Elasticity and dynamics in molecular liquids

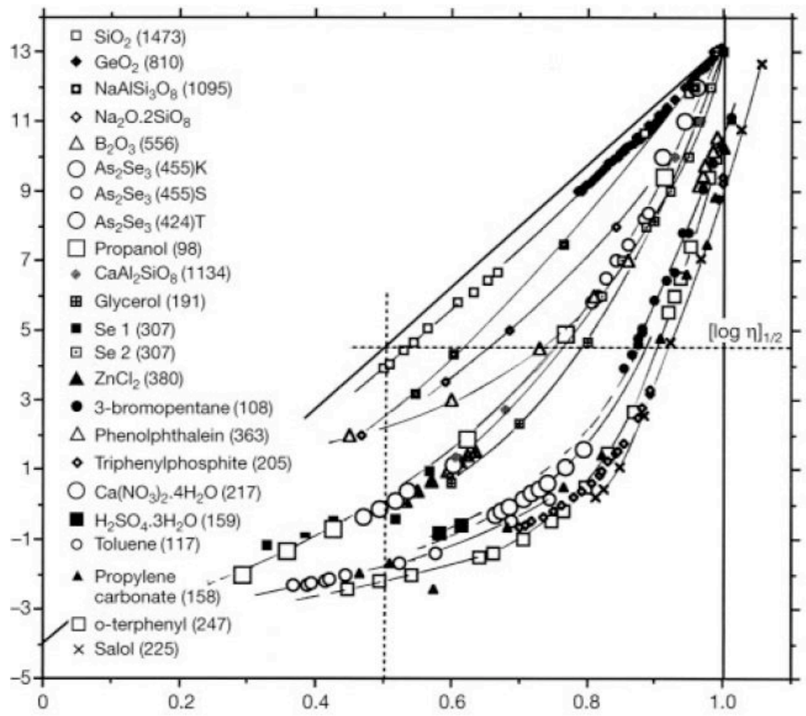
Some connections with the jamming of repulsive particles

Wyart, Phy. Rev. Lett 104, 095901 (2010)
Wyart, Silbert, Nagel and Witten PRE (2005)
Brito and Wyart, Jour. of Chem. Phys.(2009)

Matthieu Wyart

Viscosity in liquids

log(η)



T_g/T

Angell

Strong liquids:

$\boxed{\log(\eta) \sim E_a / kT}$

Arrhenius

η: Viscosity
E_a: Activation energy

Fragile liquids:

$\boxed{E_a(T) \nearrow \text{ as } T \searrow}$

Mechanism causing the increase in $E_a(T)$?

What decides if a liquid is fragile or strong? ⇒ Correlates of the dynamics as T varies

Dynamics and thermodynamics are correlated

Observations:

$S_{ex}(T)$: excess entropy= entropy liquid- entropy crystal

$$\boxed{T\ \mathrm{Log}(\eta) \sim E_a \sim 1/S_{ex}}$$

Super-cooled liquid entropy: separation of time scales $\Rightarrow$

$$\boxed{S = S_{vib} + S_c}$$

Free energy

states in [F, F+dF]

S_{vib}:Vibrational (picoseconds)

S_c : Configurational (seconds)

One interpretation for $E_a \sim 1/S_{ex}$: collective dynamics

Adam Gibbs, RFOT: less states ⇒ cooperative dynamics

$\boxed{E_a \text{ correlates to } S_c}$

$\boxed{\text{Assume} \quad S_{ex}=S_c}$

$\Updownarrow$

Vibrational entropy liquid = vibrational entropy crystal

- Since Goldstein S_{vib} known to have strong, non-trivial, dependence with temperature
- Hard spheres: $S_{crystal} < S_{liquid}$ near T ⇒ $S_c < 0$ impossible

Less stringent assumption $\boxed{S_{ex} \sim S_c}$ as problematic

Dynamics and Elasticity : elastic models

Dyre 2006

Activation energy: $\boxed{E_a = E_{scale}(T) \times f(\lambda, \ldots)}$

E_{scale} = Energy scale
f = theory-dependent factor
λ = rearrangements size

Naïve guess for energy scale:

- Rearrangements imply local strain ⇒ Energy scale ~ shear modulus G
- Rearrangements fast ⇒ vibrational time scale, THz

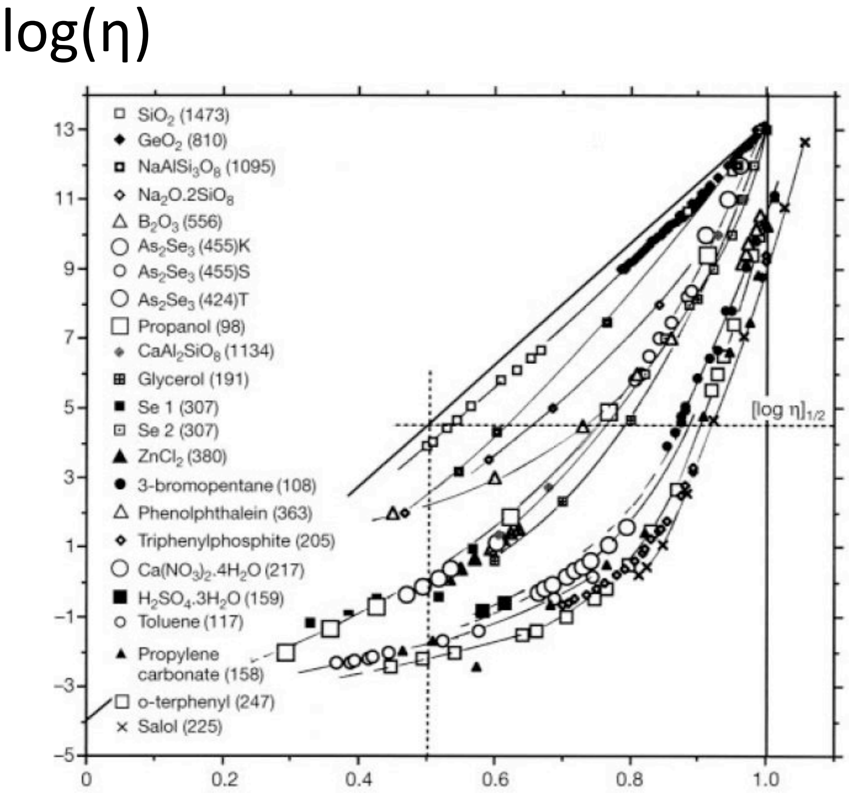
Elastic models:

