Glass transition and shear modulus in amorphous metallic systems

Konrad Samwer

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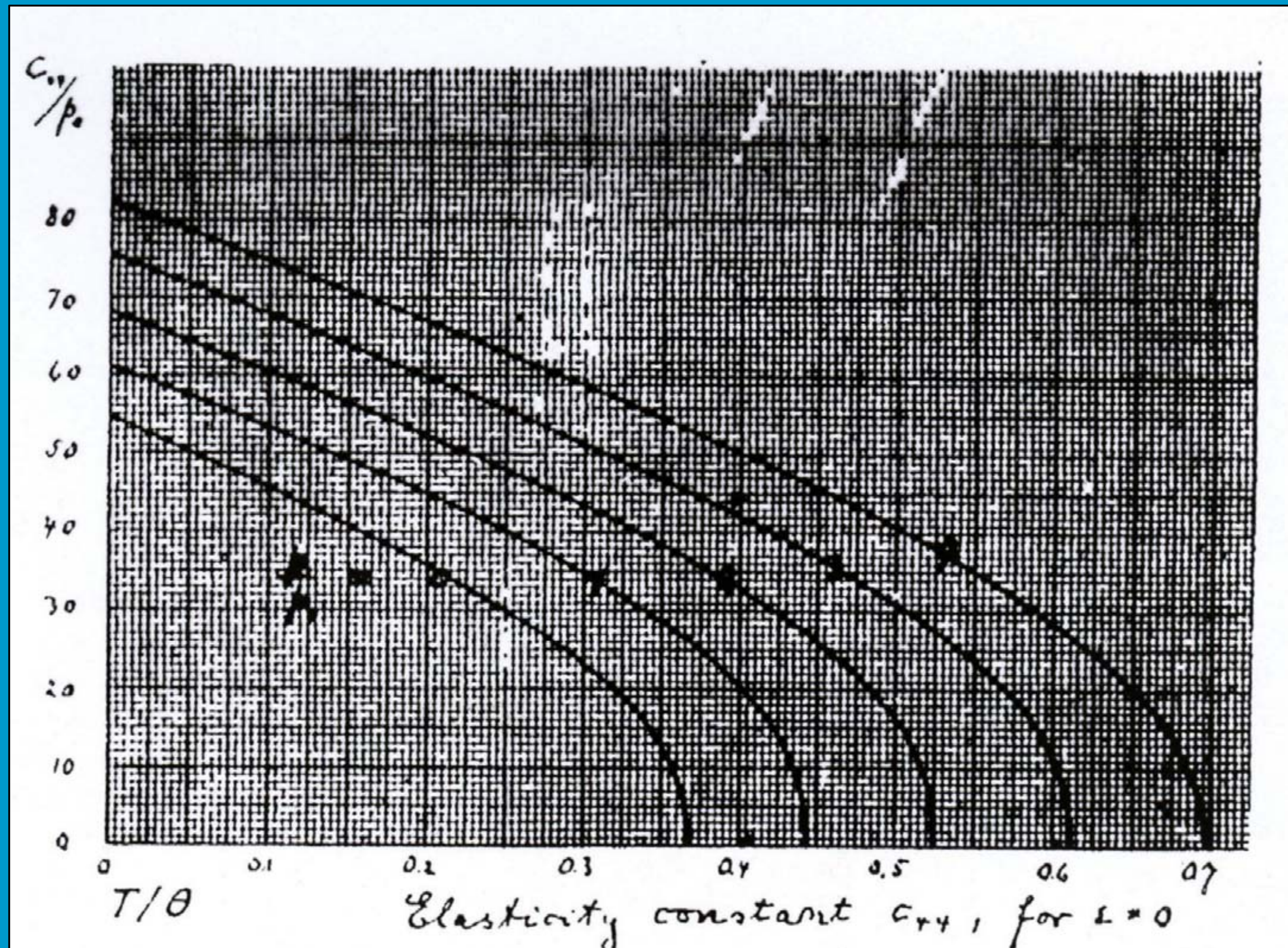
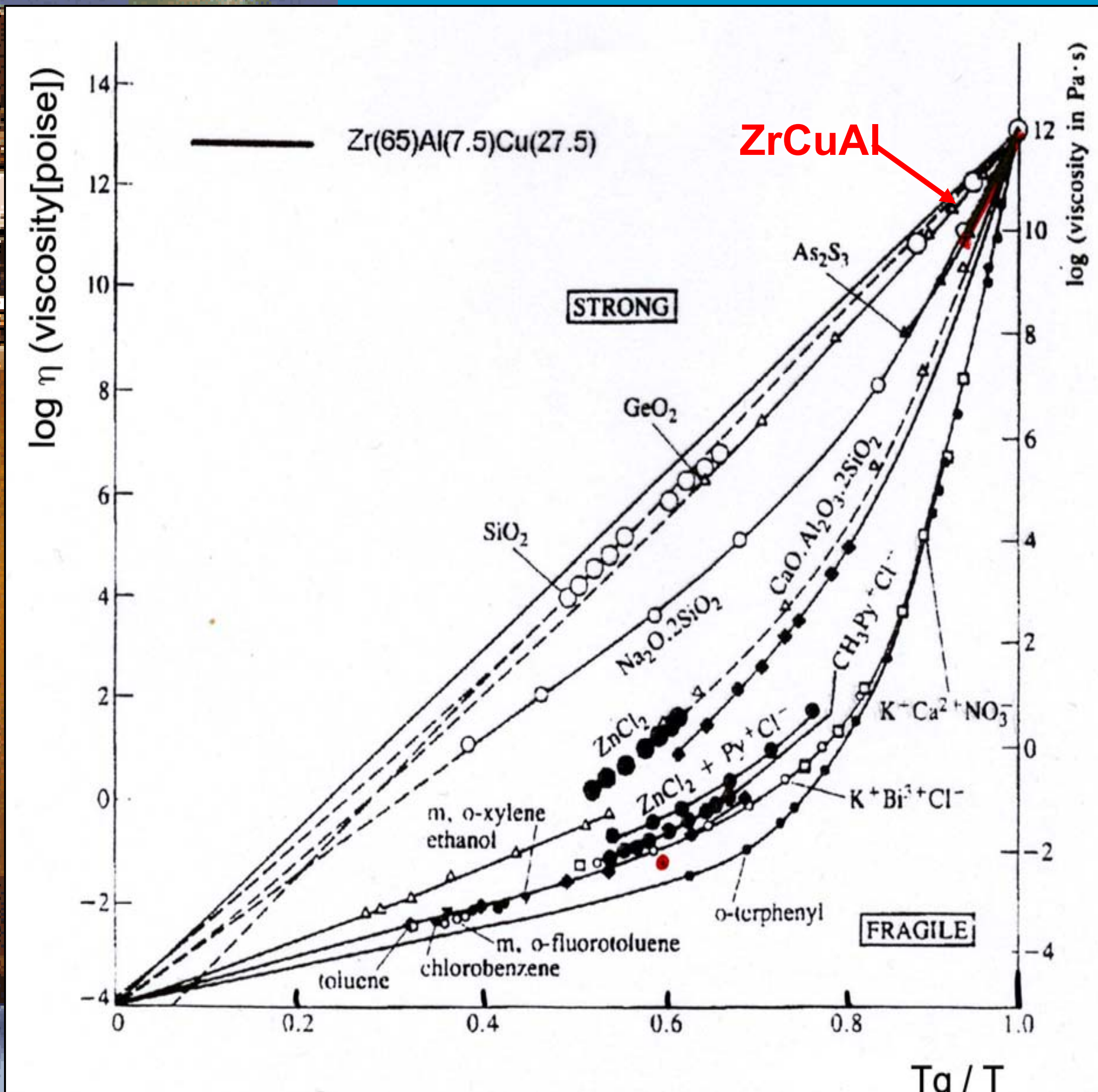
Elastic constant c_{44} vs reduced temperature T/Θ_D



