High-resolution IXS to resolve puzzles of glasses

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Content:

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1. The development of high-resolution IXS at the ESRF (ID18): monochromators and methods.
2. An example of application of the high-resolution IXS to glass dynamics.
3. Scientific cases in glass dynamics for high-resolution IXS.
4. Summary

Monochromators:

Nuclear Resonance Scattering:

(resonant scattering of x rays by nuclei with low energy (10-100 keV) nuclear transitions)

It requires ~meV monochromatization for:

(i) measurements of time spectra of nuclear scattering (to decrease load on detector)

(ii) measurements of density of vibrational states (for good energy resolution)

Energy [keV]	Isotope	Resolution [meV]	design
14.413	^{57}Fe	6.4	nested
14.413	^{57}Fe	3.1	nested
14.413	^{57}Fe	1.8	in-line
14.413	^{57}Fe	0.5	in-line
22.502	^{149}Sm	0.76	nested
21.542	^{151}Eu	1.6	nested
23.879	^{119}Sn	0.65	nested
25.651	^{161}Dy	0.9	nested
27.890	^{129}I	1.0	nested
35.493	^{125}Te	1.1	backscattering
37.1298	^{121}Sb	1.2	backscattering
39.5821	^{129}Xe	1.4	backscattering
67.41	^{61}Ni	120	nested
68.752	^{73}Ge	24	nested

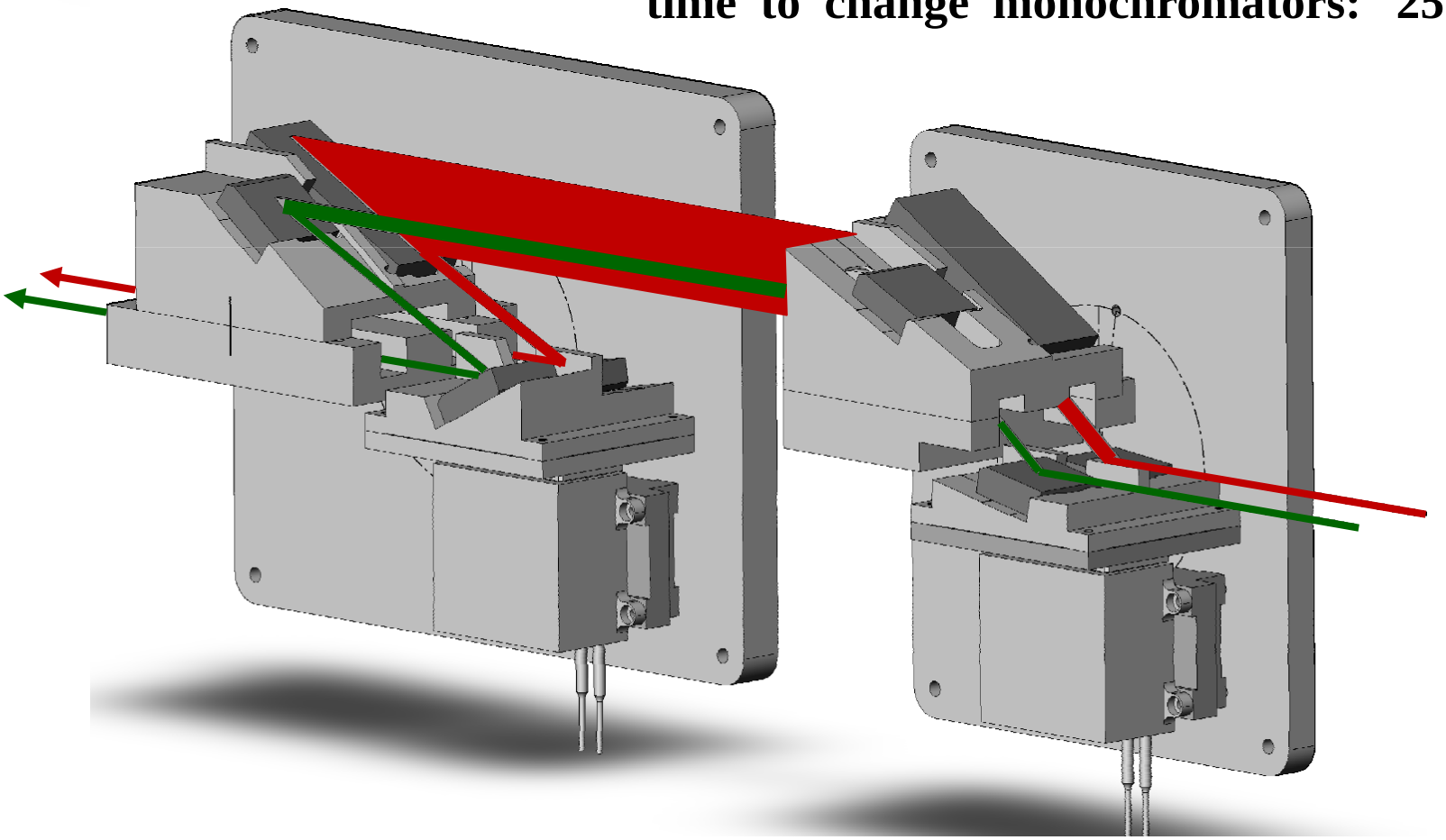
Monochromators:

Double In-line monochromator for E = 14.413 keV:

ΔE = ~0.5 meV, R = ~40%, flux = 0.9×10^{10} ph/s

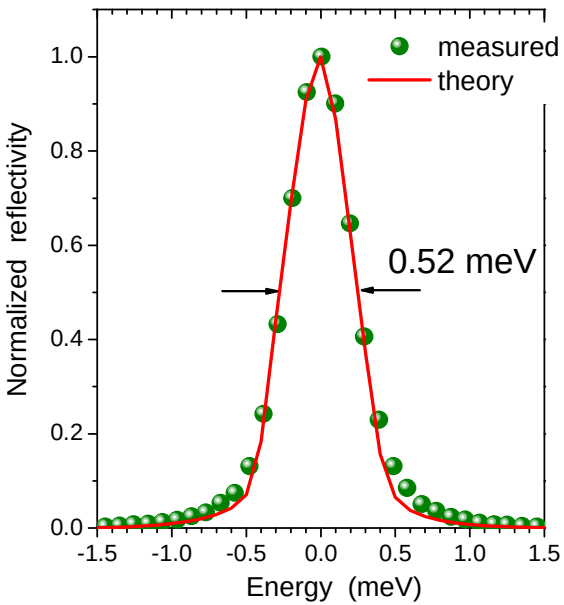
ΔE = ~1.8 meV, R = ~50%, flux = 4×10^{10} ph/s

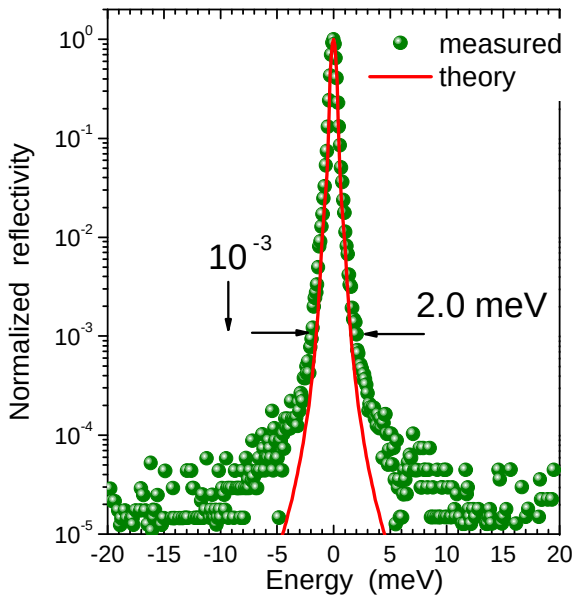
time to change monochromators: 25 sec

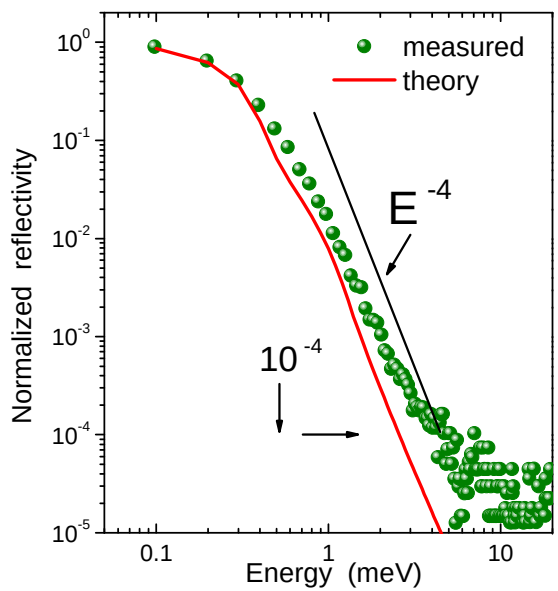


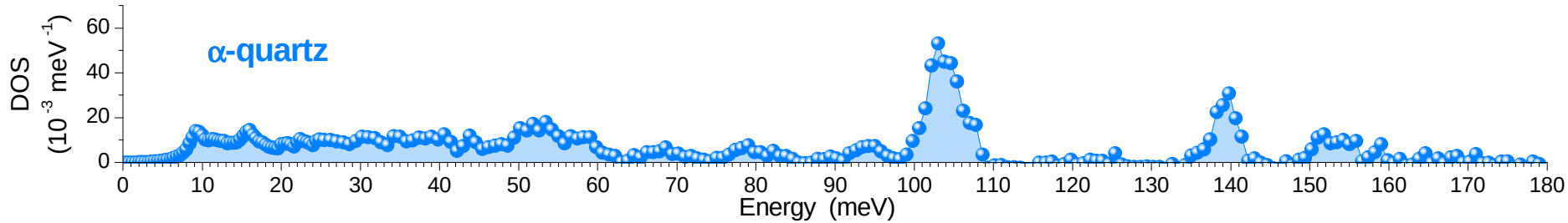
Monochromators:

