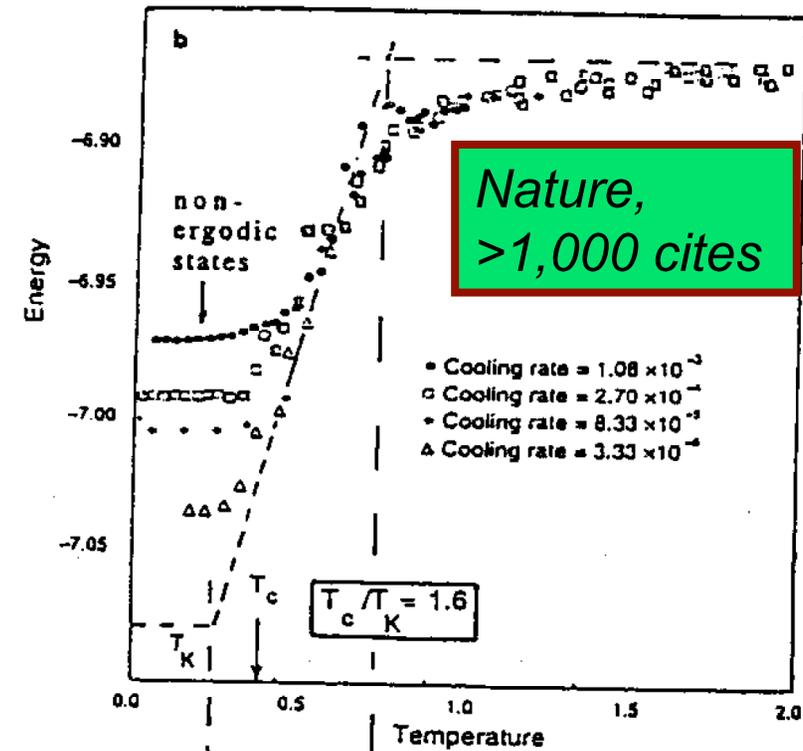
Don't doubt the power of two state models !

Simple ideal mixing cases
(and next slide)



and with one more parameter, complex cooperative cases like water
1965 Strässler and Kittel, **JCP** and
Holten and Anisimov for water in **2017 Scientific Reports**
(perfect agreement with experiment)





Binary mixed Lennard-Jones model (computer simulation) has excitation profile of two-state model.

The steeper the profile the more fragile the liquid. Steepness is determined by Δs parameter

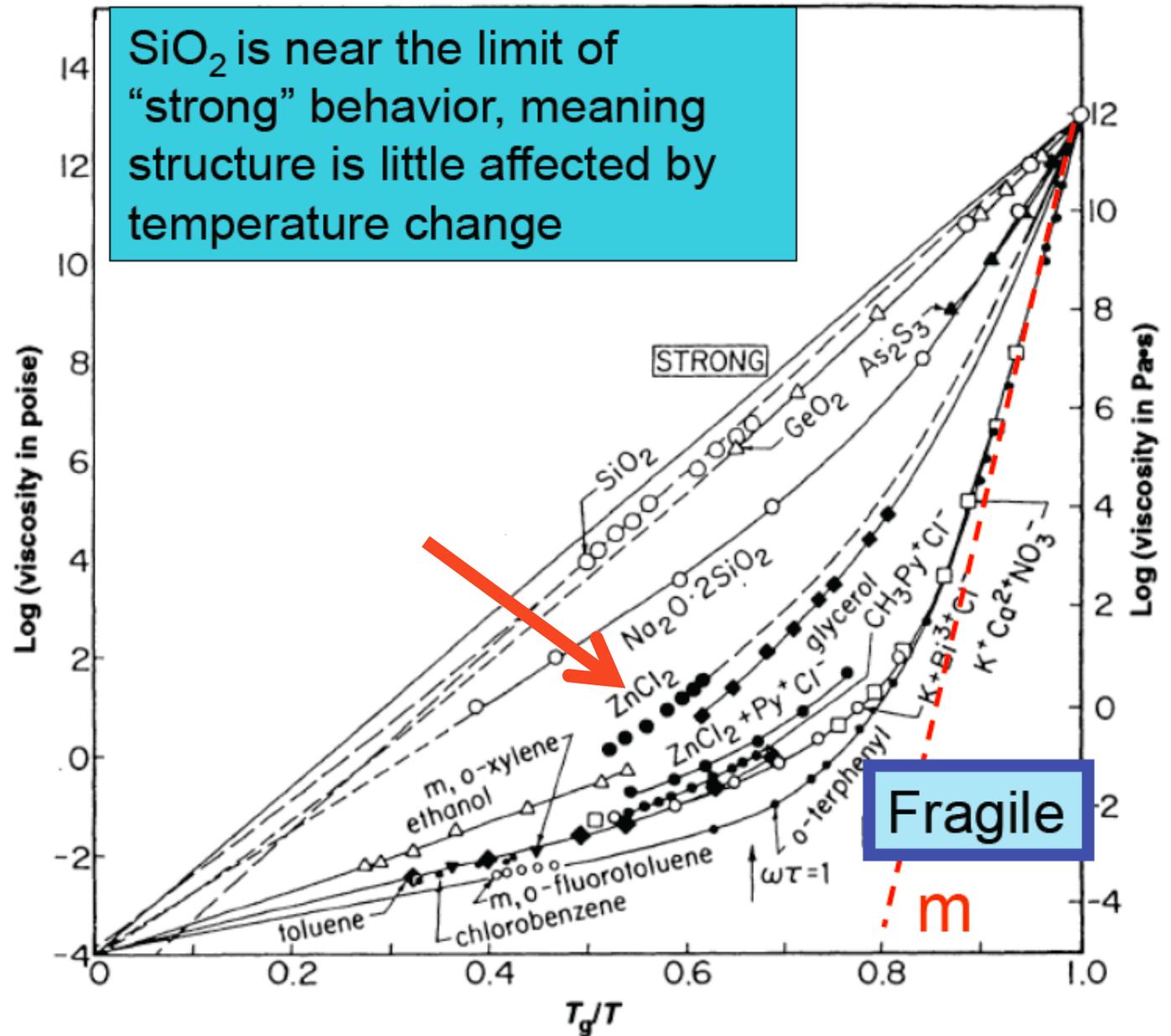
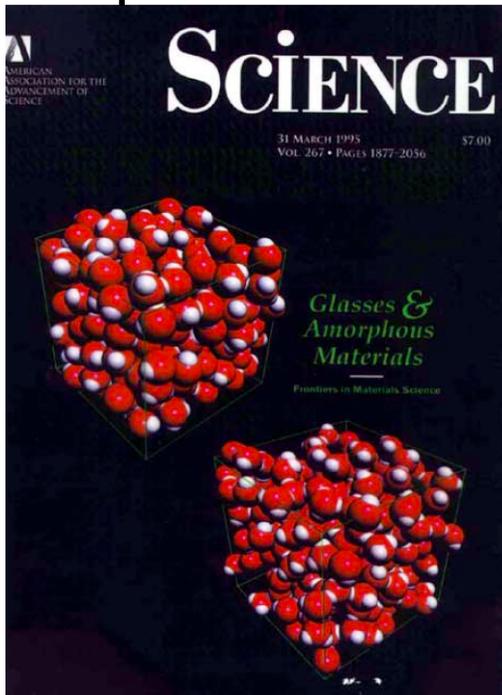
So then

Can we “see” bond defects” in glasses?

In special cases, yes, e.g. ZnCl_2 tetrahedral network with $\text{C}\equiv\text{N}^-$ probe anions

Pure ZnCl_2 , an intermediate fragility inorganic liquid

Special issue

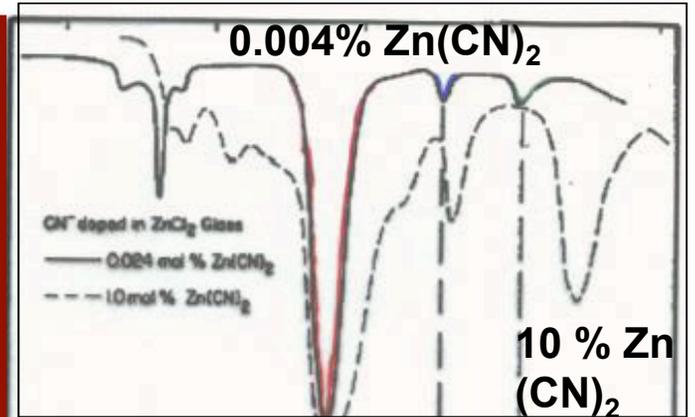


Here's an early attempt by doping a IR signalling ligand (CN-) into an "intermediate" fragility network glassformer, ZnCl₂ (Joe Wong, Purdue U)