Assume: $$\frac{d\ln(E_{scale})}{dT} \gg \frac{d\ln(f)}{dT} \Rightarrow \boxed{E_a \sim G}$$

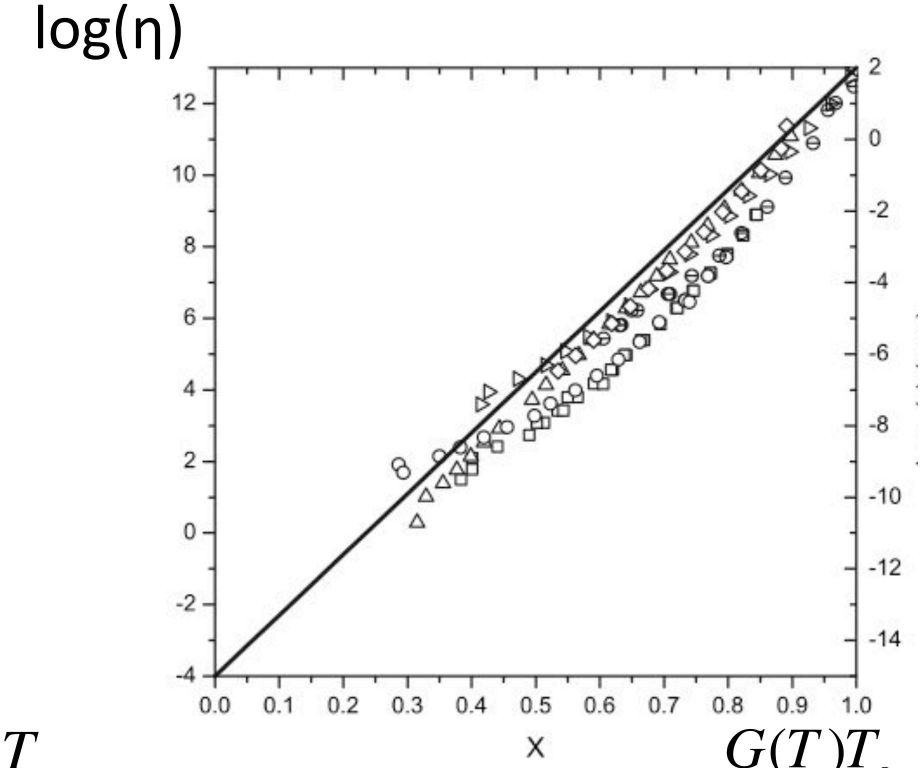
Dynamics and elasticity are correlated

Torchinsky et al (2009), Dyre et al (1998)

- shear modulus G(T) measured at GHz frequencies (Impulse Stimulated Scattering)
- 6 fragile liquids (m~90)



$$\frac{T_g}{T}$$



$$\frac{G(T)T_g}{G(T_g)T}$$

$\boxed{E_a \sim G}$ ⇒ fragile liquids stiffen under cooling

Dynamics- Thermodynamics correlations: elastic point of view

Naïve argument

$$S_{vib} = \frac{k_b}{N} \ln(\Omega_{vib})$$

$$\Omega_{vib} \propto (< p^2 >^{1/2})^{3N} (< u^2 >^{1/2})^{3N}$$

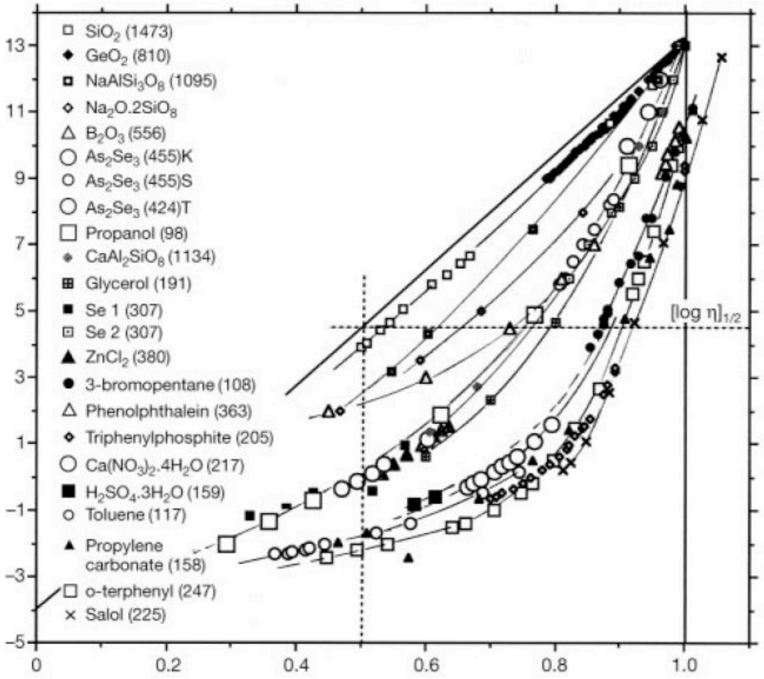
$$\Rightarrow \boxed{C_{vib} = \frac{3k_b}{2} + \frac{3k_b}{2} \frac{\partial \ln < u^2 >}{\partial \ln T} = 3k_b - \frac{3k_b}{2} \frac{\partial \ln G}{\partial \ln T}}$$

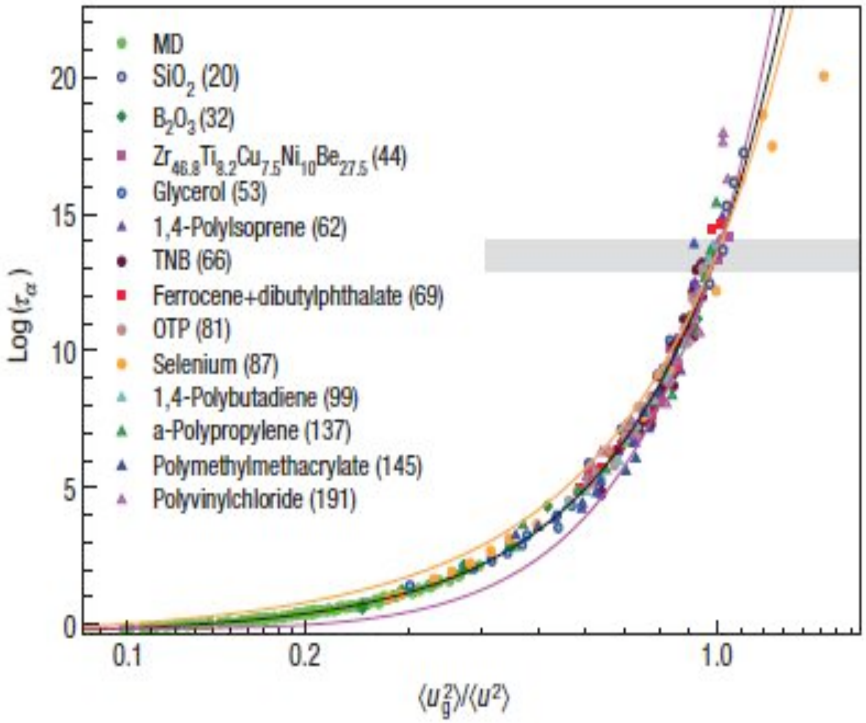
Used: $< u^2 > \propto \frac{k_b T}{G}$

⇒ Correlation dynamics and vibrational entropy predicted
⇒ but effect 3 times larger than measurements *Dyre 2006*

What went wrong? Indication of correlation dynamics-vibrational entropy in other data ?