In-line monochromator with the bandwidth of ~0.5 meV





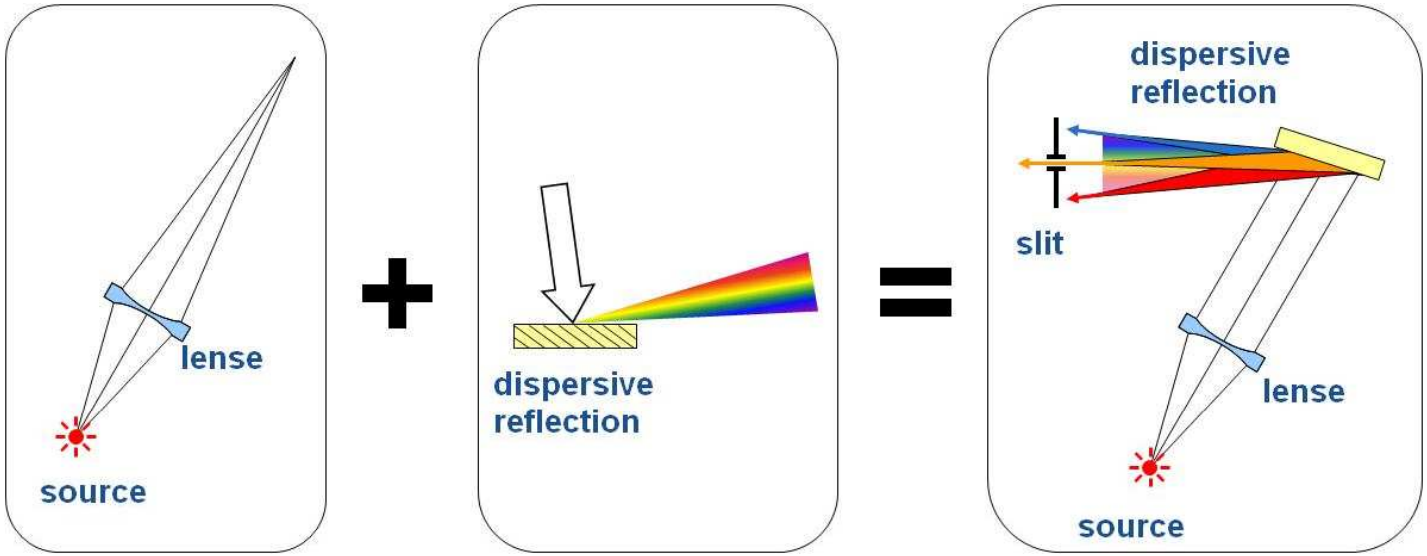


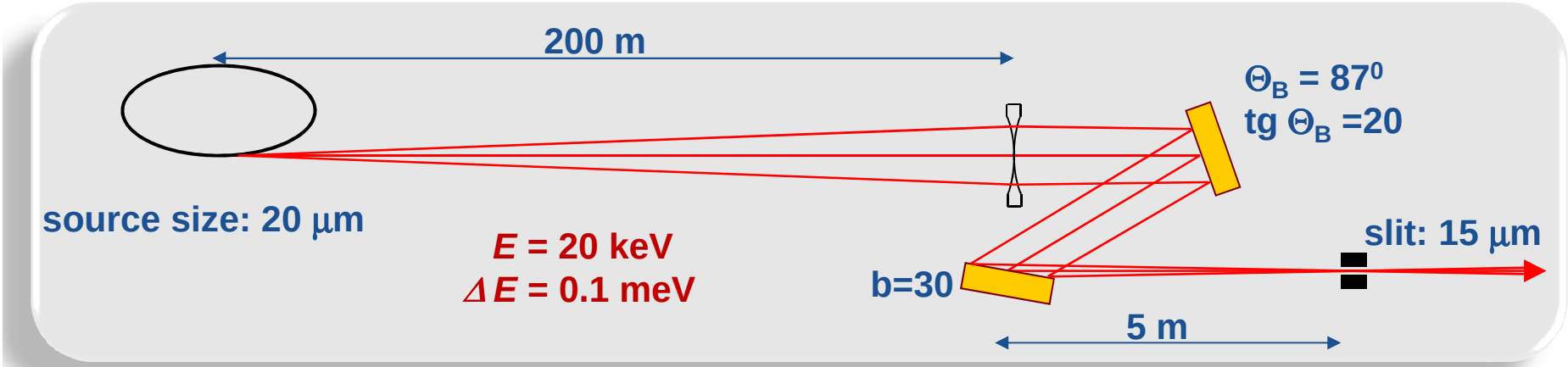


Monochromators:

"Focusing" monochromator:

V.Kohn, ac, R.Rüffer, JSR **16** (2009) 635



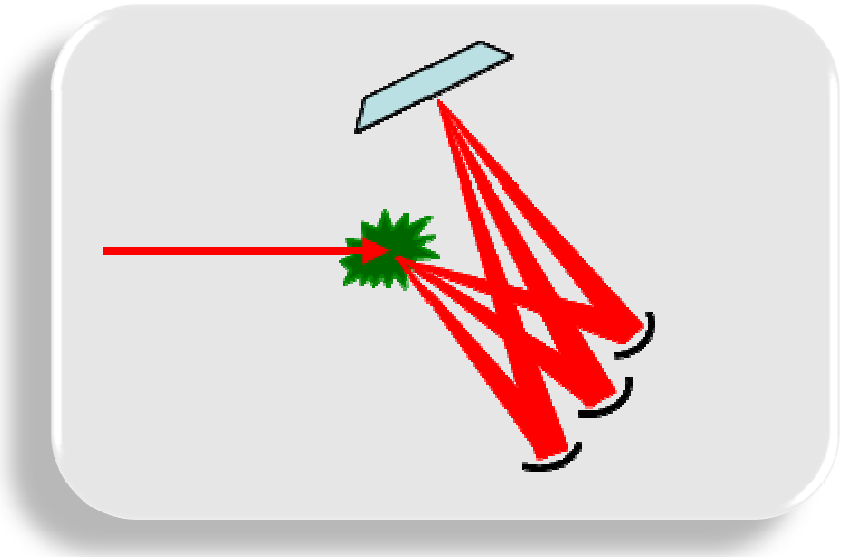


Methods:

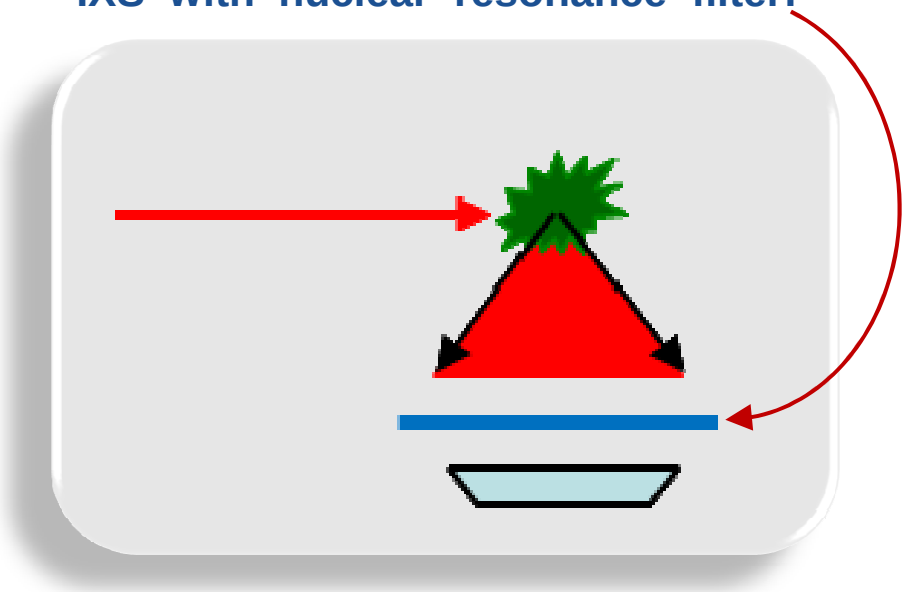
Nuclear Resonance analysis of IXS:

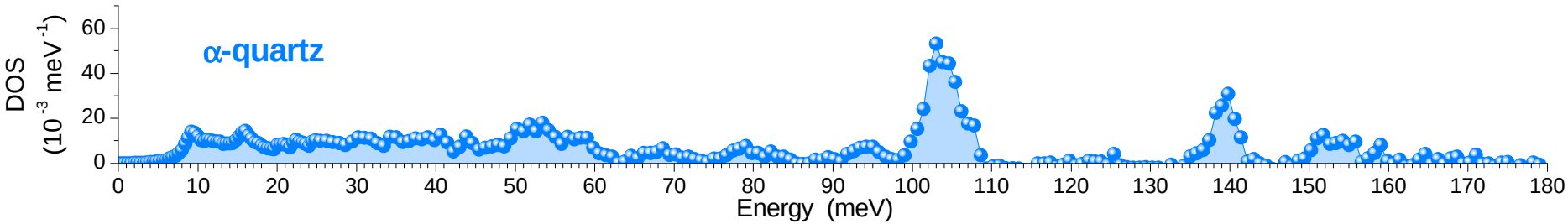
ac *et al*, PRL **76** (1996) 4258

IXS with crystal analyzers:



IXS with nuclear resonance filter:

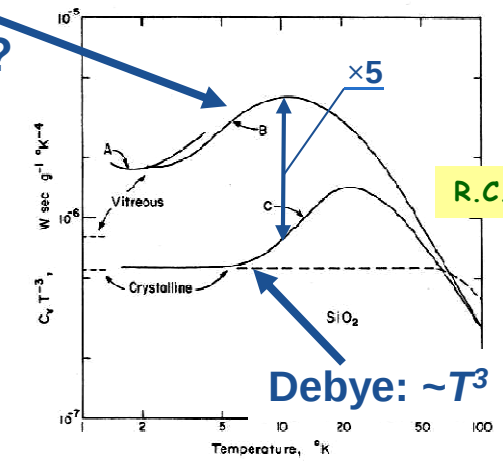




Scientific case:

additional vibrational states?

At low temperatures, heat capacity for glasses is larger than for crystals

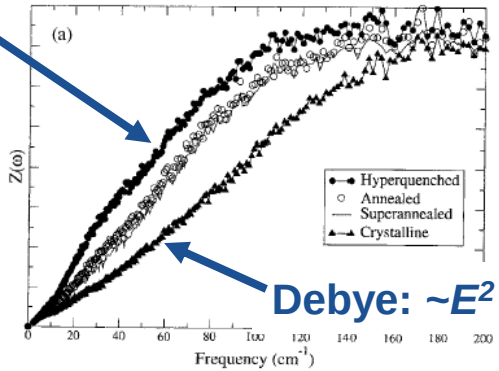


R.C.Zeller *et al.*, PRB 4,2029,1971

FIG. 4. Specific heat of vitreous SiO_2 and crystal quartz, plotted as C_pT^{-3} vs T. A: I. R. Vitreosil (Ref. 29); B: vitreous silica (after Refs. 30–32); C: α-quartz

DOS *g(E)*: additional vibrational states !

g(E)

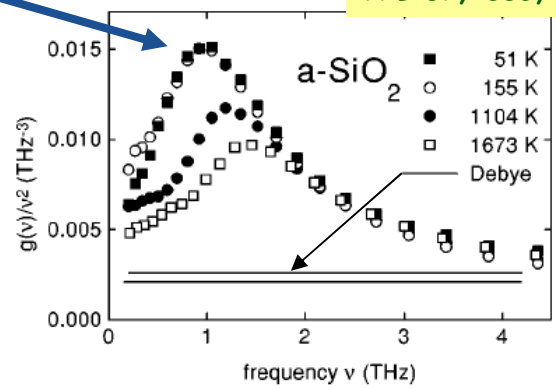


C.A.Angel *et al.*, J.Phys.:Cond.Matt. 15,S1051,2003

Reduced DOS $g(E)/E^2$: **the boson peak** !