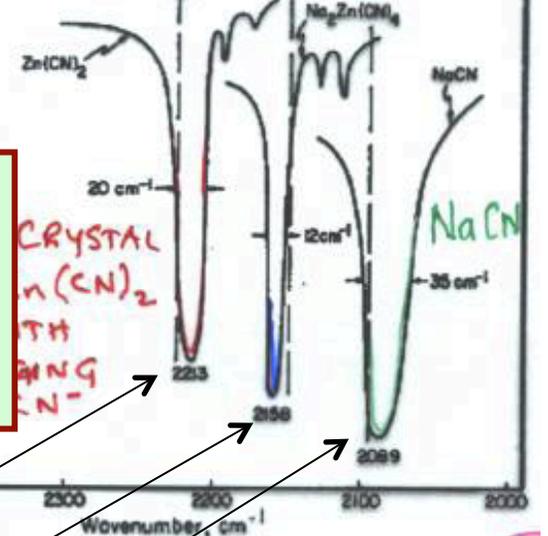
JCP 1976

Fingerprint, using crystals, Zn(CN)₂, "bridging" NaCN "free" etc

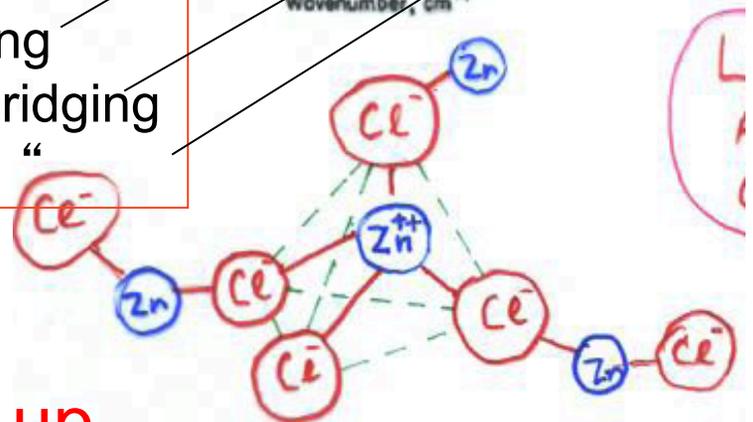
Glass Doped with CN- (J.Wong)



Crystals with different Zn-CN bond states



Bridging Non-bridging and "free"

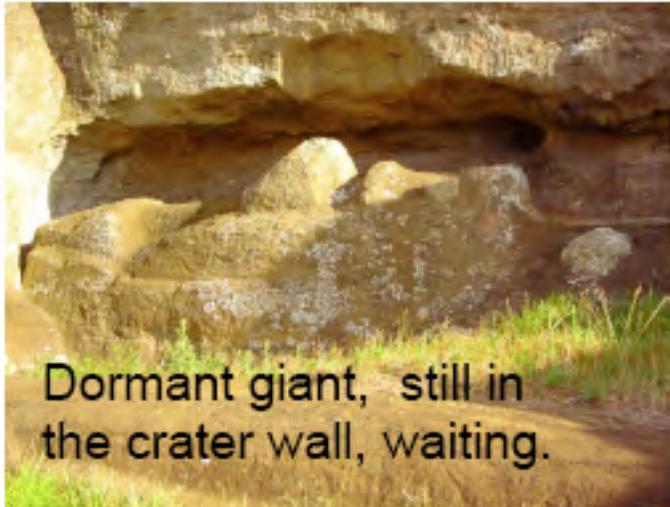


This deserves a follow-up

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Silent watch over Easter Island



Dormant giant, still in the crater wall, waiting.



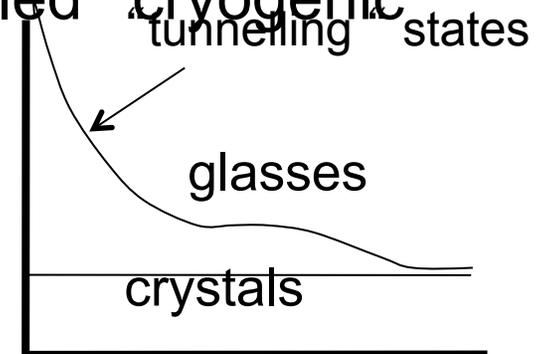
Another major mystery.
How did they move them?

Same as thinking about the criteria for the ideal glass,
(other than $S_{ex} = 0$)

(All based on observations made in the glassy state,
and mostly also first reported for a-water)

1. Absence of “two level systems” (also called “tunnelling systems”),
thought “ubiquitous” to glasses - also called “cryogenic anomalies”

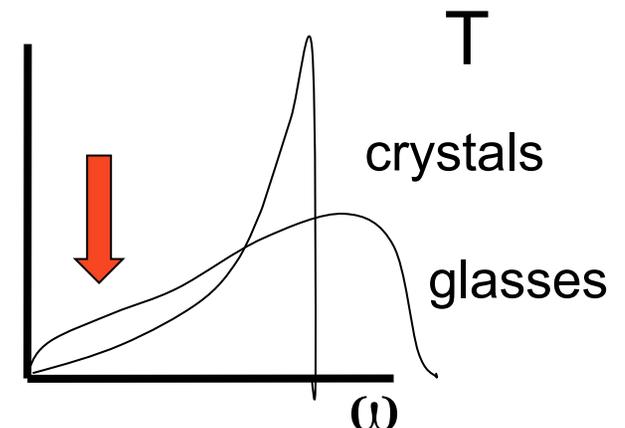
C_p/T^3
(Debye theory)



2. Absence of boson peak

An excess in the density of vibrational
density of states, over Debye theory,
Very low frequencies typically $10-20 \text{ cm}^{-1}$

$g(\omega)$



(You can think of these both as defect signatures
- absence means “defect-free” glass)

Searching for the origin of fragility in the excitation parameters (predicting the boson peak from the fragility)

$$\Delta g = \Delta h - T \Delta s$$

$$\Delta S = 5 \text{ cal/mol is fragile}$$

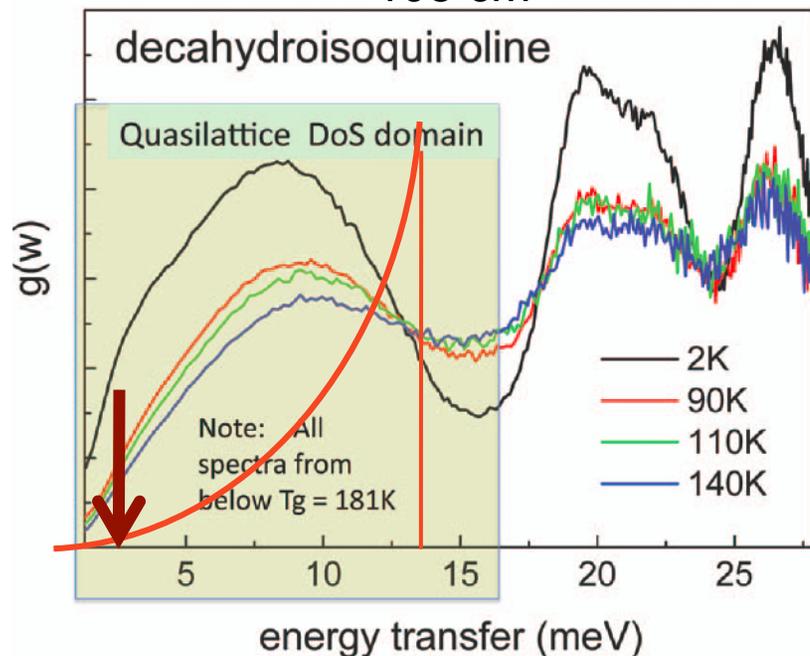
$$108 \text{ cm}^{-1}$$

Let's try $\Delta s = R \ln (\nu_1/\nu_2)$ because, next to a defect in a crystal, there are low frequency localized modes generated (due to unbalanced forces). On excitation, high frequency Debye mode is replaced by a low frequency Einstein mode.

CAA&CTM (MetMatTrans (2000))

$$\nu_2 = \nu_1 \exp (-\Delta S^*/R) \quad [4]$$

To obtain the approximate range of ν_1 , we use the observation that T_K (or the Vogel-Fulcher-equation T_0 parameter) $\sim T_{\text{Debye}}$ [28,29,30] and write $\nu_1 \sim k_B T_K/h \approx 140 \text{ cm}^{-1}$, from which, with $\Delta S^* = 5 \text{ cal/mol} \cdot \text{K}$, ν_2 should be in the vicinity of 10 cm^{-1} . Thus, the new vibrational modes should be found in the very-low-frequency vibrational density of states, at or below the much-discussed boson peak. Indeed, there is strong evidence