Correlations short-time ($<u^2>$) vs long-time dynamics





Larini et al, 2008

- mean square displacement $<u^2>$ at picoseconds
- collapse $$\boxed{\log(\tau) = f\left(\frac{<u_g^2>}{<u^2>}\right)}$$

Vibrational entropy and $<u^2>$

Wyart, 2010

- Linear approximation $$\boxed{C_{vib} \approx 3k_b(1- < \frac{\partial \ln(\omega)}{\partial \ln(T)} >_{\omega})}$$

- ω (T): spectral decomposition of the dynamics- change of inherent structures + non linearities (tested in Selenium, Phillips et al. 1989)

- $$\boxed{C_{vib} - \frac{3k_b}{2} = \alpha \frac{3k_b T}{2} \frac{\partial \ln(< u^2 >)}{\partial T}} \quad \Rightarrow \quad \boxed{\Delta C_{vib} = \frac{3k_b}{2}(\alpha m / 26 - 1)}$$

⇒ vibrational entropy and dynamics correlated

$$m = - \frac{\partial \log \tau}{\partial \ln T}_{Tg}$$

if $< \frac{\partial \ln(\omega)}{\partial T} >_{\omega}$ independent of ω $\Rightarrow \alpha = 1 \Rightarrow \Delta C_{vib} > 2\Delta C$ impossible

- α small if low-frequency spectrum soften with T.

Softening at some ω_{BP} $\Rightarrow$ $\boxed{\alpha > \omega_{BP}/\omega_D}$ ω_D: Debye frequency

- Effect known: softening around the boson peak
(excess modes with respect to Debye model):

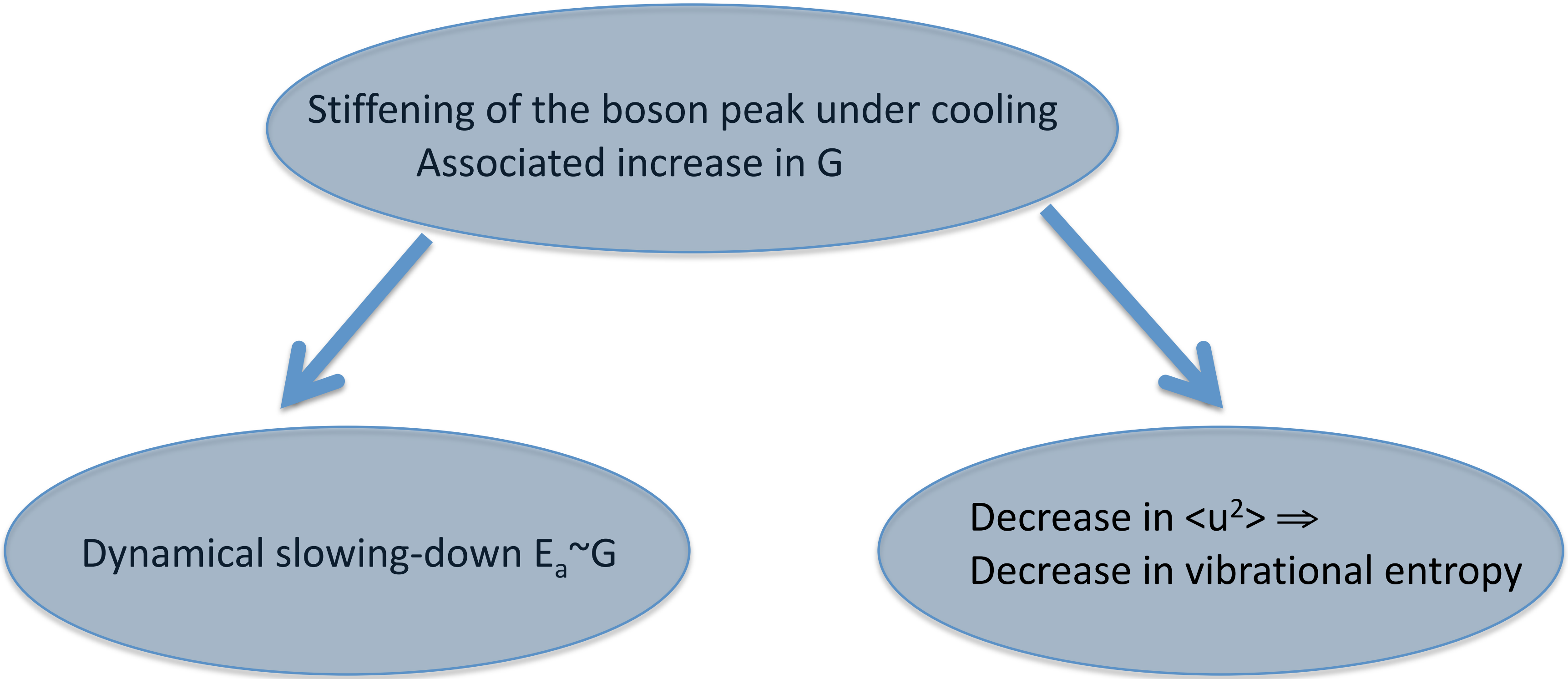
$\alpha > \omega_{BP}/\omega_D \approx 1/5$ near Tg

$\Rightarrow$ $$\boxed{\Delta C_{vib} > 40\% \Delta C}$$

Similar results in *Wang and Richert, 2007*

- Vibrational entropy and dynamics correlated
- stiffening = stiffening of the boson peak, not overall spectrum