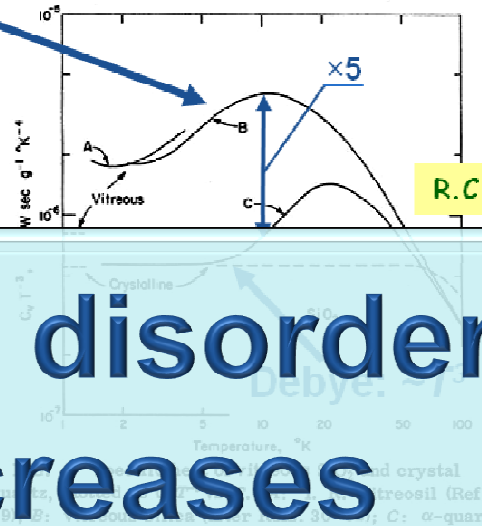
A.Wischnewski *et al.*, PRB 57,2663,1998

g(E) / E²



Scientific case:

additional vibrational states?



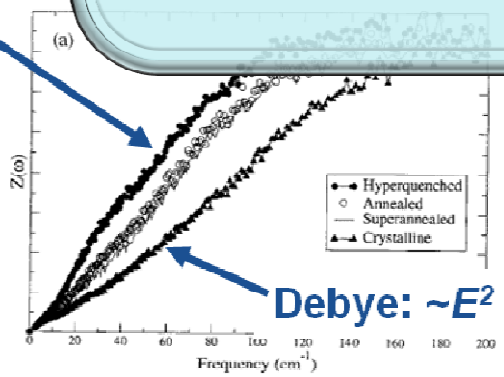
R.C.Zeller *et al.*, PRB 4,2029,1971

At low temperatures, heat capacity for glasses is larger than for crystal

How disorder increases the heat capacity?

DOS *g(E)*: additional vibrational states !

g(E)

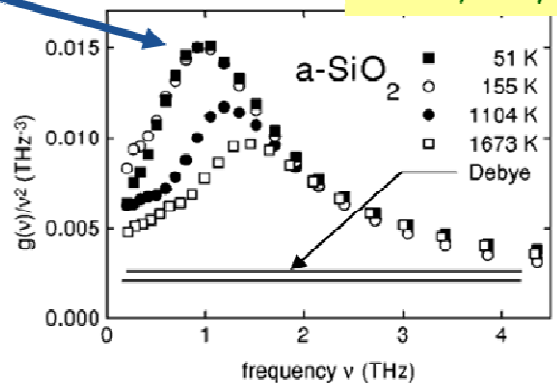


Debye: ~E^2

C.A.Angel *et al.*, J.Phys.:Cond.Matt. 15,S1051,2003

Reduced DOS g(E)/E: the boson peak !

g(E) / E^2



A.Wischnewski *et al.*, PRB 57,2663,1998

Scientific case:

WEB OF KNOWLEDGE℠ | DISCOVERY STARTS HERE

All Databases | Select a Database | Web of Science | Additional Resources

Search | Search History

All Databases

Results Topic=(boson) AND Topic=(peak) NOT Topic=(HIGGS)
Timespan=All years.
Search language=English

Results: **1,434**

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3. Title: A thermodynamic connection to the fragility of glass-forming liquids
Author(s): Martinez, LM; Angell, CA
Source: NATURE Volume: 410 Issue: 6829 Pages: 663-667 DOI: 10.1038/35070517 Published:
Times Cited: 317 (from All Databases)
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London University, Universität Bayreuth,
Max Planck Institut for the Science of Light, Aalborg University

submitted to PRL

Samples :

ambient glass

amorphous

SiO_2

densified glass

amorphous

α-cristobalite

tetragonal

α-quartz

trigonal

coesite

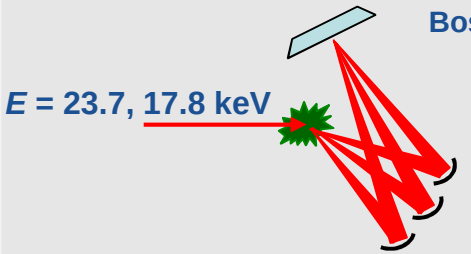
monoclinic

Methods :

- Experimental method: Inelastic X-ray scattering (two methods)

with crystal analyzers:
(momentum-differentiated approach)

Bosak & Krisch, 2005



ID28

ΔE = 1.4 meV or 3 meV
δQ = 0.03 nm^{-1}, ΔQ = [1-7] nm^{-1}

with nuclear resonance analysis:
(momentum-integrated approach)

ac *et al*, 1996

ID18

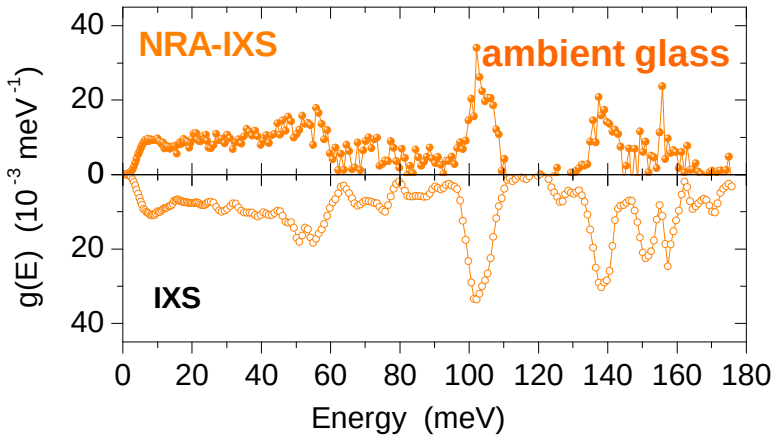
ΔE = 0.7 meV
ΔQ = [3-14] nm^{-1}

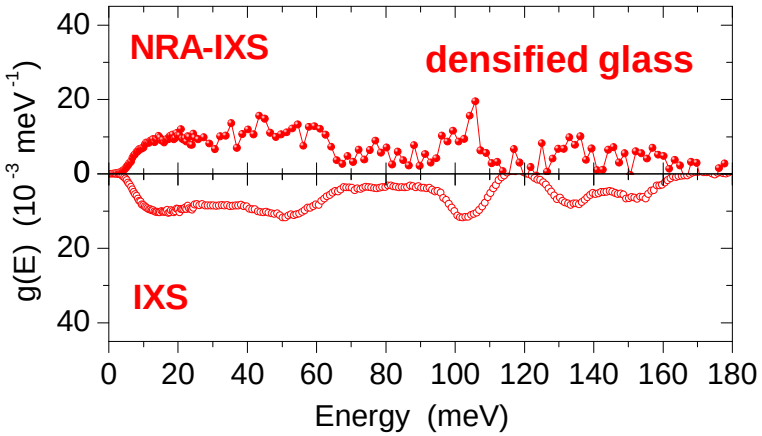
- Comparison of the data sets from <u>two methods</u>
- Comparison to <u>*ab initio*</u> calculations
- Comparison to <u>heat capacity</u> measurements
- Comparison to <u>neutron data</u>

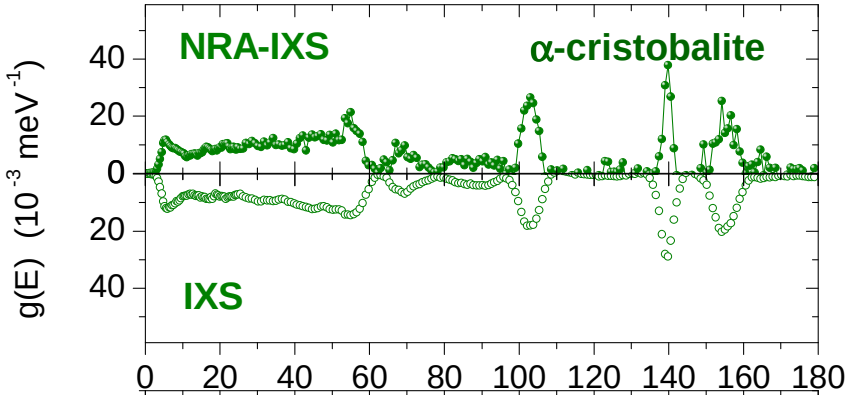
Comparison of two data sets:

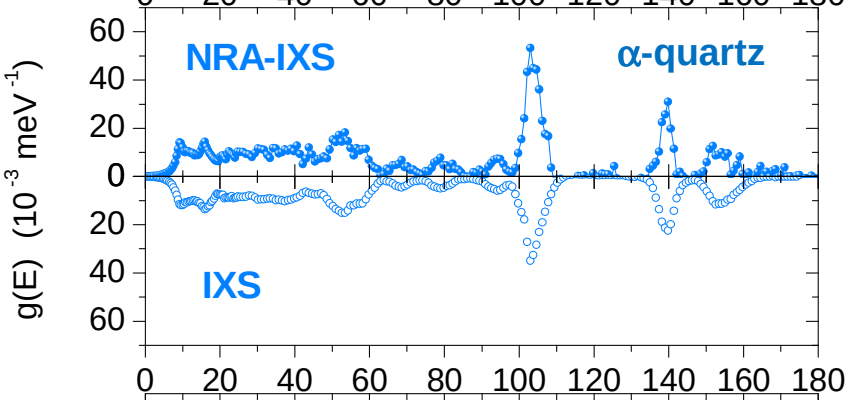
● nuclear resonance analysis

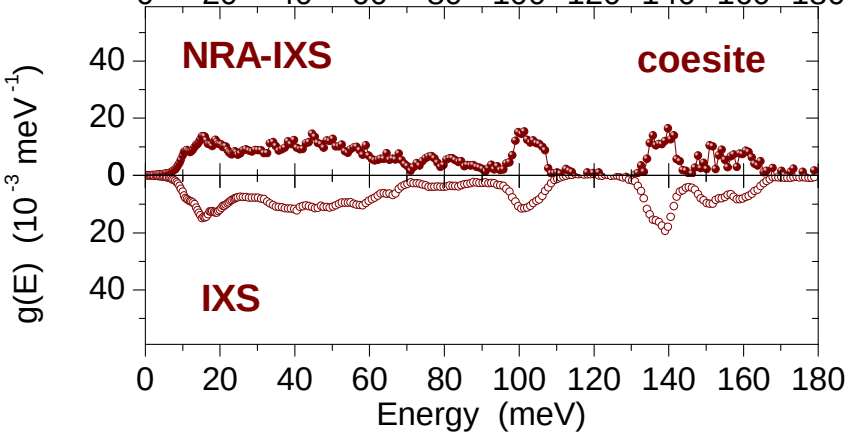
○ crystal analyzers







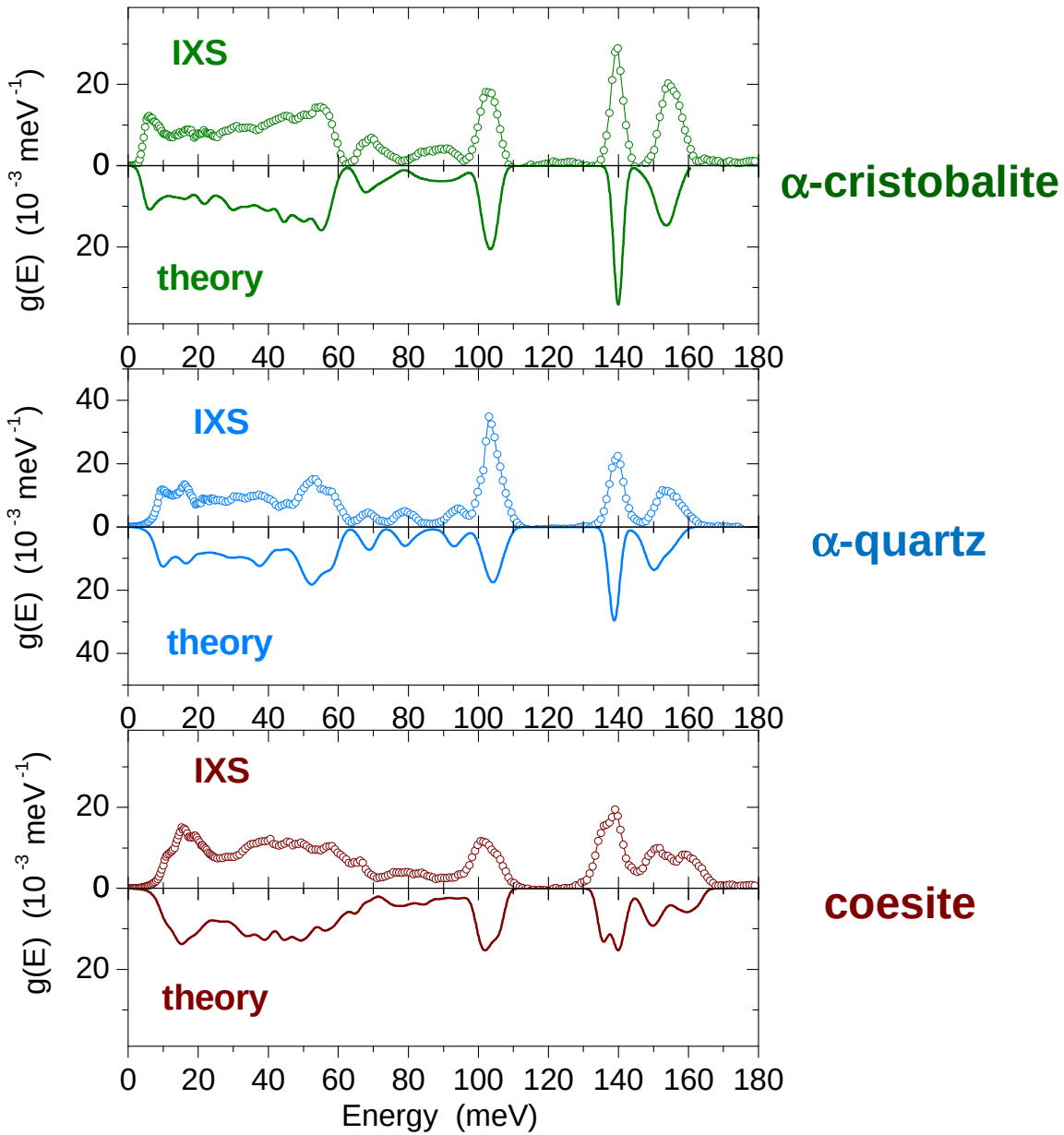




Comparison to theory :

○ IXS, crystal analyzers

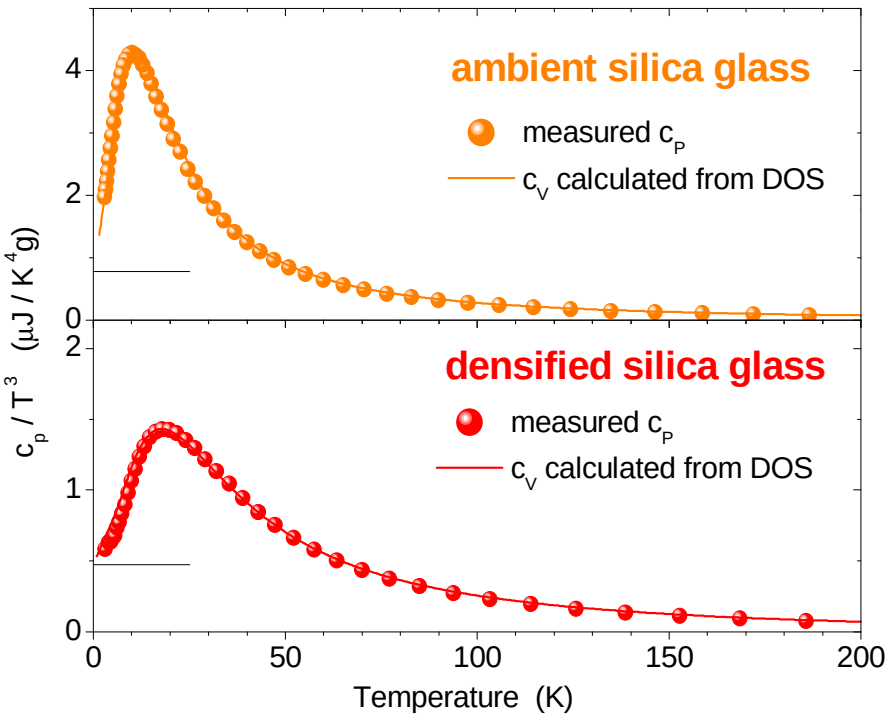
— *ab-initio* calculations convoluted with instrumental function

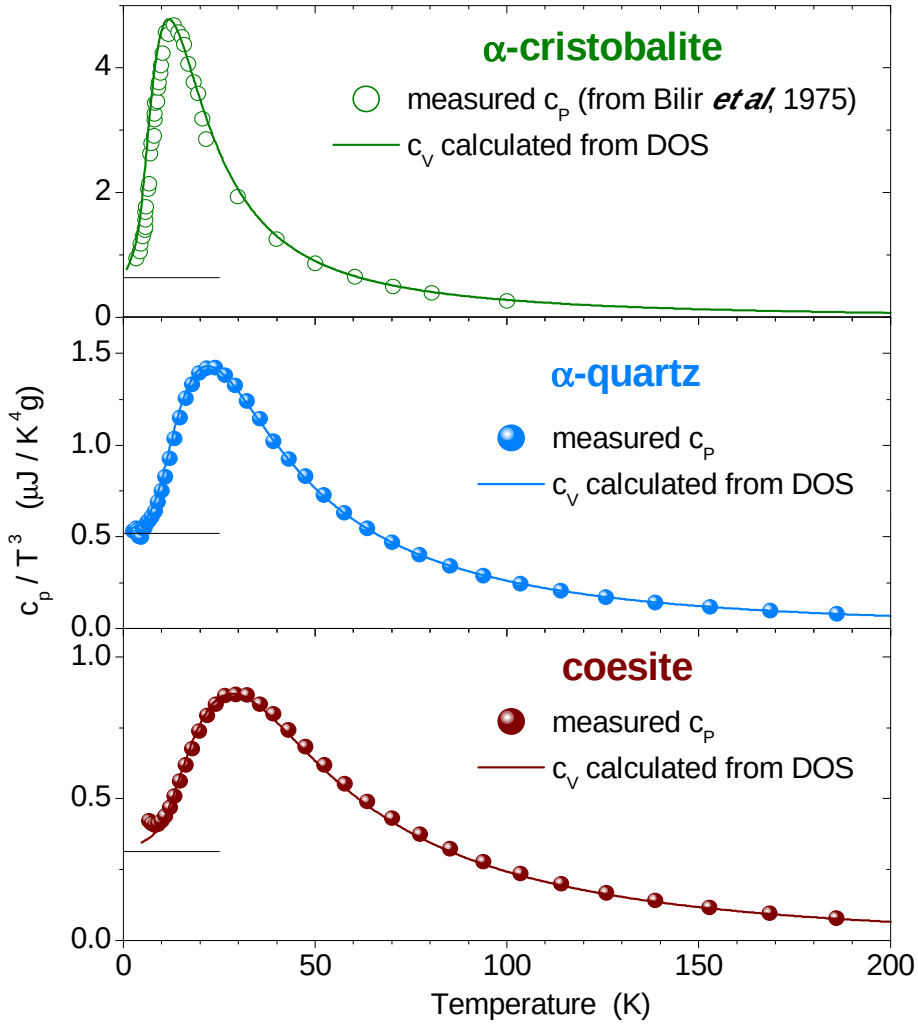


Comparison to heat capacity :