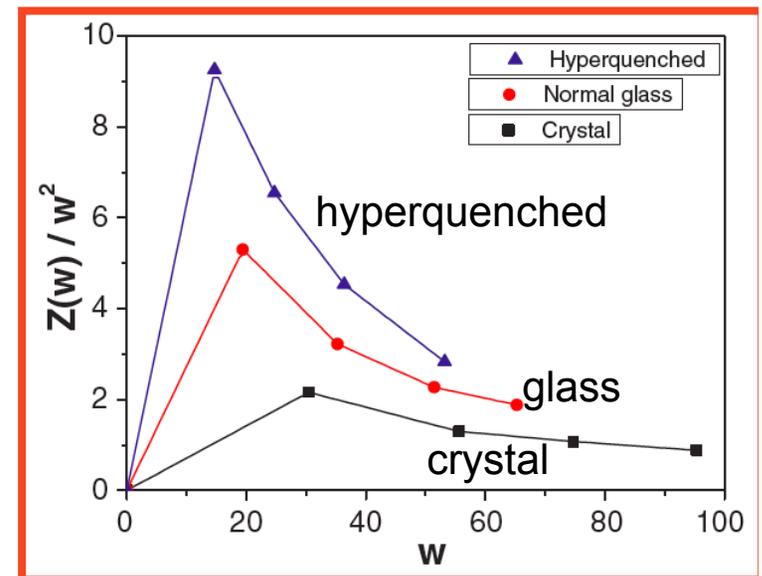
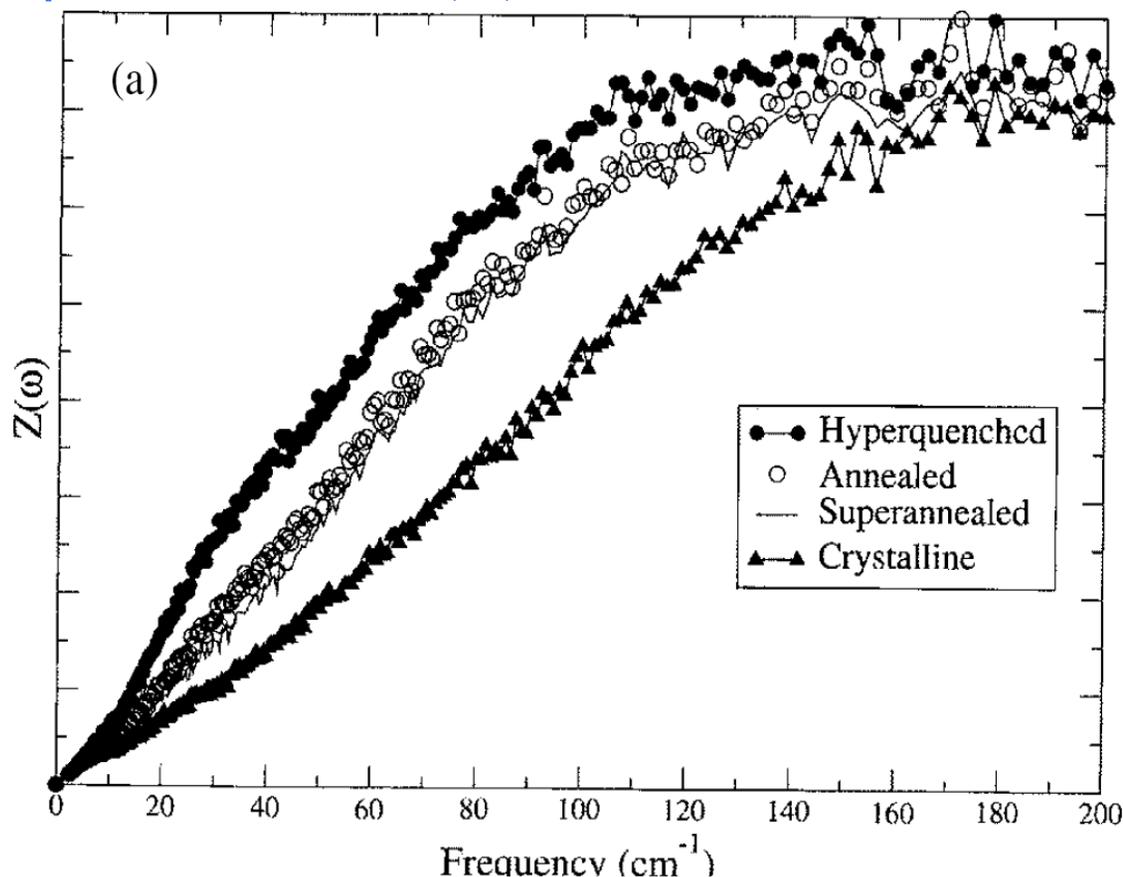
$$\nu_1 = 13.5 \times 8.0(\text{cm/meV}) = 108 \text{ cm}^{-1},$$

$$\text{So } \nu_2 = 108 \exp -(5-0/1.96) = 108 \exp -2.55108 \times 0.078 = 8,4 \text{ cm}^{-1} \approx 1 \text{ meV}$$

Effect of hyperquenching on the boson peak intensity

Potential energy, relaxation, vibrational dynamics and the boson peak, of hyperquenched glasses Collabn. with Yuanzheng Y

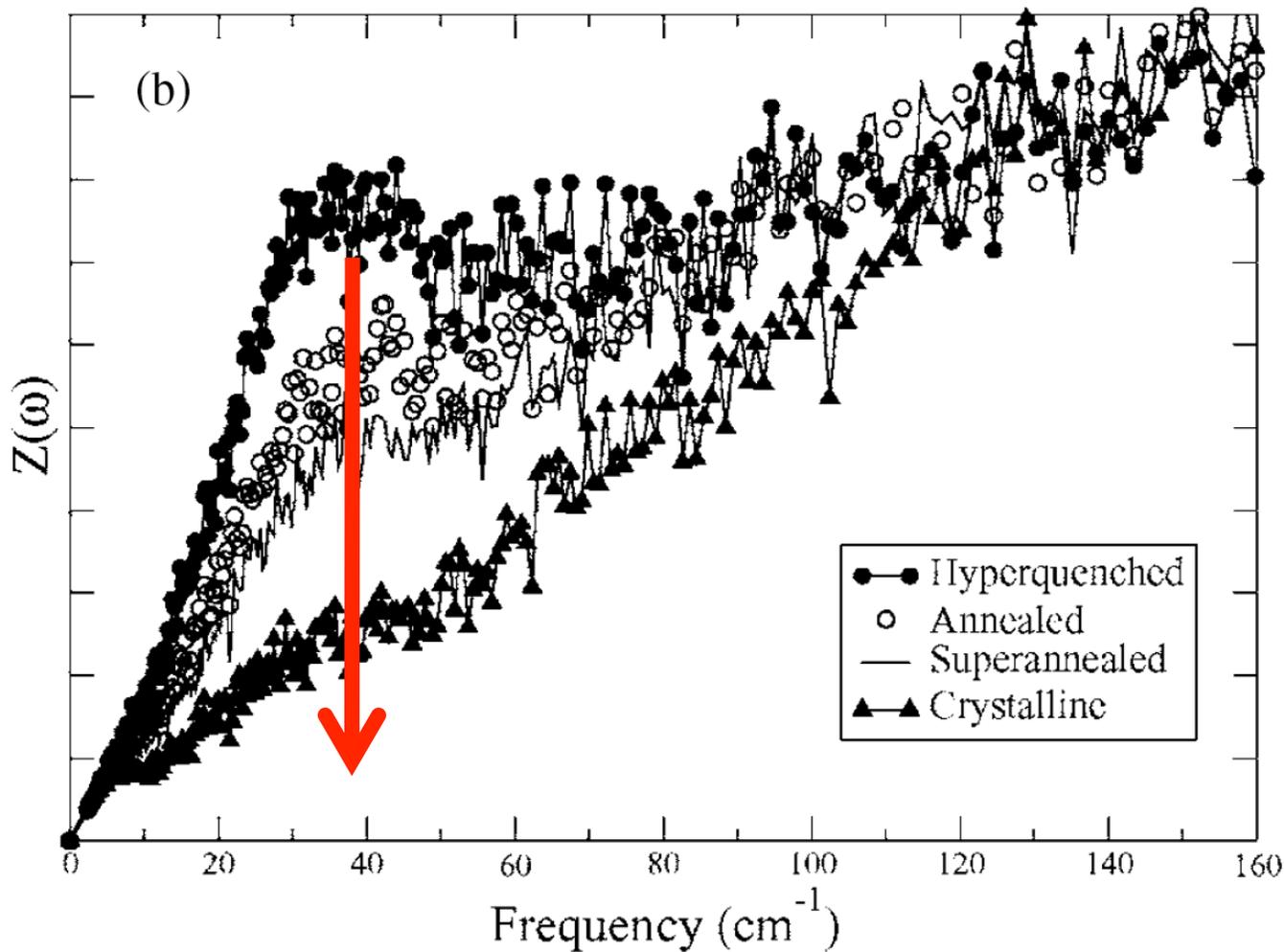
This is total DoS: For boson “peak” need $G(\omega)/\omega^2$



See Thorpe-fest

Alternative is a “restricted q ” Sampling. See next slide for $q = 0.4-0.7\text{\AA}^{-1}$.