Elastic scenario for the glass transition



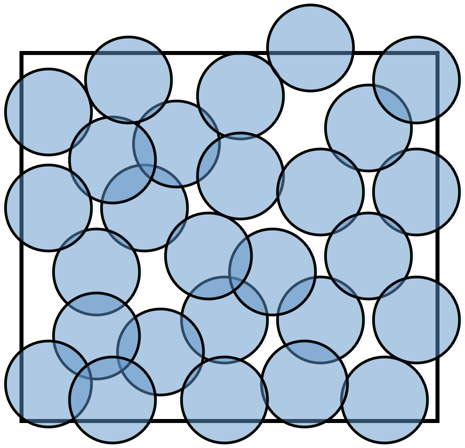
Stiffening of the boson peak under cooling
Associated increase in G

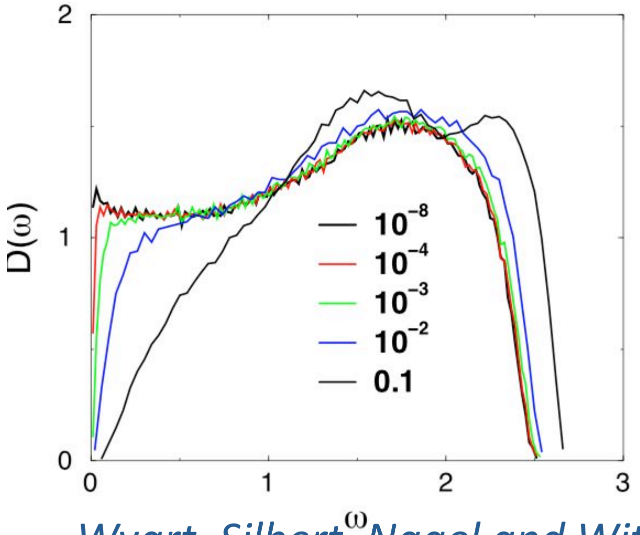
Dynamical slowing-down $E_a \sim G$

Decrease in $\langle u^2 \rangle \Rightarrow$
Decrease in vibrational entropy

- Cause for the stiffening under cooling of fragile liquids?
- Numerical evidences for relation between boson peak and dynamics?

Nature of the Boson peak in simple liquids





Granular matter, emulsion

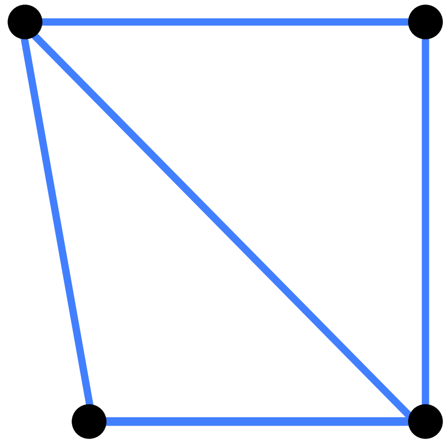
Wyart, Silbert, Nagel and Witten 2005
Silbert, Liu and Nagel 2005

Silica *Wyart 2005*

Model of metallic glasses: L-J *Wyart 2005, Xu, Wyart, Liu, Nagel 2006*

Maxwell: Rigidity and soft modes

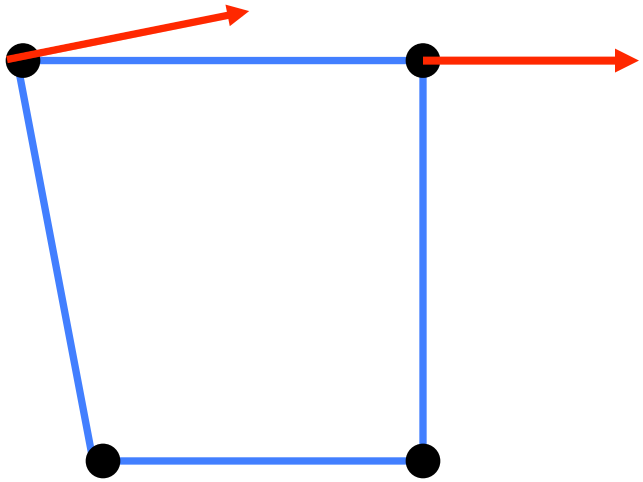
Rigid



Not rigid

⇓

soft mode



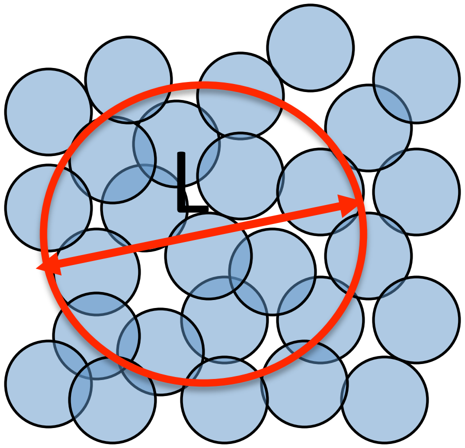
Maxwell: minimal coordination Z to be rigid?

$Z \geq 2d > d+1$ *global*

jamming: marginally connected **$z_c=2d$** “*isostatic*”

(Moukarzel, Roux, Witten, Tkachenko,...)

Variational (non mean-field) argument for weakly-connected solids



Z=2d

- Cavity: impose free boundary
- Generates L^{d-1} soft modes independent *(instead of 1 for a normal solid*)
- Distort them: create anomalous modes of frequency $\omega \sim L^{-1}$

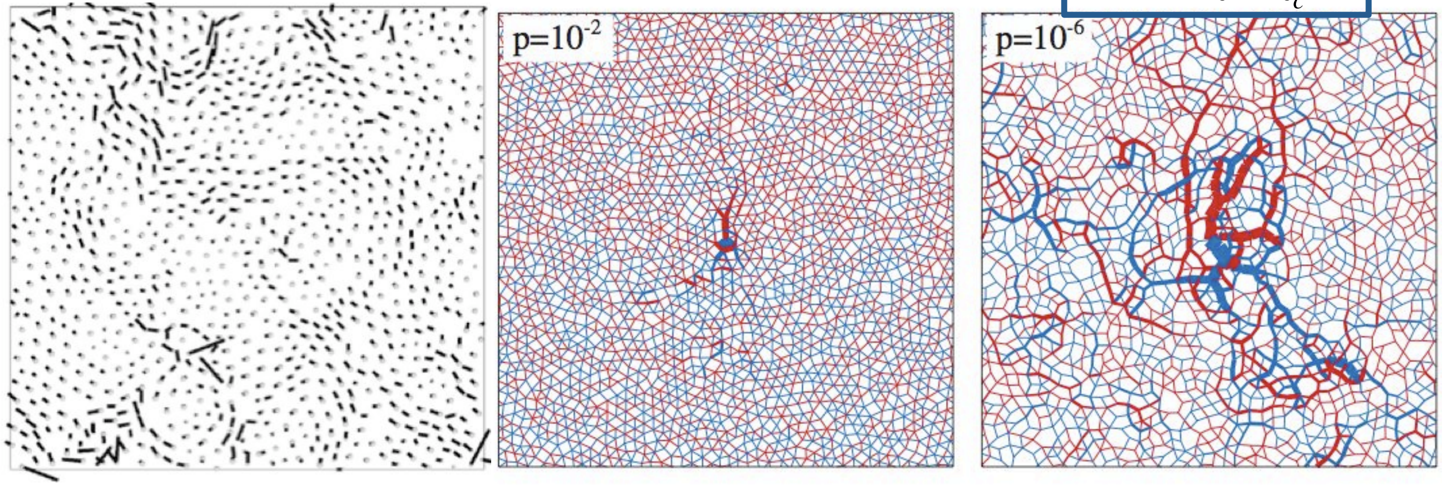
$D(\omega) \sim L^{d-1}/(L^{d}L^{-1}) \sim L^{0}$