○ measured c_P

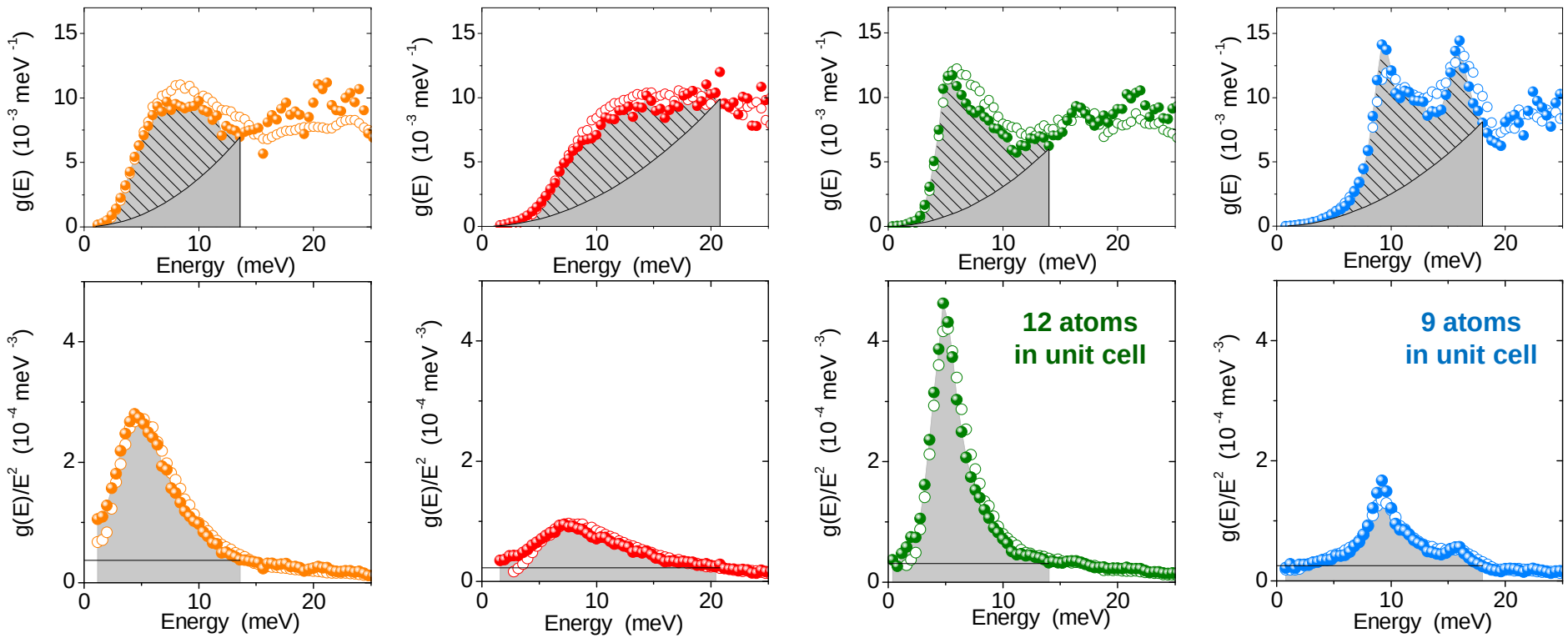
— c_V calculated from DOS



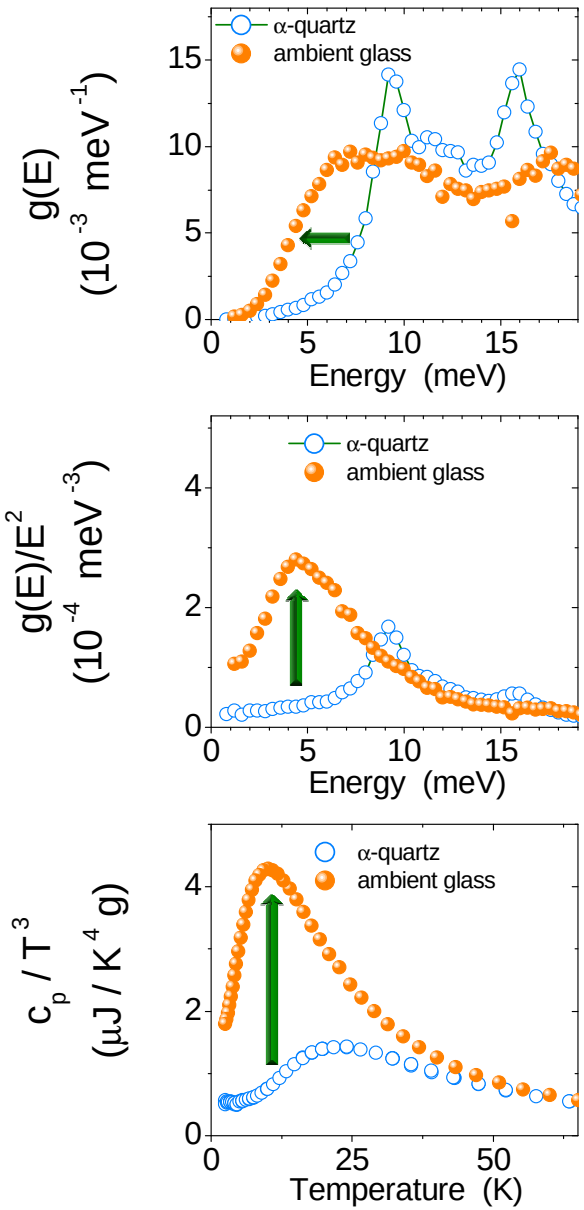


Quantitative analysis :

ambient glass	densified glass	α-cristobalite	α-quartz
excess states: 5.3(3)%	excess states: 5.9(4)%	excess states: 5.6(3)%	excess states: 6.6(4)%
all states: 8.4(5)%	all states: 12.8(8)%	all states: 8.4(5)%	all states: 11.5(7)%



Typical glass vs typical crystal:



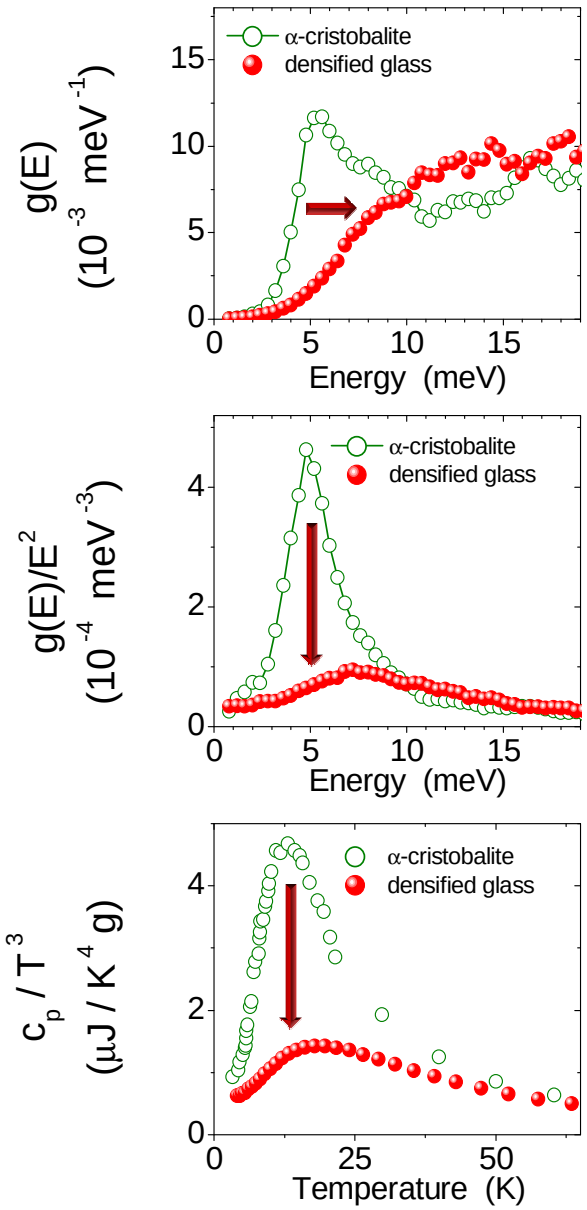
ambient glass

α-quartz

The role of disorder:

- shifts DOS to **lower** frequency,
- creates a **peak** in reduced DOS,
- provides **excess** of heat capacity.

Another glass vs another crystal:



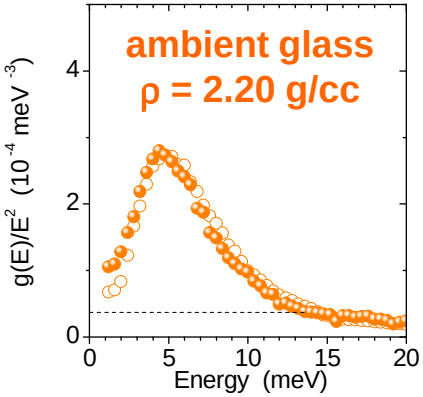
densified glass

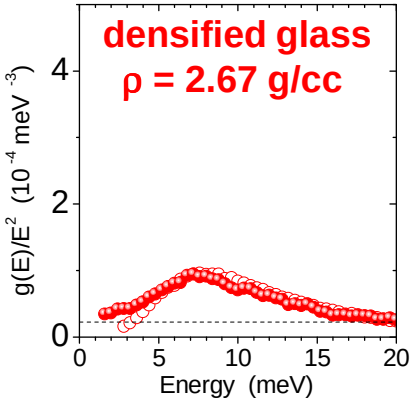
α-cristobalite

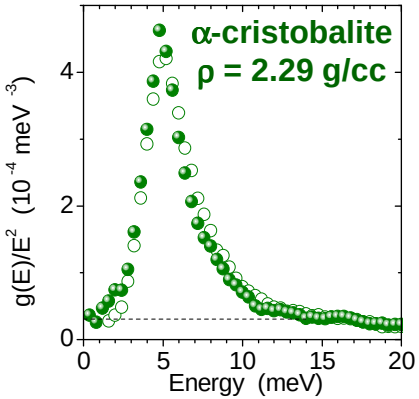
The role of disorder:

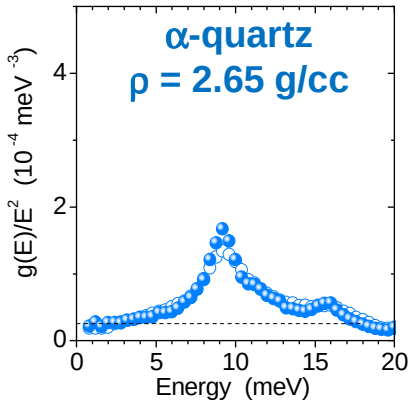
- shifts DOS to **higher** frequency,
- creates **flat** reduced DOS,
- provides **deficit** of heat capacity.

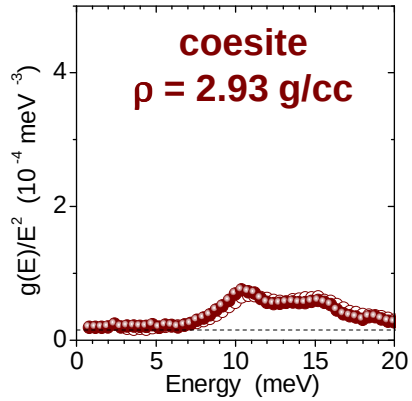
Where is the problem ?





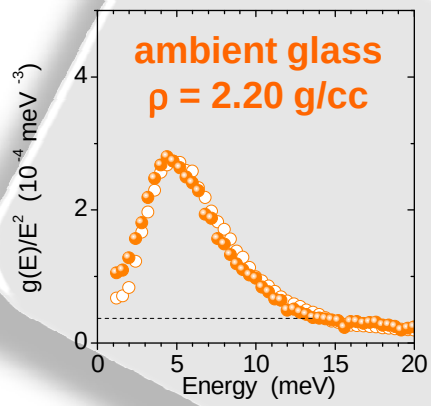


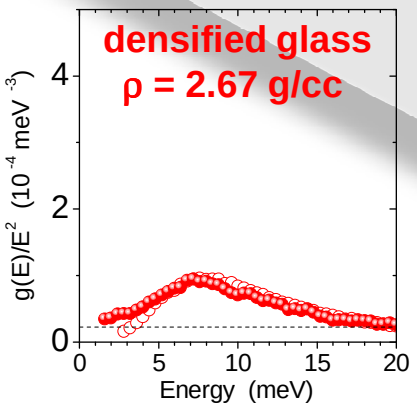




DOS, *reduced DOS*, and heat capacity depend also on *density*:

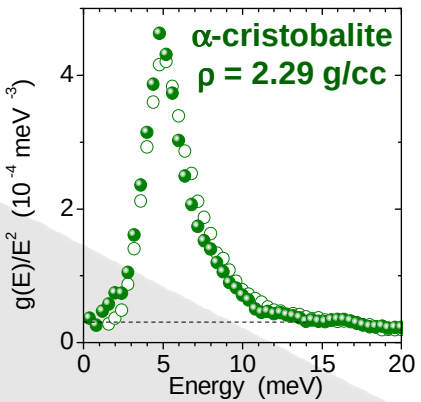
Where is the problem ?