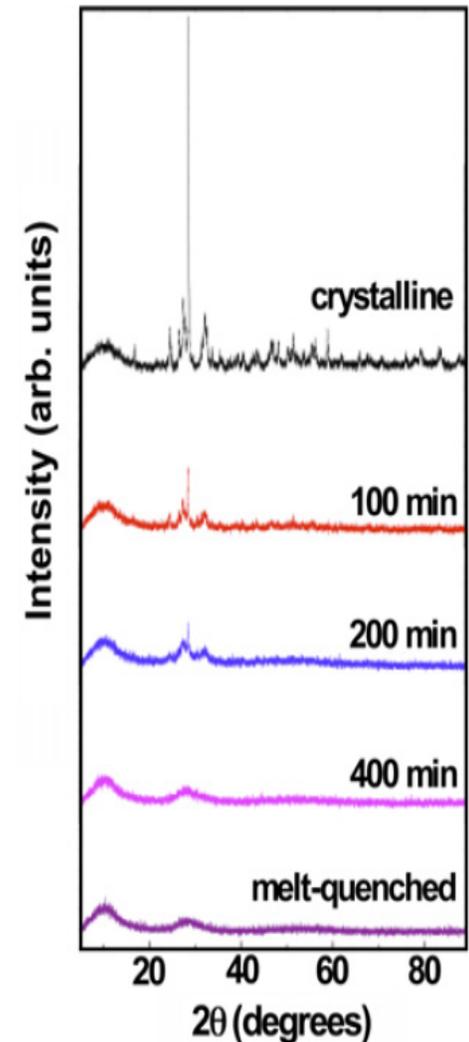
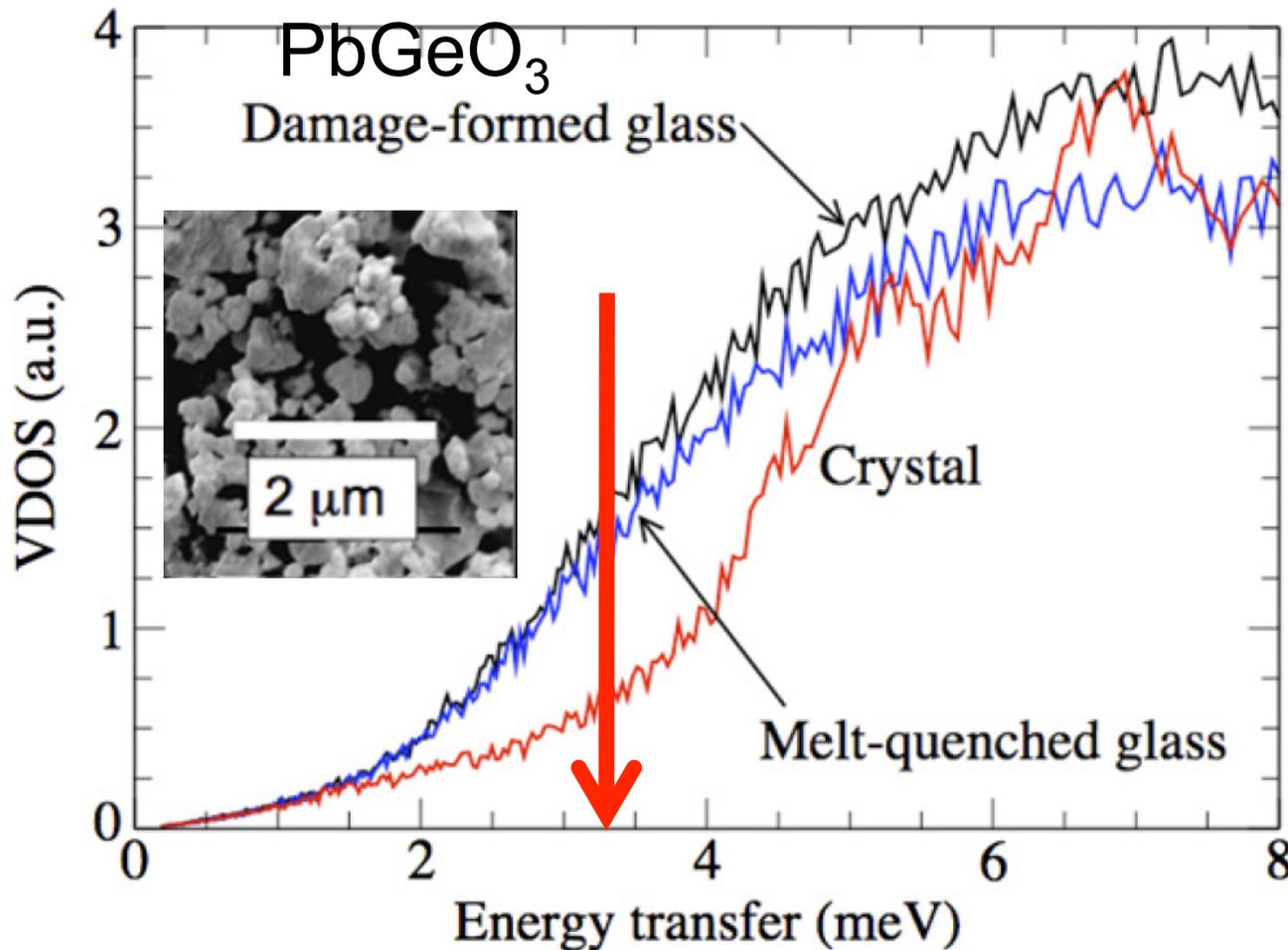
“Restricted q ” sampling, for
 $q = 0.4-0.7 \text{ \AA}^{-1}$.



Implies
dimension of
excitations
being locked in
during
hyperquenching
is of order
 $1.5-2.5 \text{ \AA}$

One more case: low frequency excitations being introduced during mechanical damage, by ball milling

“The Boson peak in Melt-formed and Damage-formed Glasses: a Defect Signature?” Harish Bhat, Inmaculada Peral John R. D. Copley, and C. Austen Angell, *J. Non-Cryst. Sol.*, 352, 4517-4524 (2006)



3×8 or 24 cm^{-1}

Let's try another line, which
actually connects up with what
you just heard

Outline

- A. **STARTING UP**: What is meant by “glass”. How formed? Degrees of freedom. The “entropy problem”, the three “nons”, and the glass transition. Are there “perfect glasses?” glassy water
- B. (a) fragile vs strong liquids. Fragility from thermodynamics. Two state thermodynamics and origin of fragility. Soft spots, defects, configurons, and phase transitions .
(b) Origin of fragility (shocker: it’ s probably in the vibrations)
- C. Other ideas on fragility .(a) The shear modulus, its temp. dependence and the origin of this temperature dependence.
(b) Shear and bulk moduli, infinite and low frequency,
(c) confusion on Poisson ratio of glasses and other materials,
MECHANICAL PROPERTIES OF GLASS-FORMERS (brittle and ductile glasses
-)D. Gels: fragile and tough,

Views on Fragility involving mechanical properties

1. Dyre and coauthors: the “shoving” model

$$\tau = \tau_0 \exp\left(\frac{G_\infty V_c}{k_B T}\right).$$

$$V_c = \frac{2}{3} \frac{\Delta V^2}{V},$$

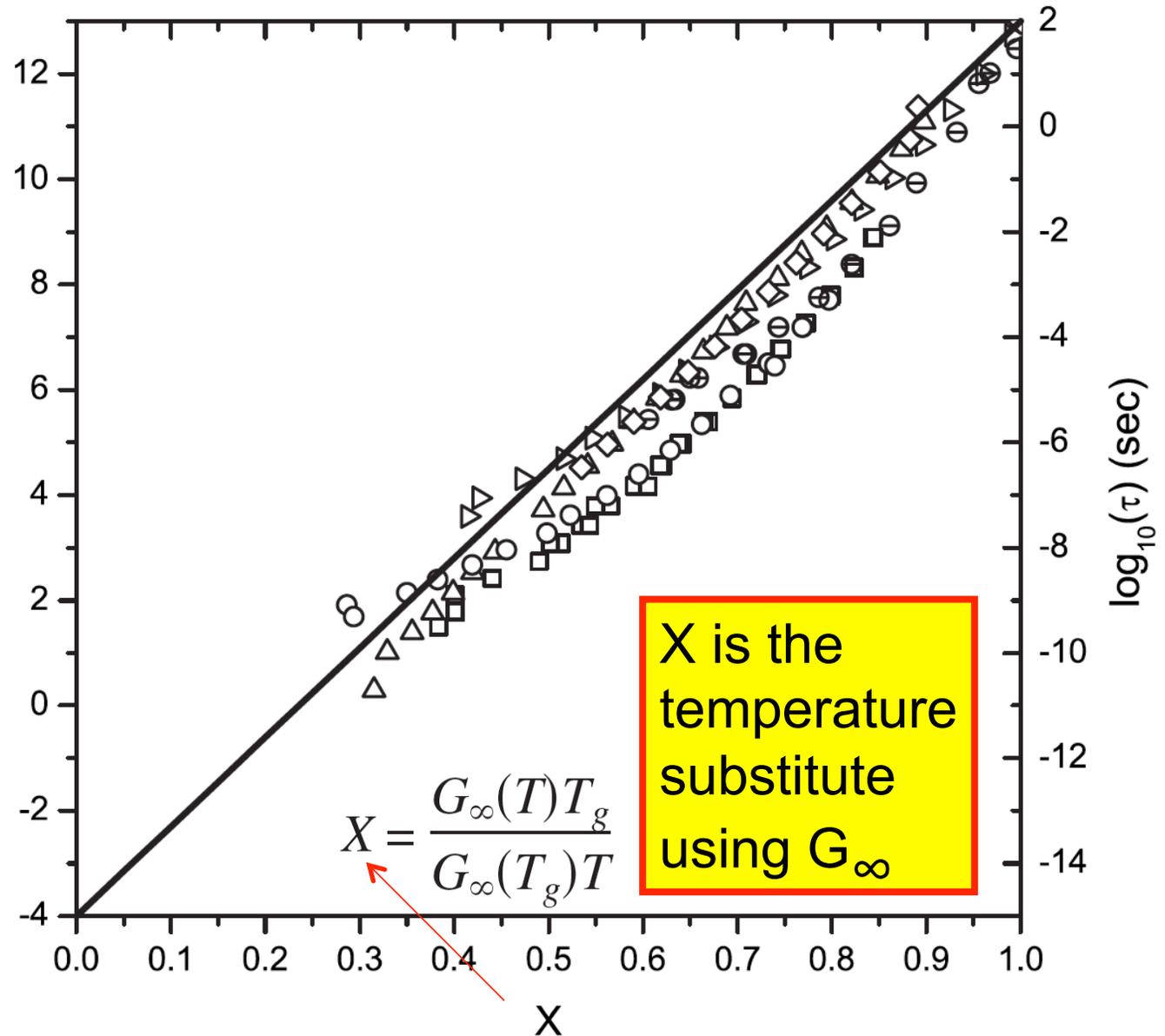
where ΔV is the change in volume during the flow event
 V is the volume of the flowing region before flow.