Z>2d

Argument brakes down for length scale

$$\boxed{l^* \sim \frac{1}{z - z_c}}$$

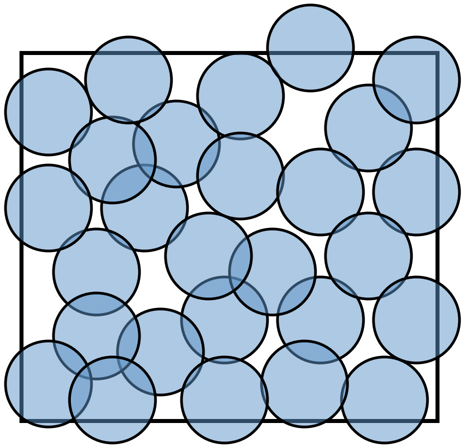
$$\boxed{\omega^* \sim z - z_c}$$



Ellenbroek et al 2006

Nature of the Boson peak in simple liquids

Wyart, Nagel and Witten 2005



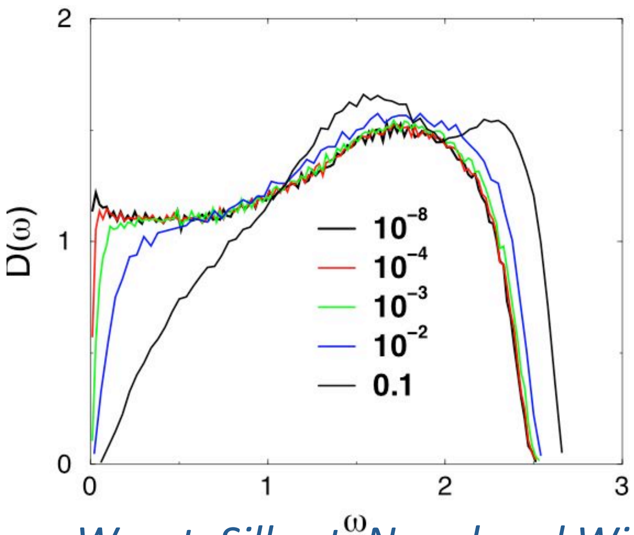
Anomalous modes, governed by coordination:

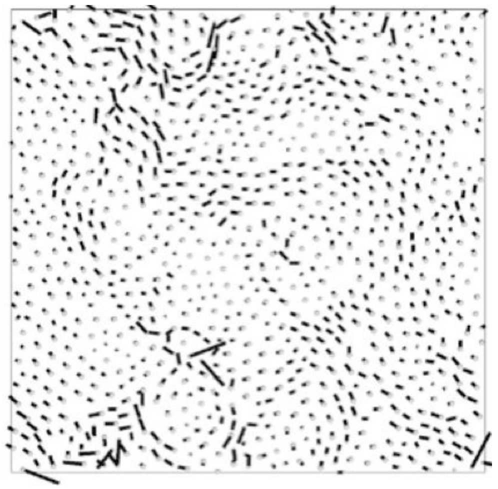
Extended on length scale: $\boxed{l^* \sim \frac{1}{z - z_c}}$