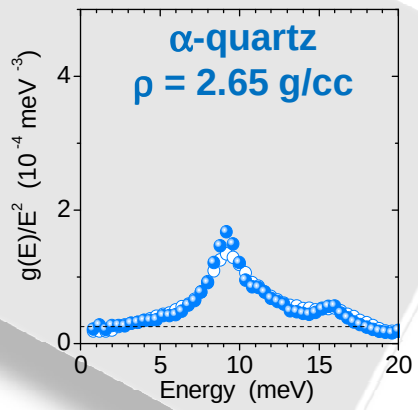


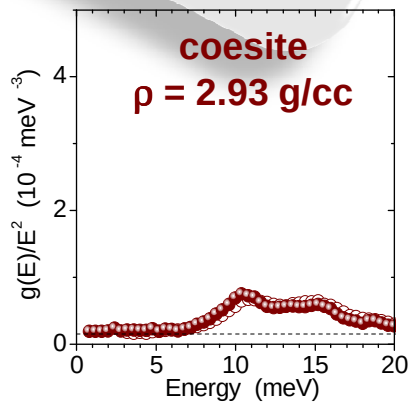


low-density glass
versus
high-density crystal:

disorder effect
plus
density effect

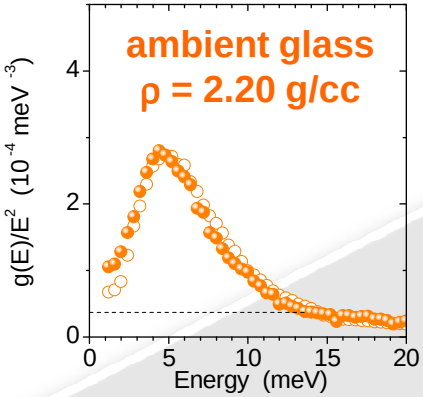


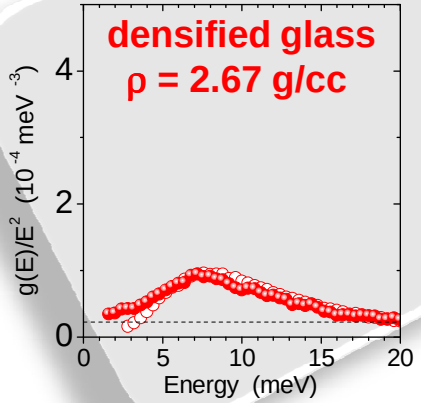




DOS, *reduced DOS*, and heat capacity depend also on *density*:

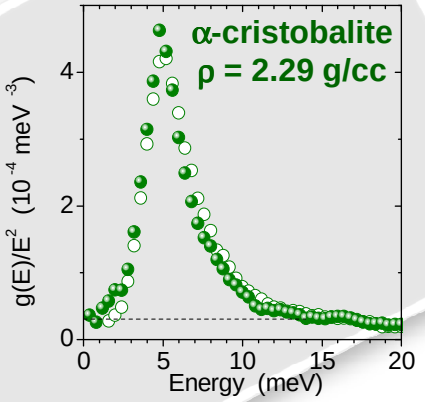
Where is the problem ?

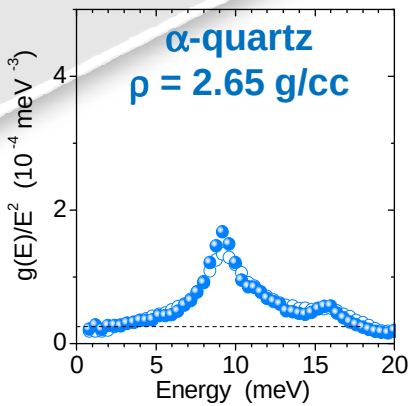


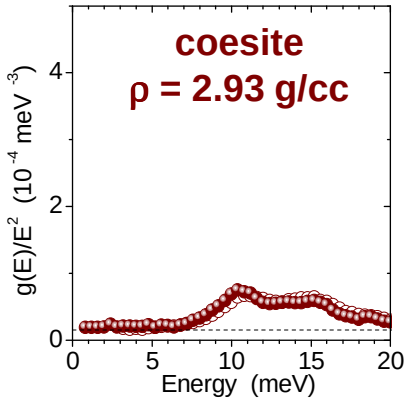


high-density glass versus low-density crystal:

disorder effect minus density effect

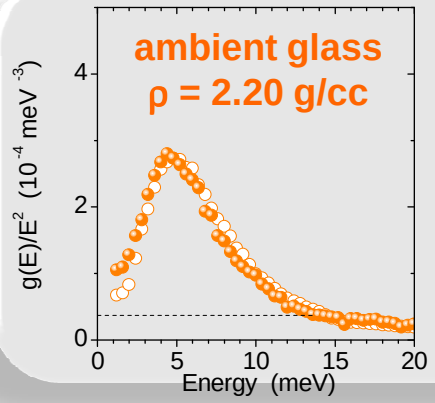




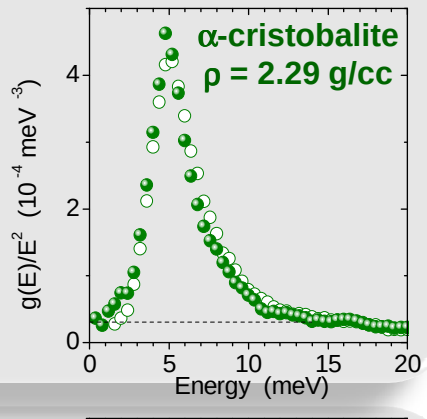


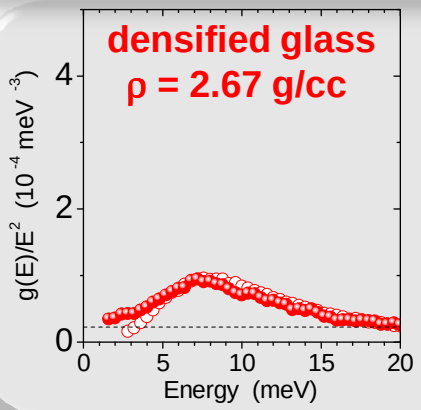
DOS, *reduced DOS*, and heat capacity depend also on *density*:

What should we compare?

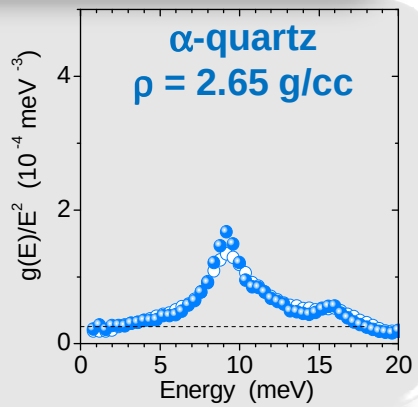


The low-density glass and crystal: only the disorder effect

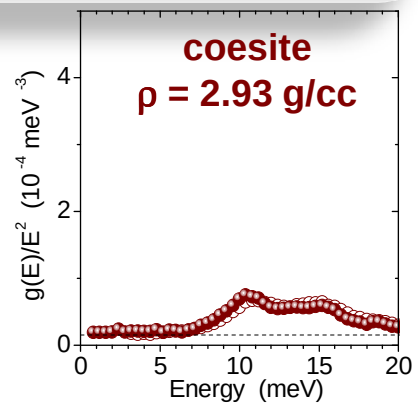




The high-density glass and crystal: only the disorder effect



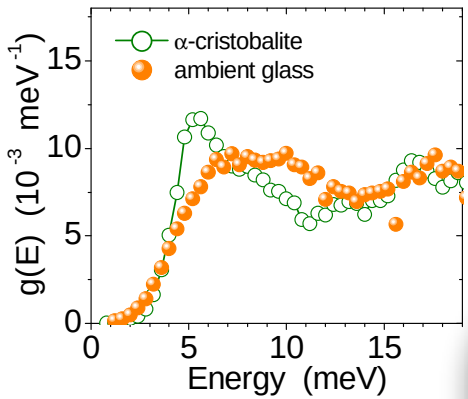
DOS, *reduced DOS*, and heat capacity depend also on *density*:

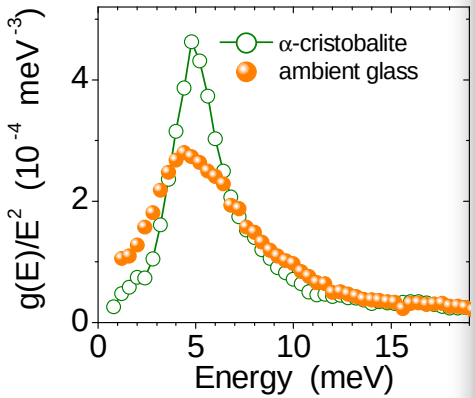


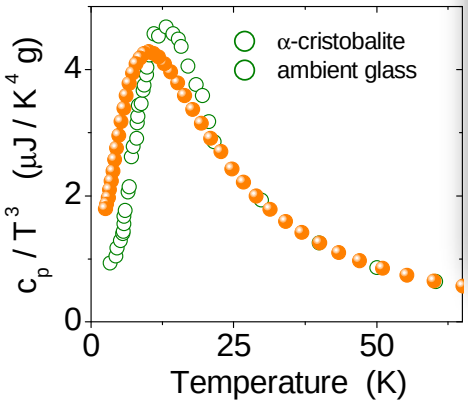
Comparison for matched density:

ambient glass
α-cristobalite

densified glass
α-quartz

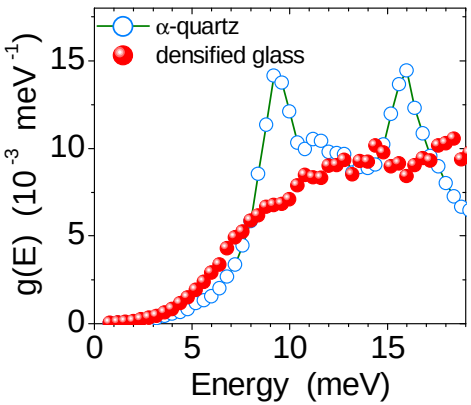


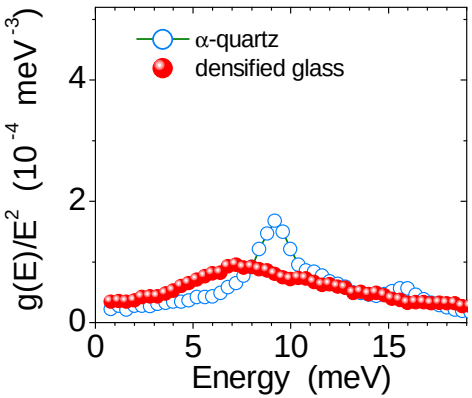


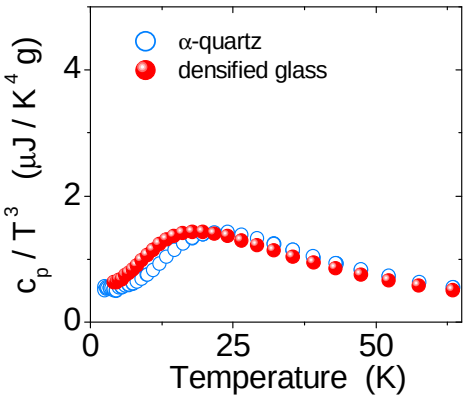


The role of disorder:

- does NOT make DOS softer,
- does NOT create peak in the reduced DOS, the peak is already there,
- it smears out the DOS and the reduced DOS,
- Disorder does NOT change the heat capacity.