Argued that the relaxation process was activated, i.e. $\tau = \tau_0 \exp(E/RT)$ and the activation energy was purely elastic - and determined by the shear modulus G_∞ which is temperature-dependent. The difference between fragile and strong liquids therefore lay in the different temperature dependences of the shear modulus

Torchinsky & Nelson, JCP 130, 064502 2009

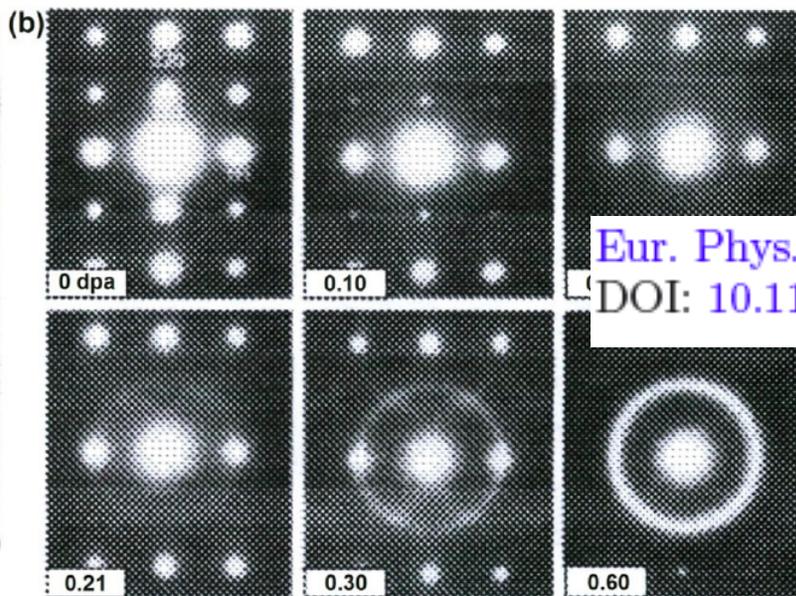
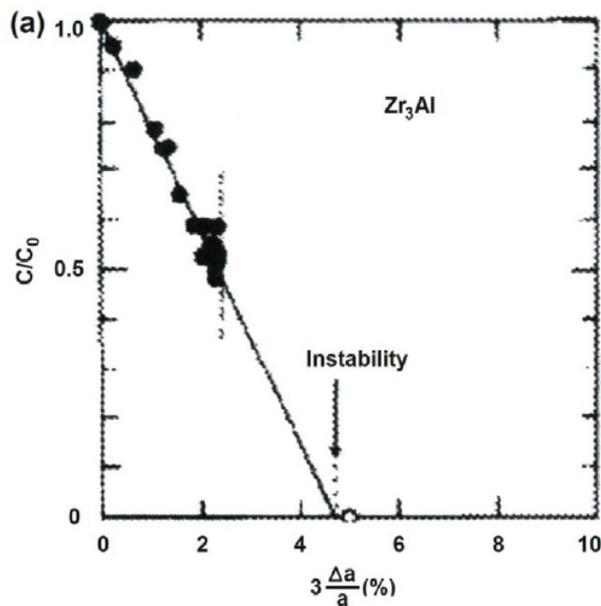
Measured G_∞ over extraordinary range using femtosecond pulses

NOT BAD, but...
then we must ask
what determines
the temperature
dependence of
 G_∞



Bangalore, 2013 “Symposium on Fragility”

“In mechanics, for instance, there is a direct relation between the rate at which the shear modulus decreases with increasing temperature, and the rate at which interstitial defects are created. So the temperature dependence of the shear modulus, which accounts for the non-Arrhenius viscosity temperature dependence according to the “shoving model”^{75 78}, could itself be interpreted in terms of the entropy-driven excitation rate of amorphous state analogs of interstitials. And so on.”



After
Andy Granato

[Eur. Phys. J. B \(2014\) 87: 18](#)
[DOI: 10.1140/epjb/e2013-41024-1](#)

Watching what
defects do

ion of Zr_3Al [21]. (a) Shear modulus vs. lattice parameter change with irradiation. (b) Laue X-ray diffraction
nction of displacements per atom (dpa).

“The fragility of glassforming liquids: thermal vs athermal systems, and kinetic vs thermodynamic origins.” C. Austen Angell, in *Fragility of glass forming liquids* Editors: A. L. Greer, K. F. Kelton, S. Sastry Publisher: Hindustan Book Agency, New Delhi, India (700 pp). Chapter 1. 2014

Concluding remarks

Liquids can be fragile because, in contrast with other condensed phases, their structures can change so much without destroying the integrity of the phase. If one prevents the structure from changing, everything becomes simple Arrhenius again, for instance, the ionic conductivity of a superionic glass. Consistent with this observation, systems studied at constant volume are always found to be less fragile than systems studied at constant pressure (although keeping the volume constant is certainly not the same as keeping the structure constant).

Basically because $X/(1-X) \neq X$

Outline

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MECHANICAL PROPERTIES OF GLASS-FORMERS (brittle and ductile glasses)
- D. Gels: fragile and tough,

Mechanical properties of glass
("glass" is a non-relaxing state that depends on observation time)

Thoughts about Poisson's ratio, timescales, and the liquid state

A 2011 paper and cited 479x

"Highly cited"

**nature
materials**

REVIEW ARTICLE

PUBLISHED ONLINE: 24 OCTOBER 2011 | DOI: 10.1038/NMAT3134

Poisson's ratio and modern materials

G. N. Greaves^{1,2*}, A. L. Greer¹, R. S. Lakes³ and T. Rouxel⁴

I know mechanical properties of glasses are important, but I get into trouble with the very first figure

Relationships to measurables

The elastic moduli were calculated from the measurements of the longitudinal, V_l , and transverse, V_t , ultrasonic wave velocities with a better than $\pm 2\%$ relative error by means of 10 MHz piezoelectric transducers. Young's modulus, E , and Poisson's ratio, ν , derive from the classical elasticity relationships [8]