Frequency: $\boxed{\omega^* \sim z - z_c}$ averaged on l^*

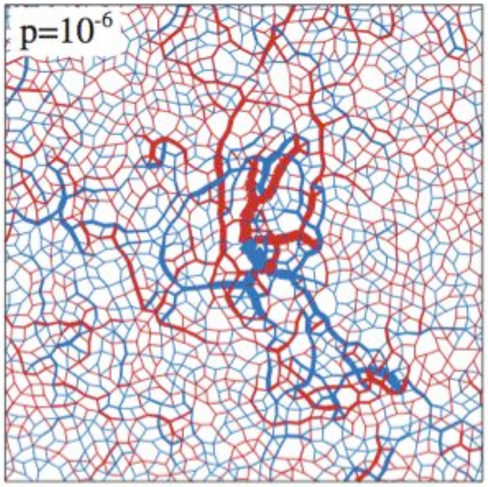
Shear modulus $\boxed{G \sim z - z_c}$

Z_c=6 in 3 dimensions





Wyart, Silbert, Nagel and Witten 2005
Silbert, Liu and Nagel 2005

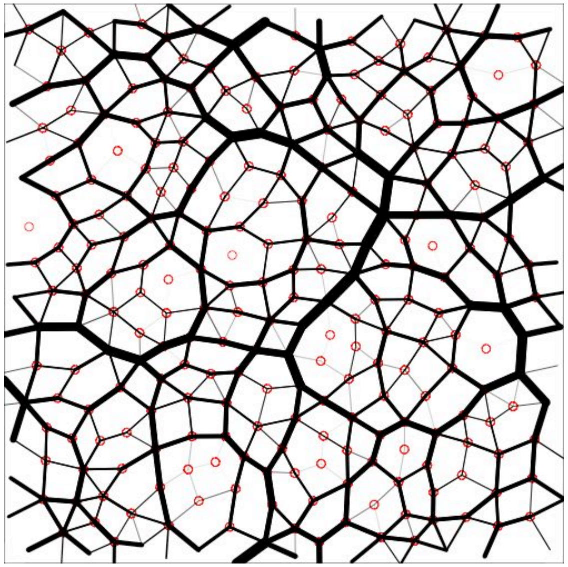


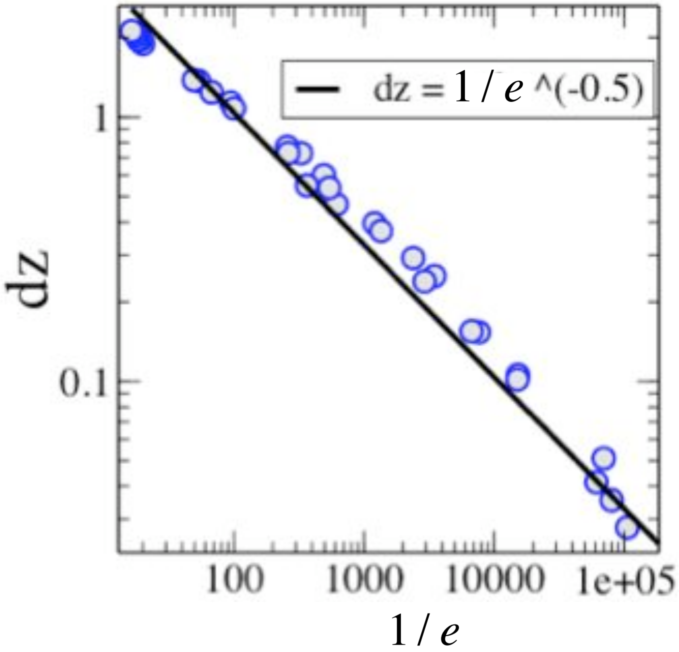
Ellenbroek et al 2006

Beyond Maxwell: Meta-stability stems from a balance between coordination and pressure *Wyart, Silbert, Nagel and Witten 2005*

- Pressure: <u>important</u> effect on anomalous modes
- Criterion for meta-stability $\boxed{z - z_c > Ae^{1/2}}$ e: strain in contact

On all subsystem of size l*





Analogy Free energy hard spheres, Energy elastic network with logarithmic springs *Brito and Wyart, 2006*

Hard sphere glass marginally stable ⇒ Dynamics controlled by stability of anomalous modes *Brito and Wyart, 2007,2009*

Physical picture for the mechanical stability of a hard sphere glass

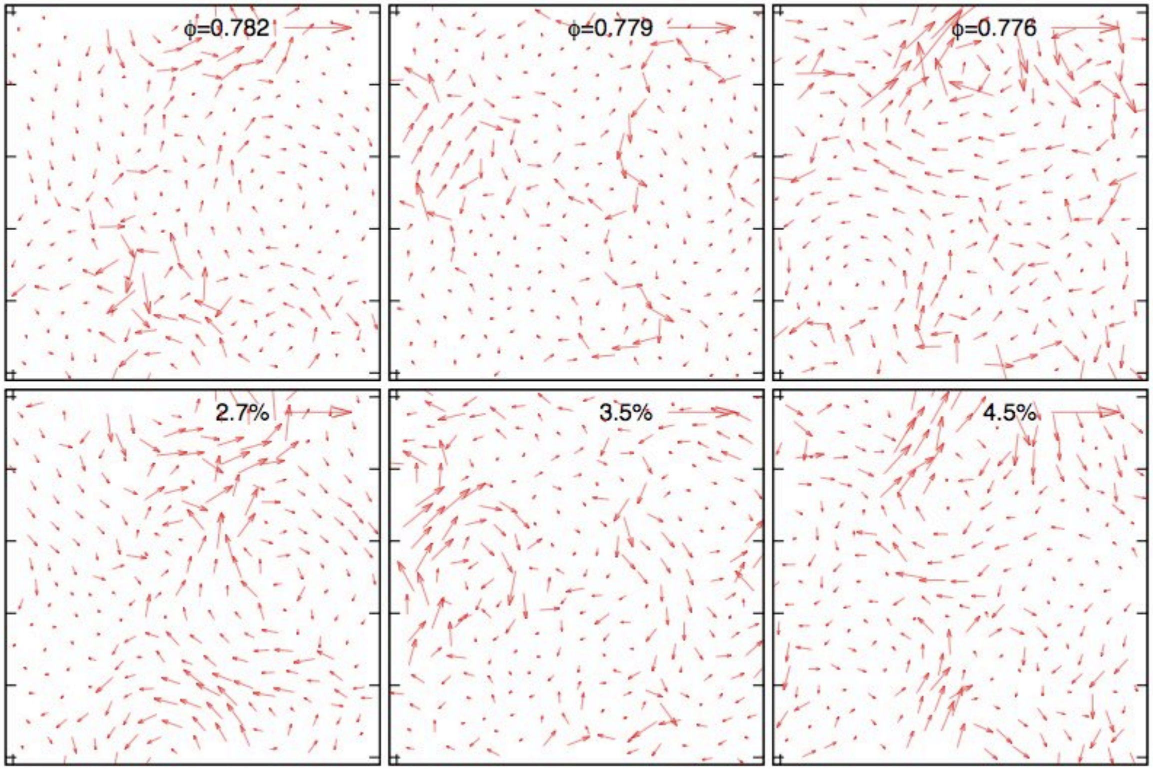
- <u>Not</u> the formation of cages

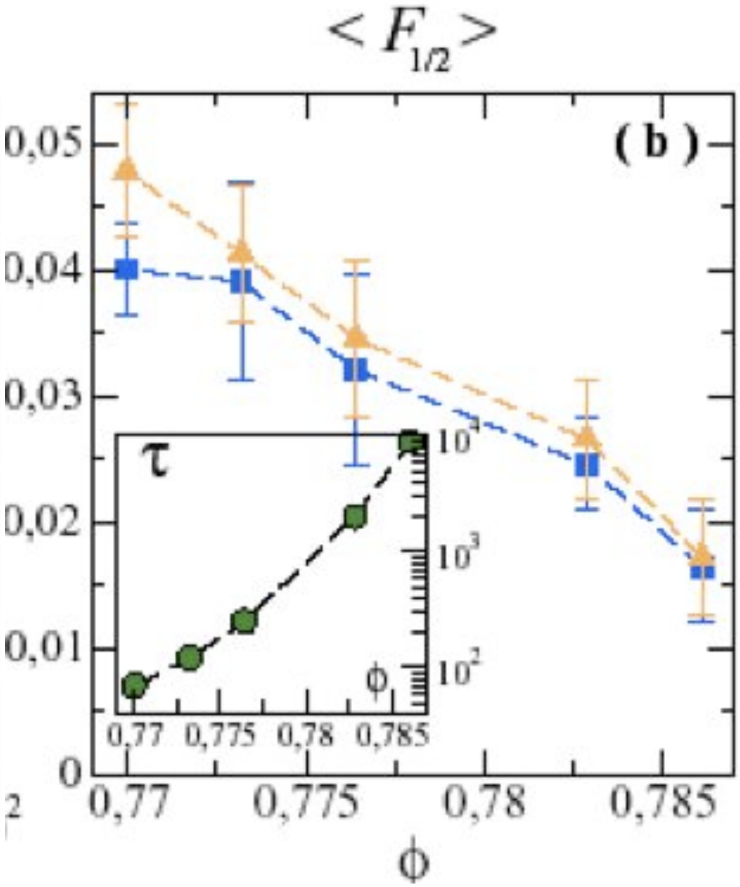
- Establishment of a contact force network sufficiently connected
to resist the destabilizing effect of positive pressure in the contacts