Conclusion:

How disorder increases the heat capacity?

At low temperatures, heat capacity for glasses is larger than for crystals

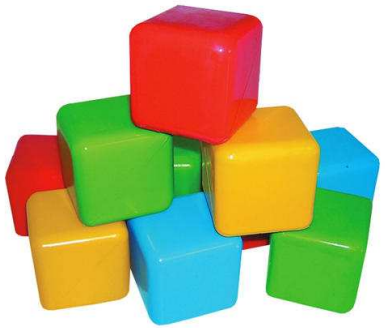
R.C.Zeller *et al.*, PRB 4,2029,1971

DOS *g(E)*: additional vibrational states !

It does not do it:

the higher heat capacity of glasses is caused by their lower density

A.Wischnewski *et al.*, PRB 57,2663,1998



ngel *et al.*, s.:Cond.Matt. 15,S1051,2003

Scientific cases:

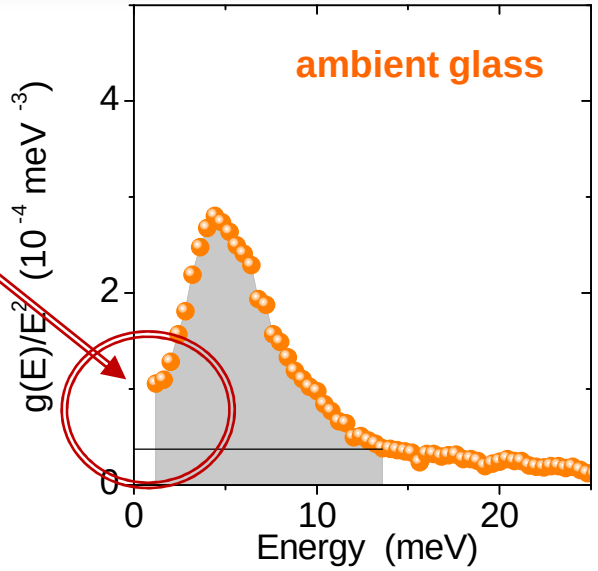
Are there any unusual soft modes at lower energy?

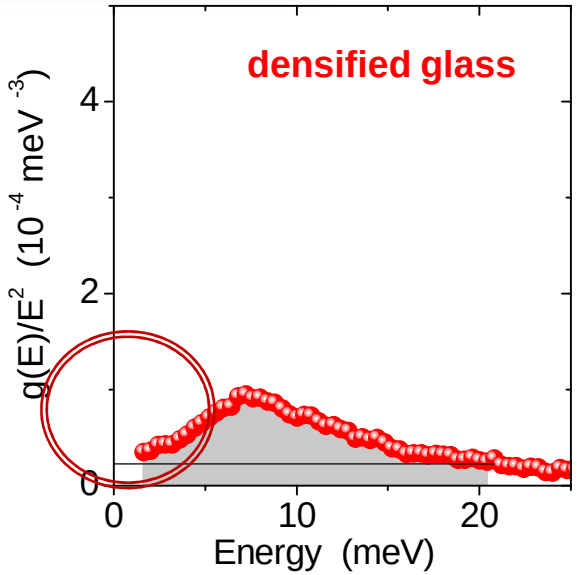
What is that?

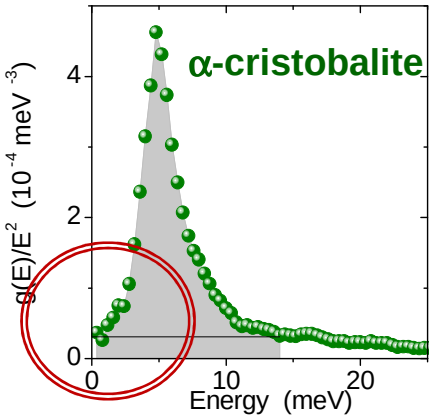
onset of instability?

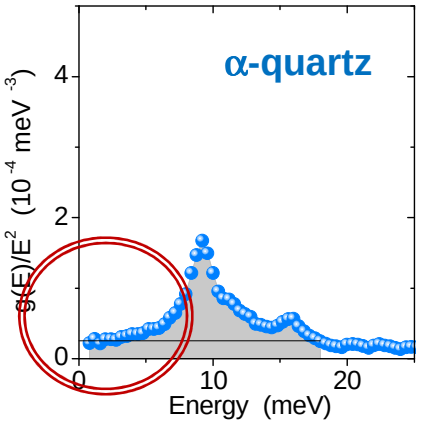
anharmonic effects?

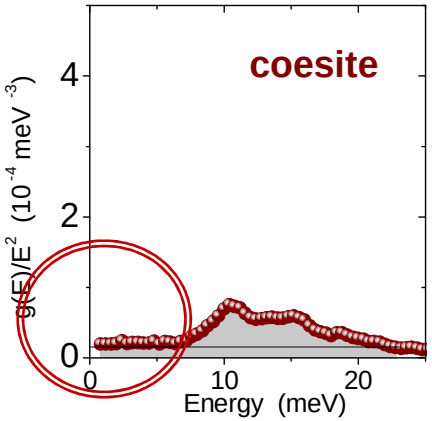
Does reduced DOS go to the Debye level?











Scientific cases:

What is the origin of quasi-elastic scattering?

B.Frick *et al*, PRB **47** (1993) 14795

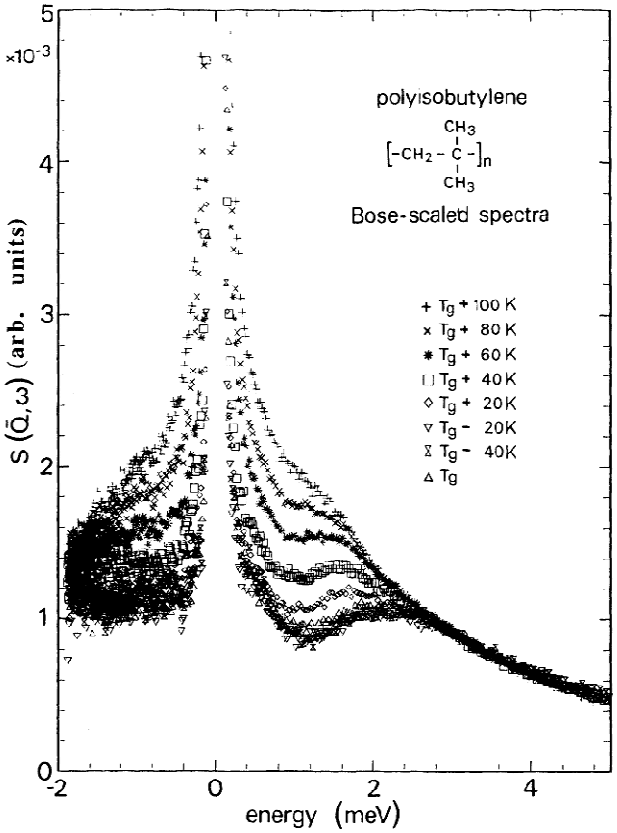


FIG. 6. Dynamic structure factor $S(Q,\omega)$ of PIB corrected for Debye-Waller factor and Bose factor as measured on IN6, ILL. The measured curves are presented for $T=200$ K, the glass-transition temperature of PIB, as a reference temperature.

relaxation?

vibrations?

A.P.Sokolov *et al*, PRB **57** (1997) 5042

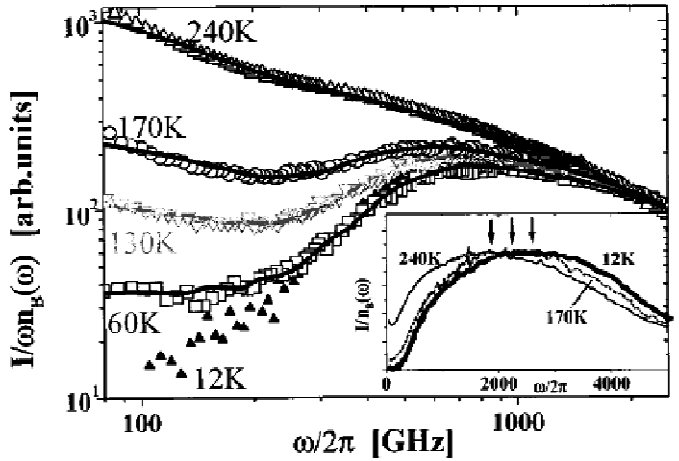


FIG. 3. The Raman spectra of PB at different temperatures (symbols) and results of the fit (lines). The inset shows the Raman susceptibility spectra and the arrows show the shift of Ω_{end} with temperature.

Scientific cases:

Can we directly observe dynamical heterogeneities?