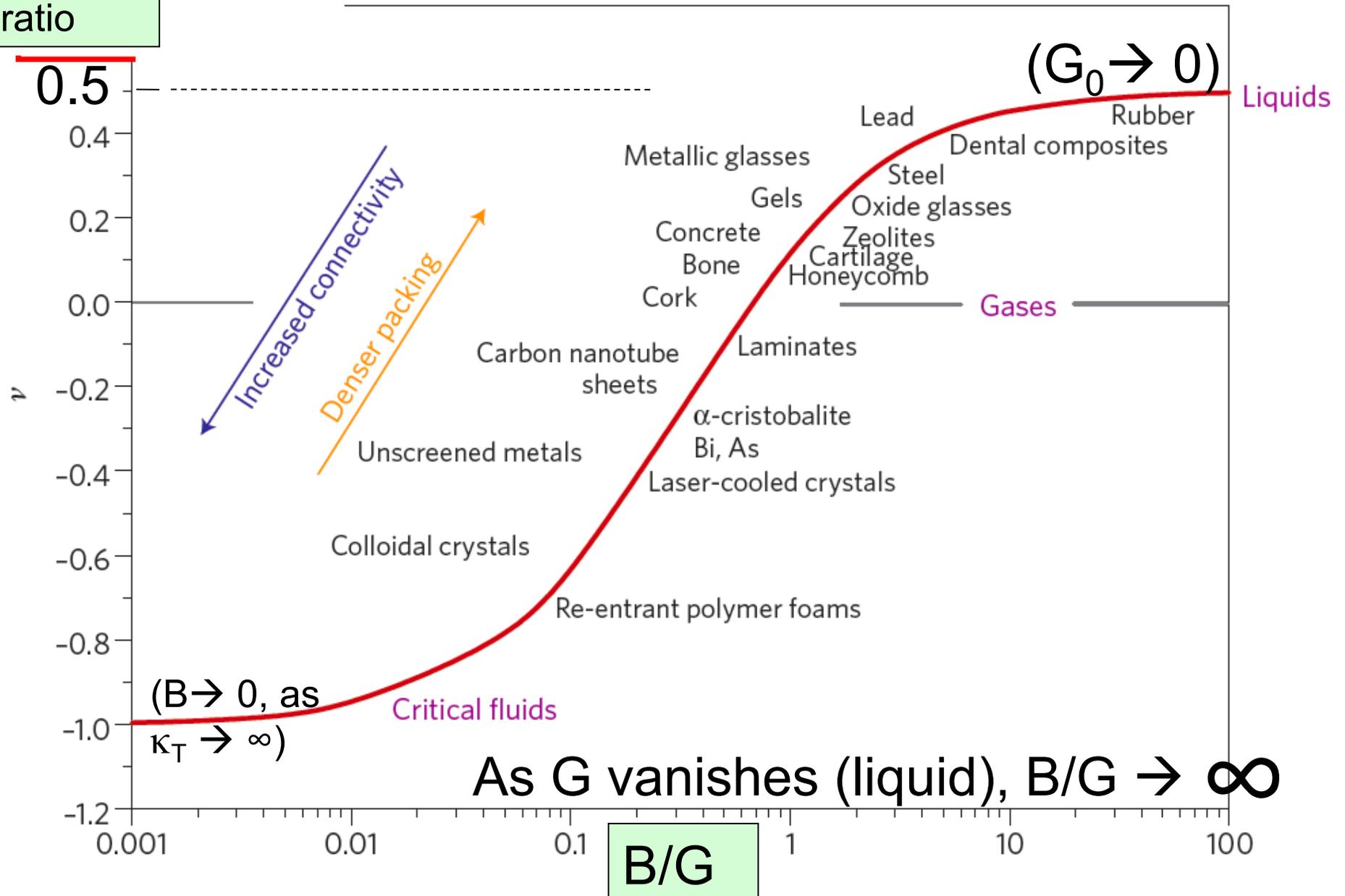
$$E = \frac{9KG}{G+3K} \approx 0.9K.$$

$$E = \rho \frac{3V_l^2 - 4V_t^2}{(V_l/V_t)^2 - 1}, \quad (1)$$

$$\nu = \rho \frac{3V_l^2 - 4V_t^2}{2(V_l^2 - V_t^2)} - 1, \quad (2)$$

Poisson's ratio, ν

Poisson ratio



MECHANICAL SPECTROSCOPY OF GLASSY SYSTEMS

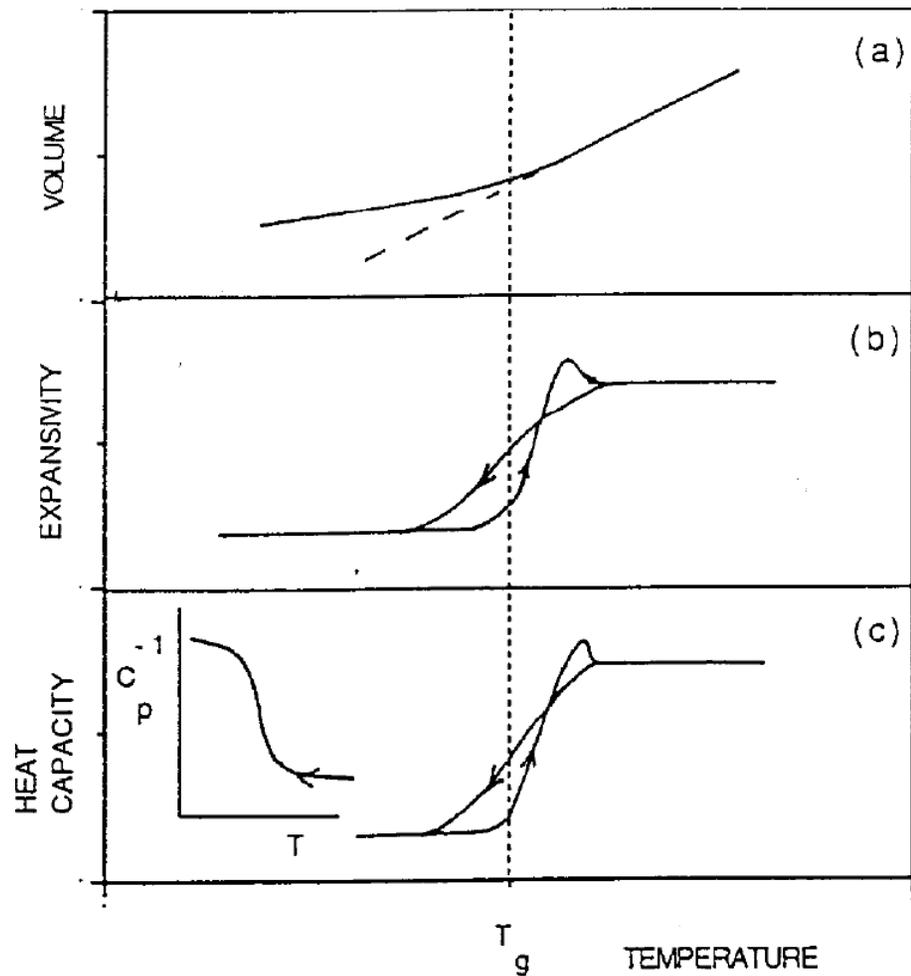
C. A. ANGELL

*Department of Chemistry, Arizona State University, Box 871604,
Tempe, AZ 85287-1604*

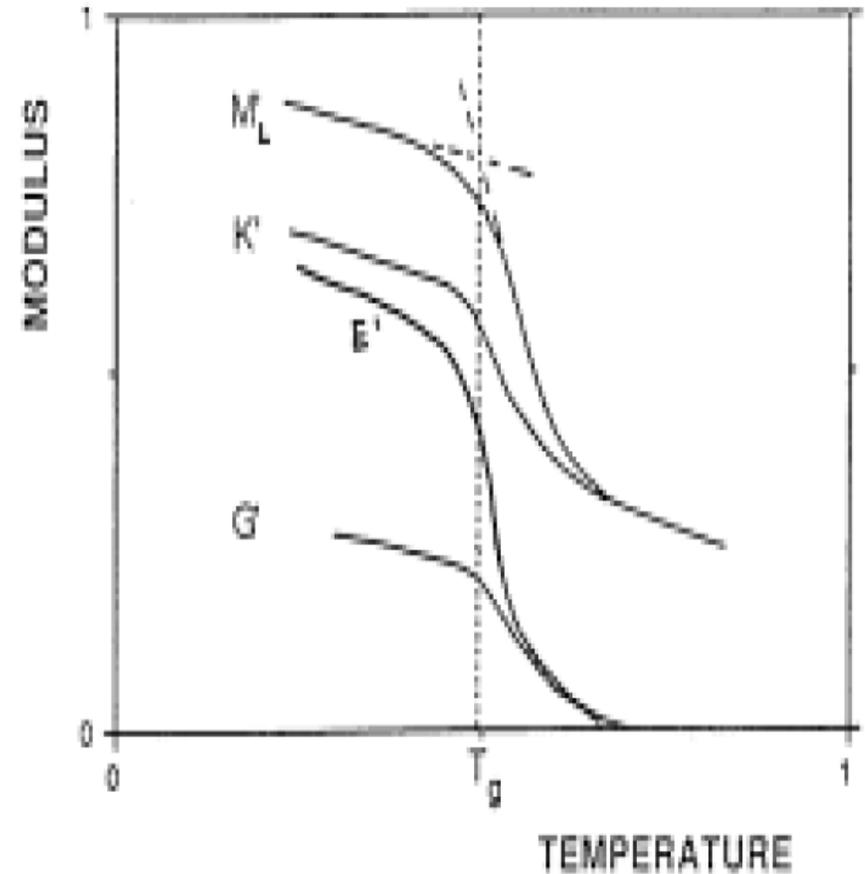
R. BÖHMER

*Institut für Festkörperphysik Technische Hochschule,
D6100 DARMSTADT
GERMANY*

Response functions
and moduli ($1/C_p$ is the
thermal modulus)



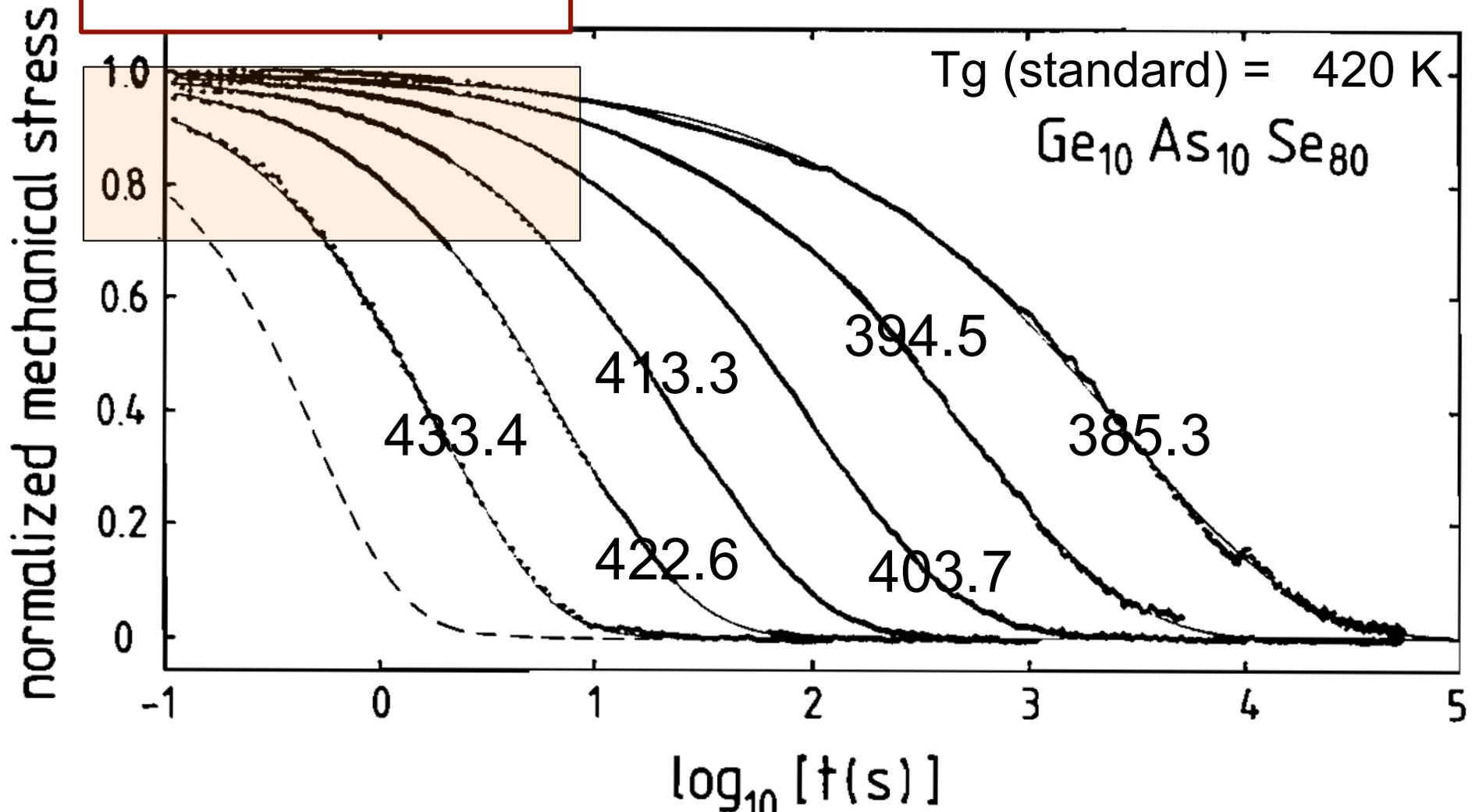
These are moduli measured on the
time scale of the glass transition 100s