- Stability not a local property, characterized by a length l* that can be large

Soft modes of the free energy dominate relaxation more and more as viscosity increases

Brito and Wyart 2007, 2009

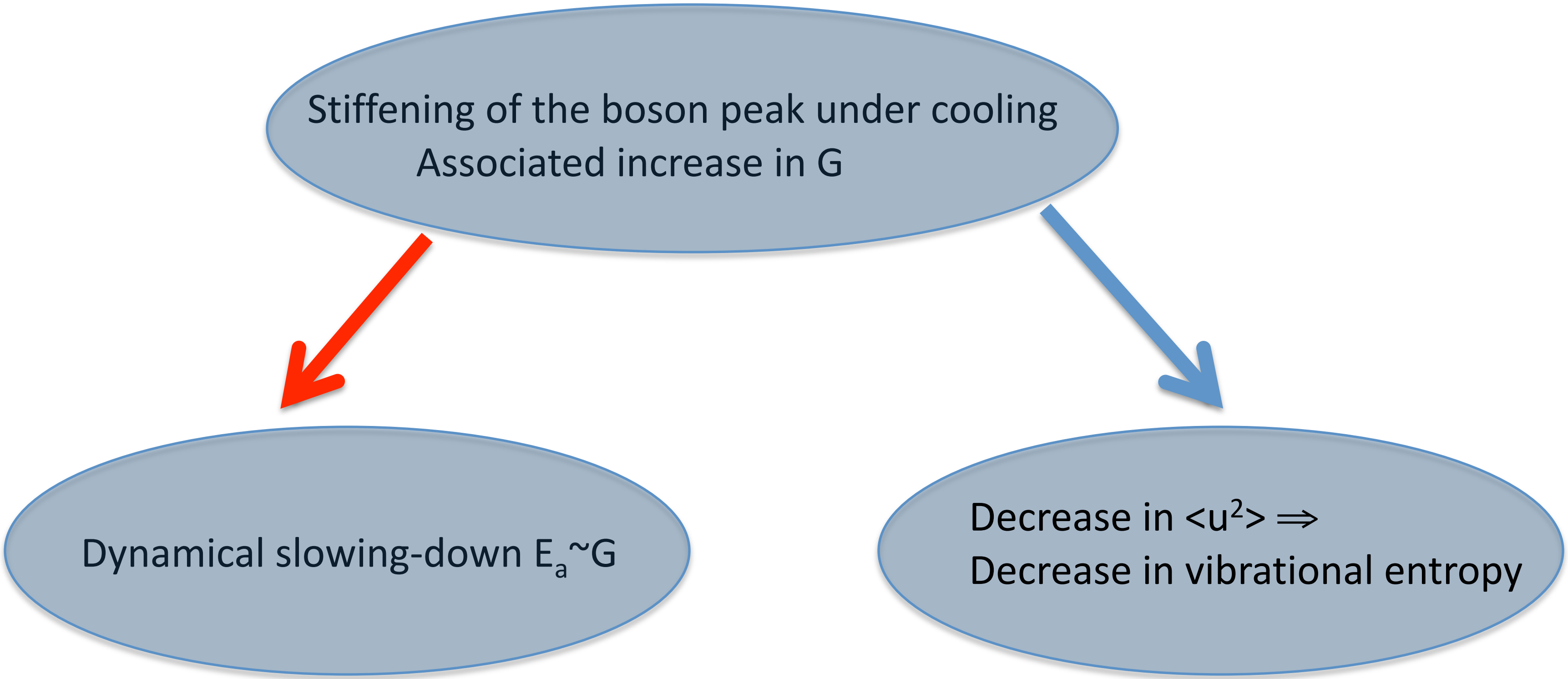




$F_{1/2}$: fraction of the modes contributing to rearrangements

$F_{1/2}$ decreases as viscosity increases: fewer and fewer degrees of freedom contribute To relaxation

Scenario for the glass transition



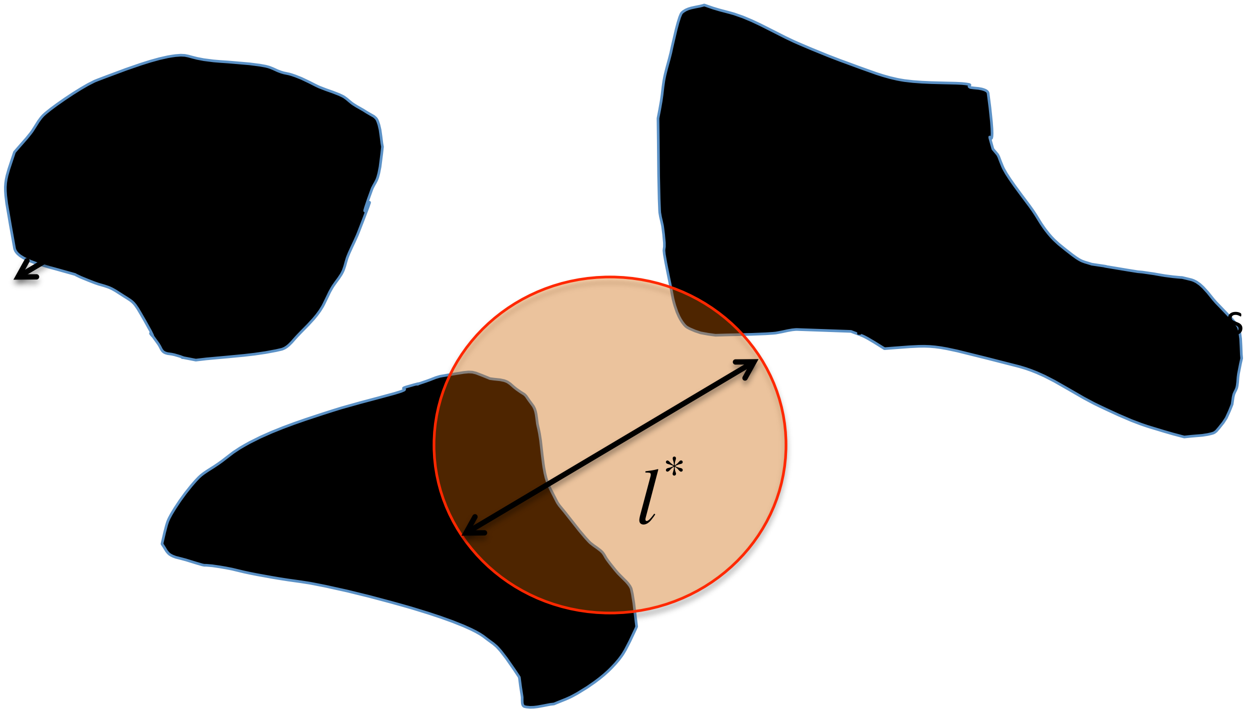
Stiffening of the boson peak under cooling
Associated increase in G