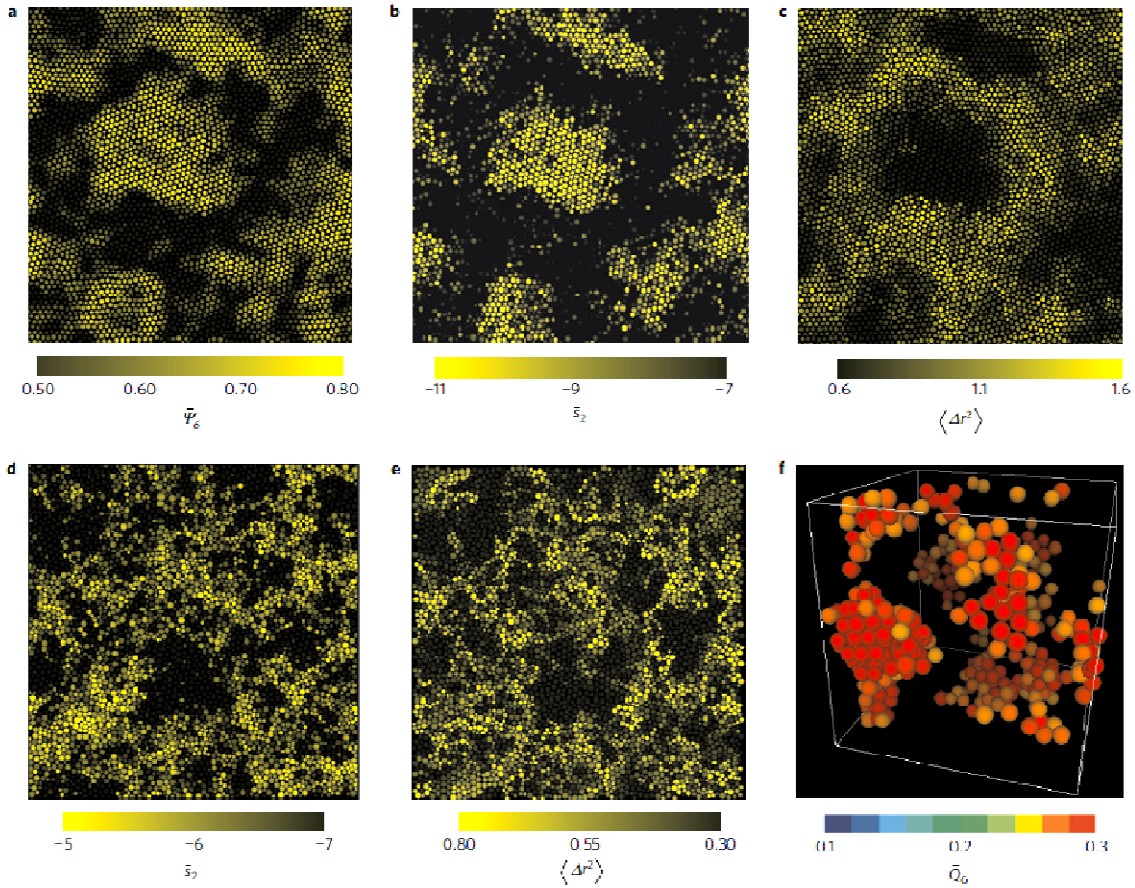


Figure 1 | Structural order in glass-forming liquids. **a**, Spatial distribution of $\bar{\Psi}_6$ for 2DPC with $\Delta_{2DPC} = 9\%$ at $\phi = 0.740$. See Supplementary Video S1 for dynamical fluctuations of $\bar{\Psi}_6$. **b**, Spatial distribution of $\bar{s}_2$ for the same system as in **a**. **c**, Spatial distribution of the mean-square displacement $\langle \Delta r^2 \rangle$ over $t = 10\tau_\alpha$ for the same system as in **a**. **d**, Spatial distribution of the local structural entropy $\bar{s}_2$, which is averaged over $10\tau_\alpha$. **e**, Spatial distribution of the mean square displacement $\langle \Delta r^2 \rangle$ over $10\tau_\alpha$, $\langle \Delta r^2(10\tau_\alpha) \rangle$. **f**, Spatial distribution of $\bar{Q}_6$ for 3DPC with $\Delta_{3DPC} = 6\%$ at $\phi = 0.557$. Here, less ordered particles are not shown for clarity. See also Supplementary Fig. S1a,b for 2DGL and 2DSL, respectively.

H.Tanaka *et al*, Nmat **9** (2010) 324

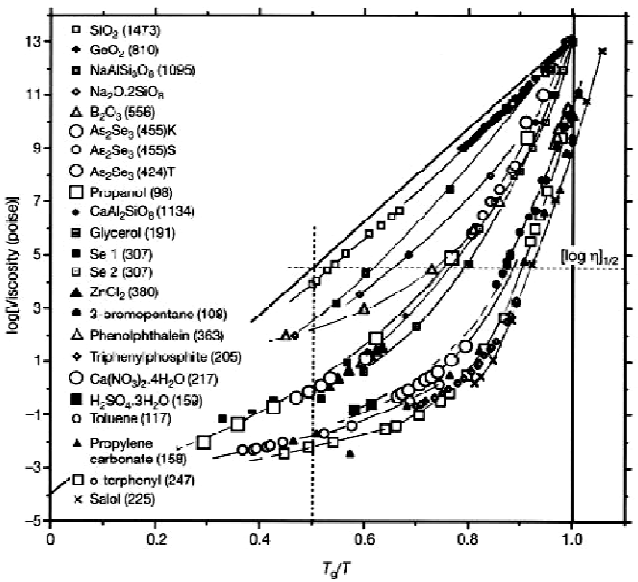
can we see this?

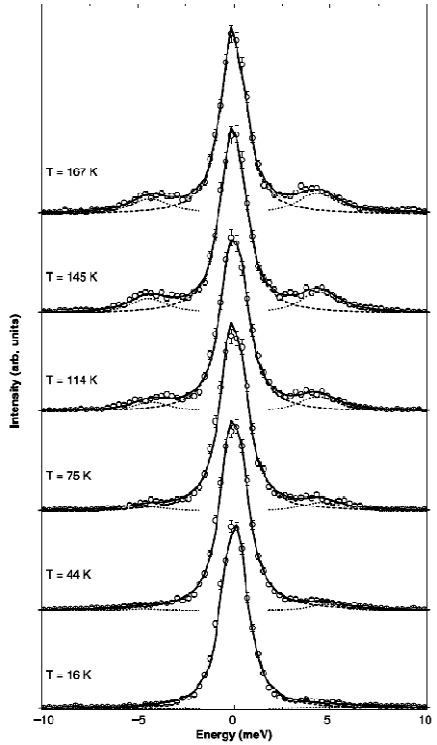
Why "slow" viscosity correlates with fast atomic vibrations?

L.-M.Martivez and C.A.Angell, Nature **410** (2001) 663

T.Scopigno *et al*, Science **302** (2003) 849

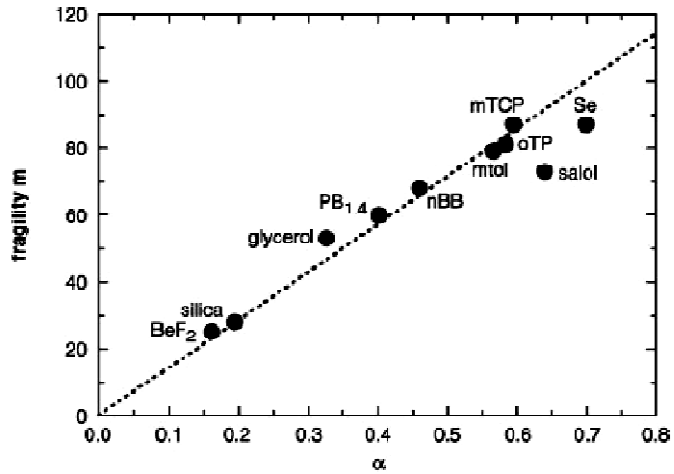
$$m = \lim_{T \to T_g} \frac{d\log(\eta)}{d(T_g/T)}$$



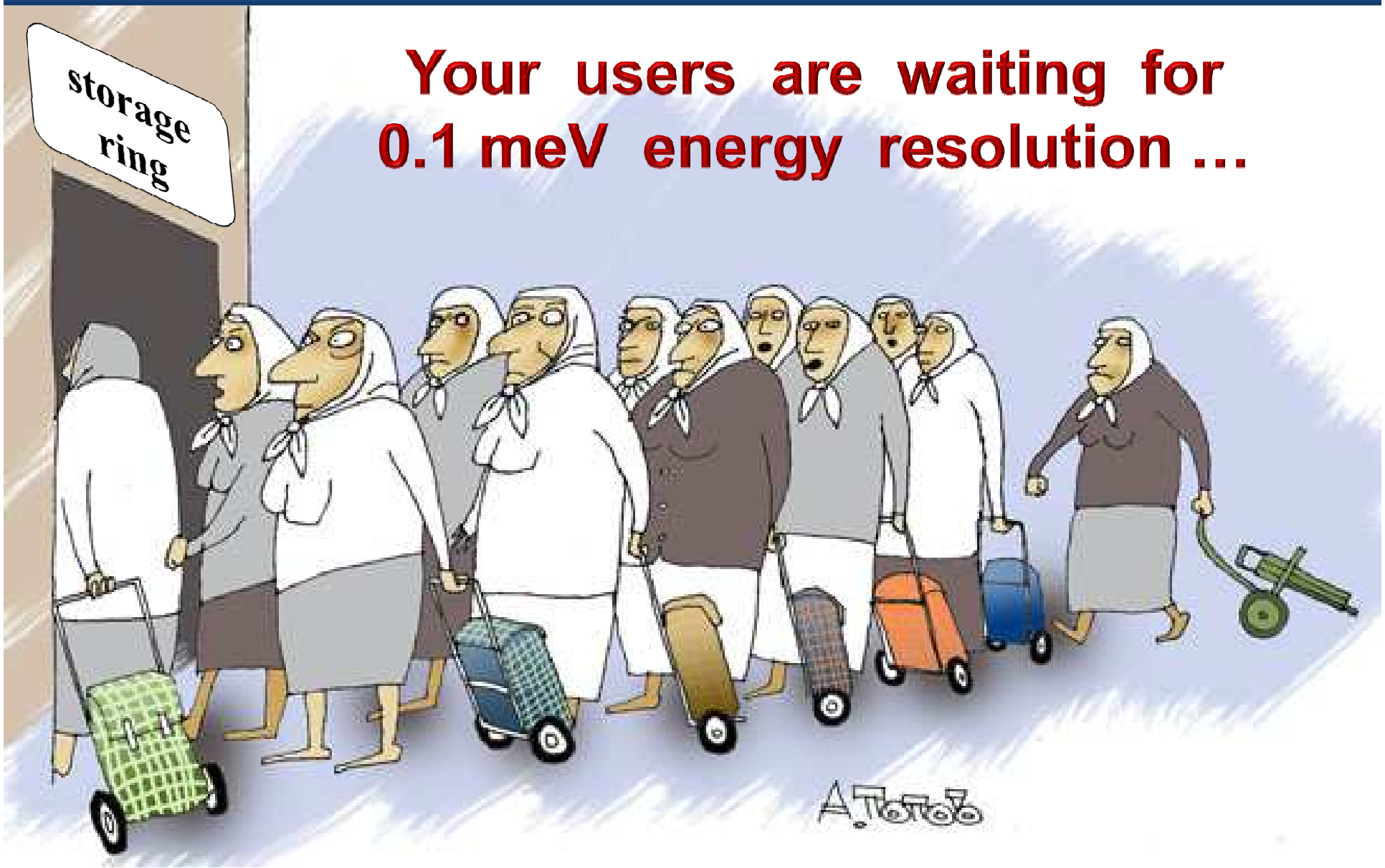


$$f(Q,T) = \lim_{t \to \infty} \Phi_Q(t) =$$

$$\lim_{t \to \infty} \frac{S_{IS}(Q) + F_{incl}(Q,t)}{S_{IS}(Q) + S_{incl}(Q)} = \frac{1}{1 + S_{incl}(Q)/S_{IS}(Q)}$$



Summary:


storage ring
Your users are waiting for 0.1 meV energy resolution …

Time to stop now...