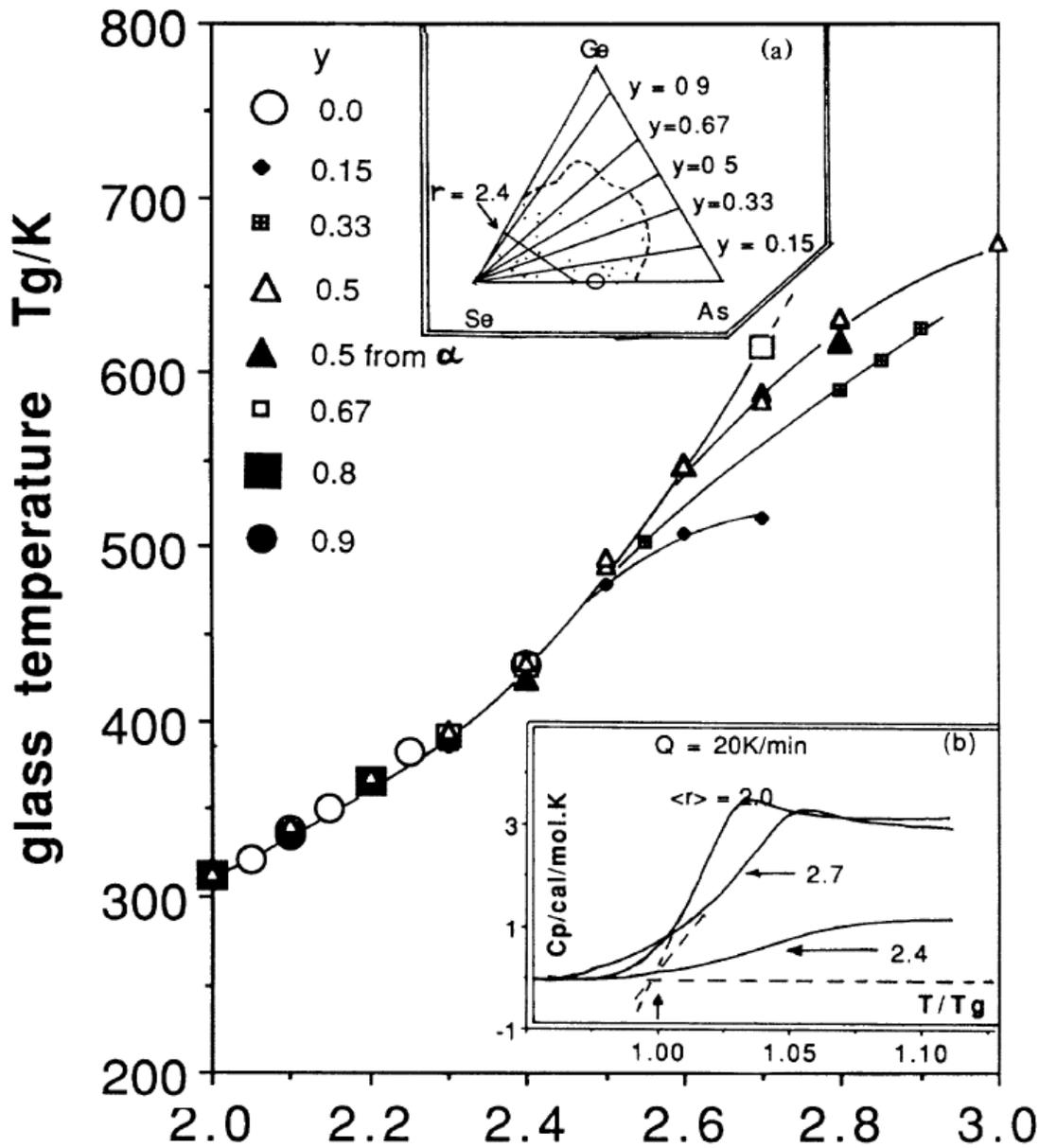


Tensile moduli vanishing at T_g

$$E = \frac{9KG}{G+3K} \approx 0.9K.$$

So E must vanish in the liquid state where $G \rightarrow 0$

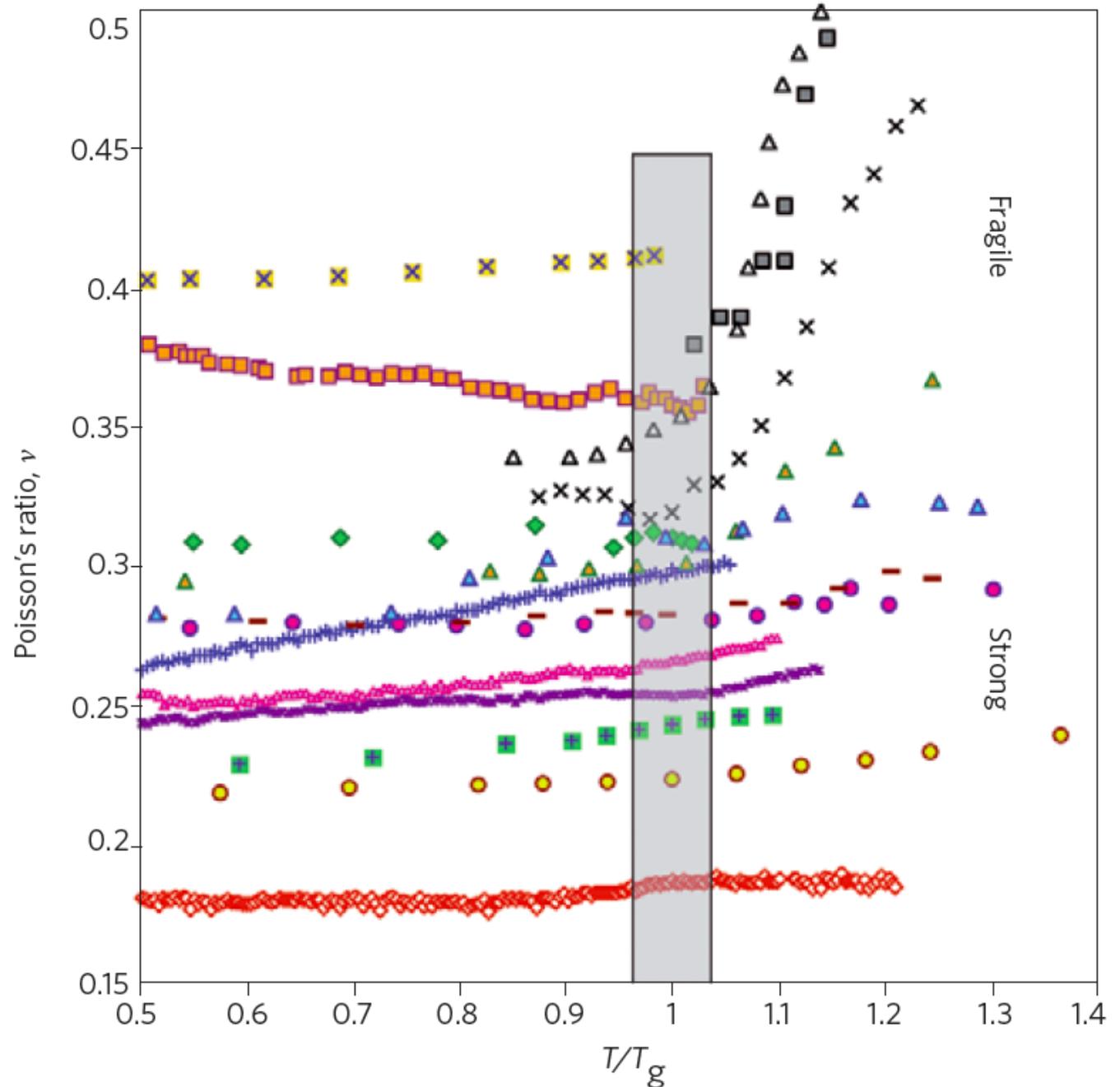




Tatsumisago et al
 (Lindsay, CAA)
 Fragility and constraint
 counting in glass-
 formers above T_g
 (first ASU paper)