Dynamical slowing-down $E_a \sim G$

Decrease in $\langle u^2 \rangle \Rightarrow$
Decrease in vibrational entropy

Numerical evidences for relation between boson peak and dynamics:
-Relaxation occurs along soft modes
-Marginal stability of the structure

What causes stiffening of the boson peak?

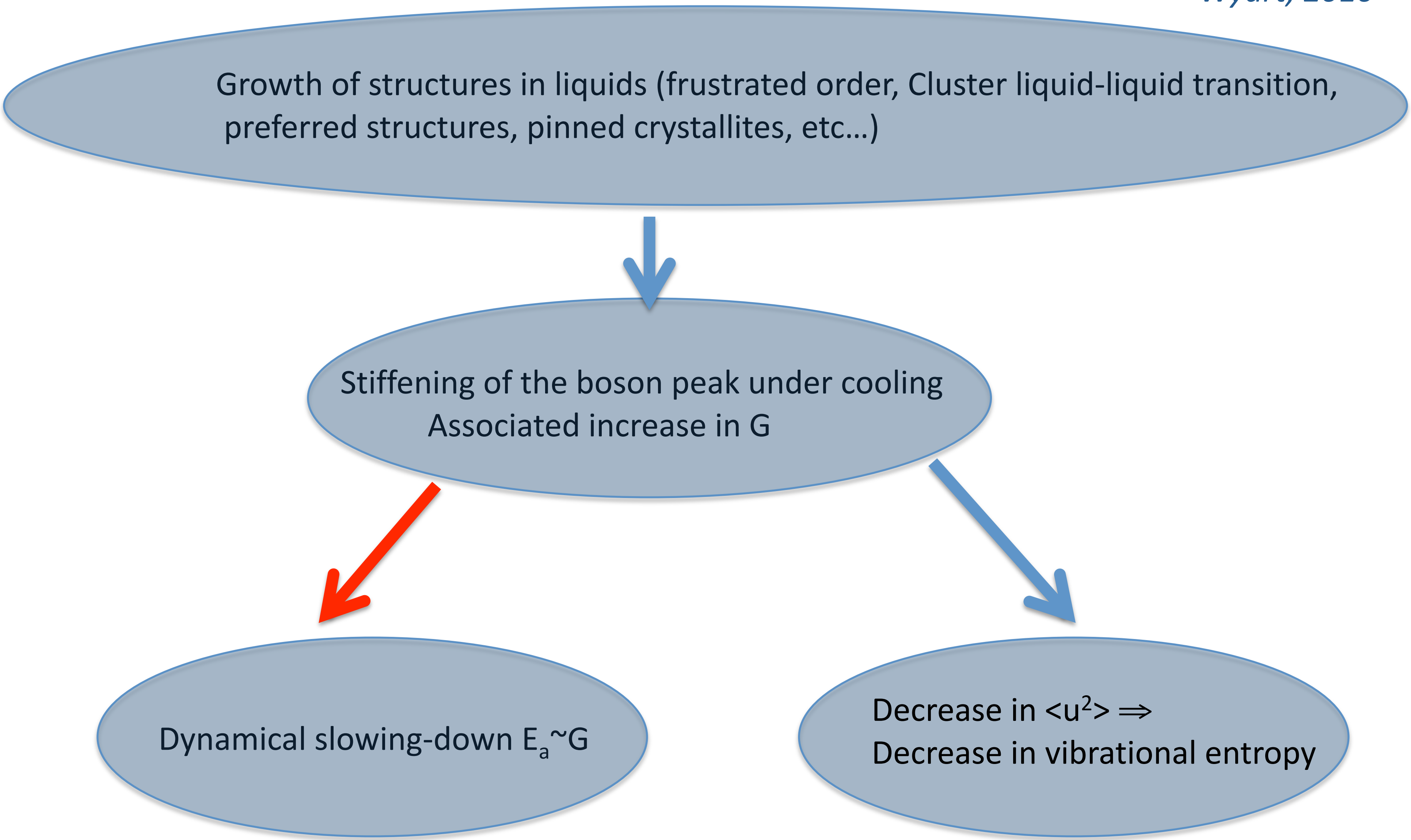


- Growth of more coordinated structures in liquids (frustratation-limited domains, Cluster liquid-liquid transition, preferred structures, pinned crystallites, etc…)

- Softer in the interstices, but stiffened by the structures

Scenario for the glass transition

Wyart, 2010



Growth of structures in liquids (frustrated order, Cluster liquid-liquid transition, preferred structures, pinned crystallites, etc…)

Stiffening of the boson peak under cooling
Associated increase in G

Dynamical slowing-down $E_a \sim G$

Decrease in $\langle u^2 \rangle \Rightarrow$
Decrease in vibrational entropy

Discussion

Experimental questions:

- Elasticity measured a GHz frequency, not THz. Same results?
- Better estimate of the vibrational specific heat:

dependence on T of spectra near Tg for various liquids

Apparent contradiction:

- *Mossa et al (2002), Angell et al (2003)*: Boson peak evolves very little at constant volume, liquid still fragile (but less).

⇒ Effects of non-linearities not included. Measure the vibrational spectrum (and entropy) directly from the dynamics.

Conceptual question:

- Hypothesis of elastic model: Stiffening of soft modes well captured effectively by a change in G. Accurate? Crude approximation?

⇒ temperature dependence of G does not capture all the fragility

⇒ *Larini et al (2008)*: log(τ) increases faster than $1/\langle u^2\rangle \sim G$