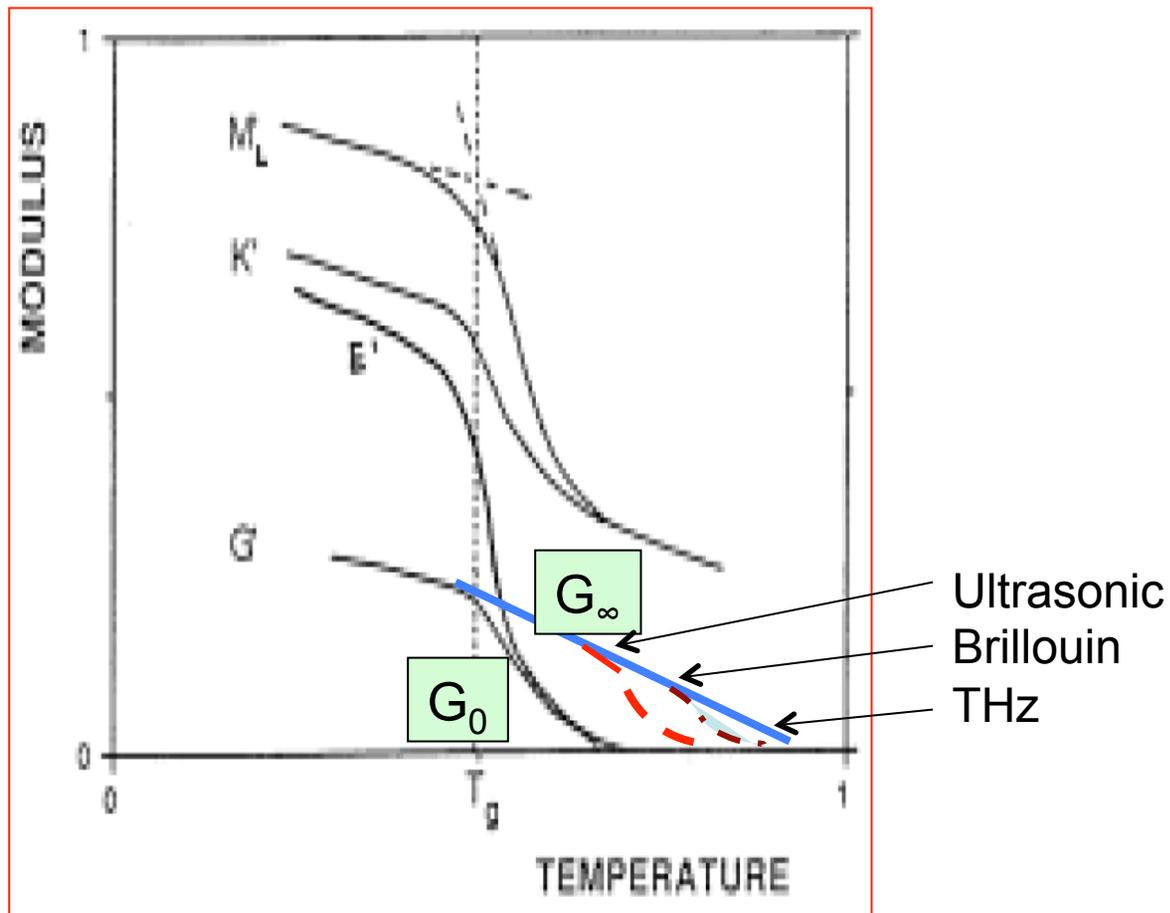
Poisson's ratio vs T across the (standard $\tau = 200s$) T_g

- × Glycerol
- △ (Ca,Na) aluminosilicate - Al/Si= 0.35
- × (Ca,Na) aluminosilicate - Al/Si= 0.29
- + (Ca,Na) aluminosilicate - Al/Si= 0.50
- ZrCuAlNi bulk metallic glass
- ◇ α -SiO₂ (Spectrosil, Saint-Gobain)
- Bitumen
- △ Glassy polystyrene
- Window glass
- ◆ ZBLAN (Zr,Ba,Al,Na) fluoride
- × PdNiCuP bulk metallic glass
- ▲ α -B₂O₃
- Borosilicate (Pyrex) glass
- (Ca,Mg) silicate (diopside)
- (Ca,Al) silicate (grossular)
- ▲ Glassy H₂O

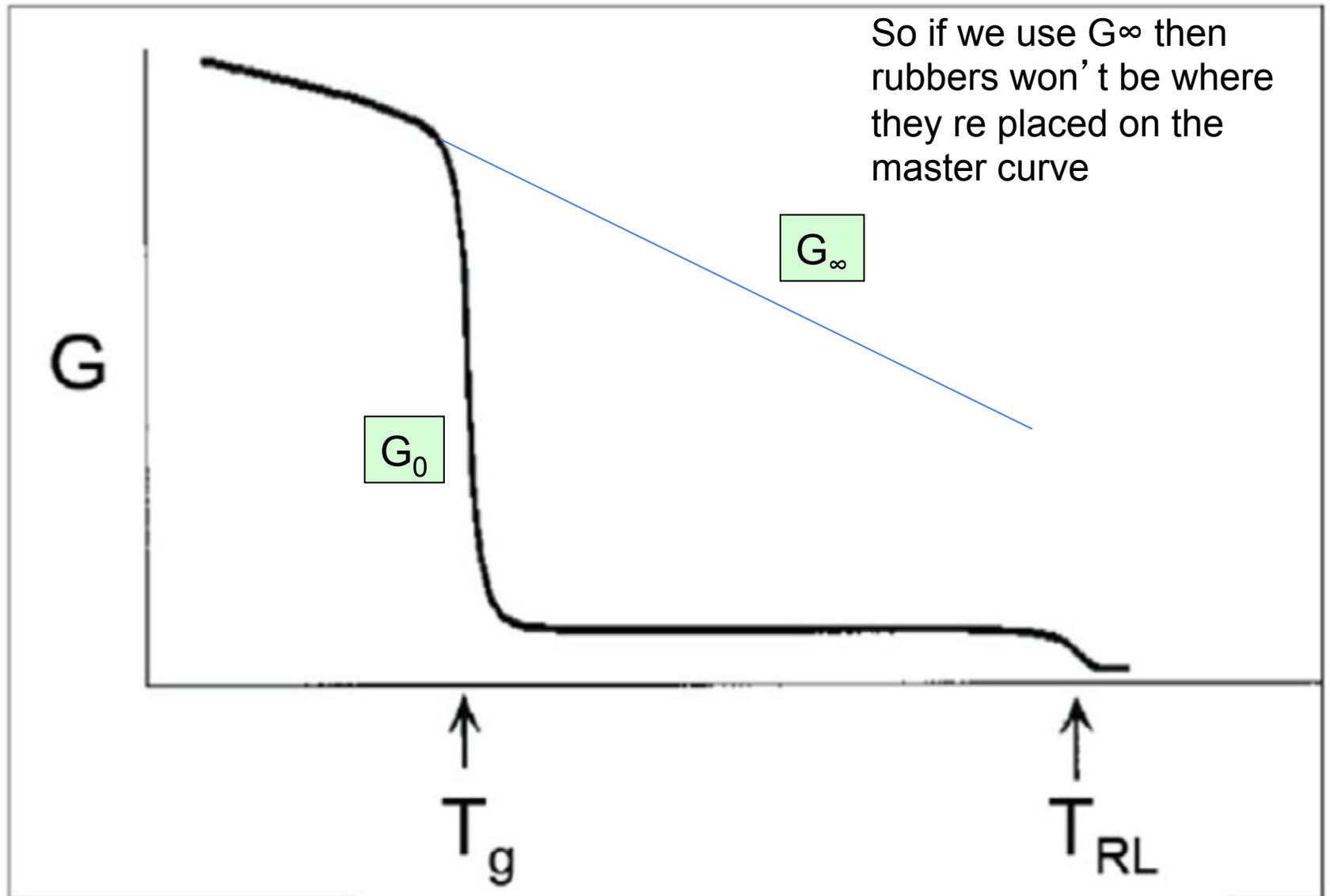


Let's think about this a bit

Moduli: adding in the time dependence



Polymers and rubbers



Summary, conclusions

1. Fragile behavior in liquids is mirrored in their entropy production
Models for entropy, are simpler than models for dynamics
2. Two state models are powerful. Excitation of quasilattice accompanied by degeneracy. Sources in the lattice vibrations.
3. Fragility of the liquid has origin in the vibrational manifold
4. Success of elastic models, targetting shear modulus, begs the Question, why is the shear modulus so much more temperature dependent for some liquids than others?
5. Shear moduli and Poisson's ratio..
Care with timescales, G^∞ vs G_0
6. Ductile vs brittle behavior??? Metallic glasses

**Response
functions.
Moduli, and
fluctuations,**

Landau and Lifshitz (1958) demonstrated that the compressibility is determined by the mean square fluctuation in the volume, according to

$$\kappa_T = \overline{\langle \Delta V \rangle^2} / V k T \quad (2)$$

while the heat capacities are related to the kinetic energy fluctuations

$$C_v = k T^2 / \overline{\langle \Delta T \rangle^2} \text{ (at constant volume)} \quad (3)$$

and the entropy fluctuations,

$$C_p = \overline{\langle \Delta S \rangle^2} / k \text{ (at constant pressure)} \quad (4)$$

The moduli are the inverse of the response functions

From “The glass transition”, Pergammon Encyclopedia of Materials: Science and Technology, 3365 (vol 4), (2001) .