M.Born, J.Chem.Phys. 7 (1939) 591

Equilibrium – viscosity of different glass-forming systems

Angell – Plot



ZrAlCu …………Pd Cu Si metallic undercooled liquid between „strong“ and „fragile“ glass forming system

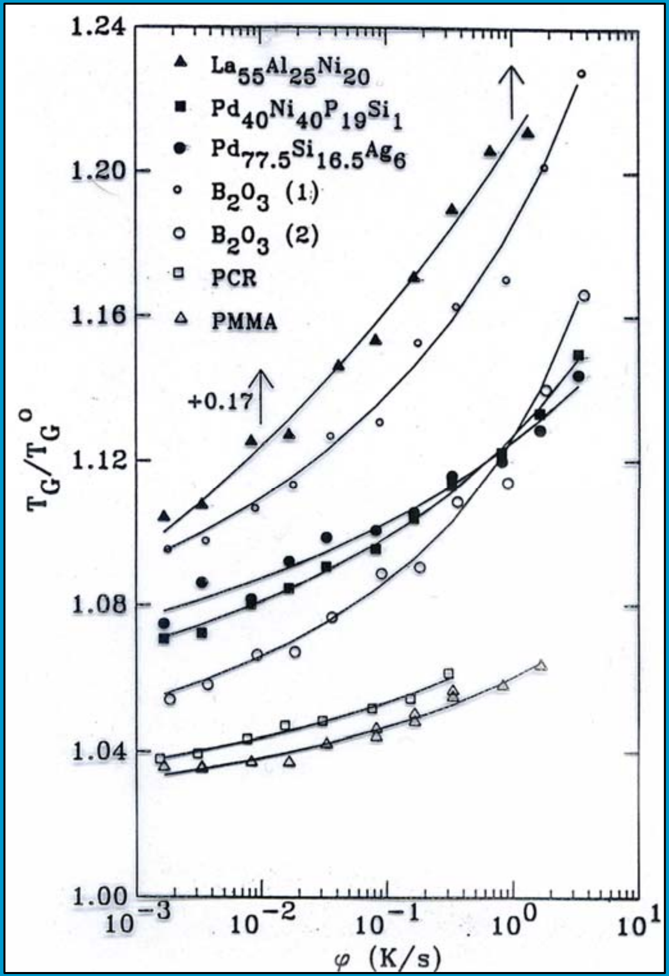
„strong“ **„fragile“**

Arrhenius law **Vogel-Fulcher law**

m = 16 … [36.4] … 200

$$m = \frac{d \log \langle \eta \rangle}{d\,(T_g/T)}$$

Dependence of Tg vs heating rate Θ(K/s)

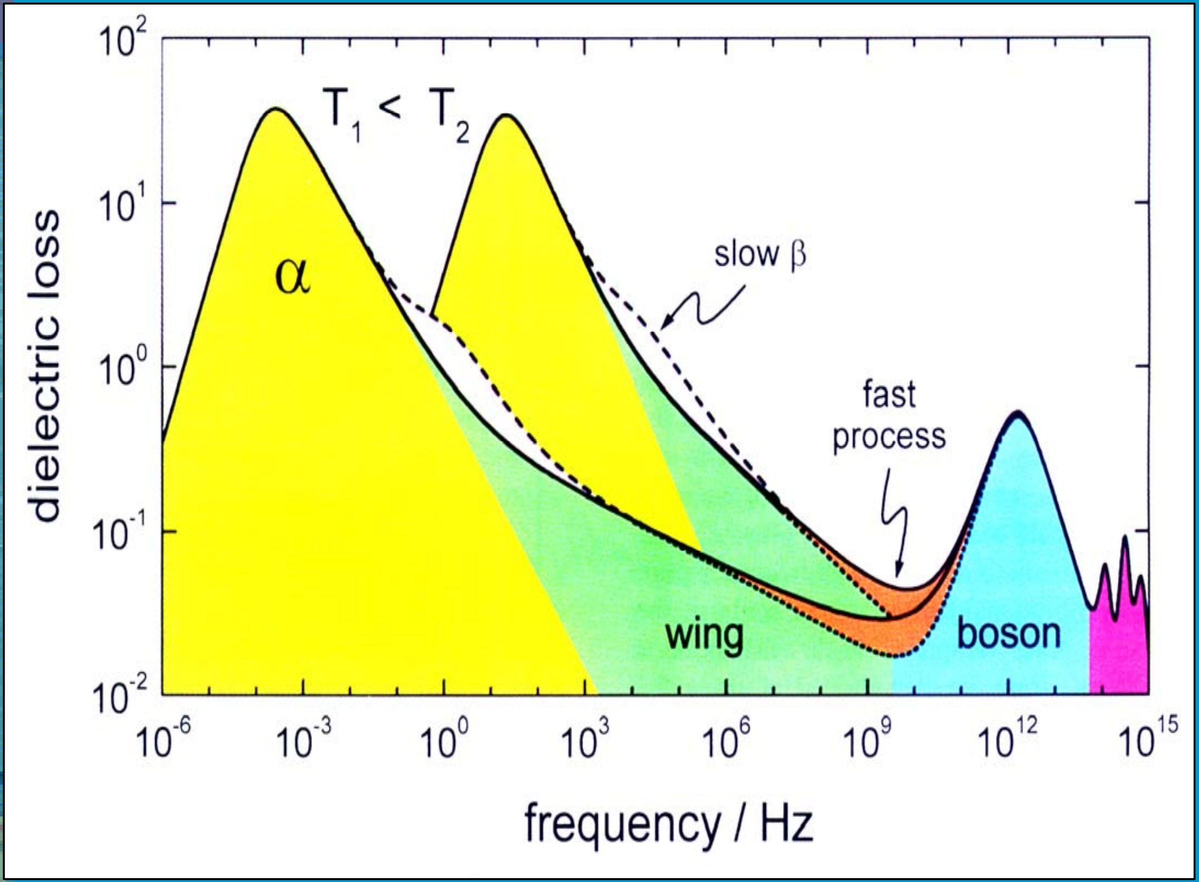


R.Brüning and K.S., Phys.Rev. B.46 (1992)

Dependence of the onset of T_G on the logarithm of the heating rate. For each system T_G is scaled with the value of T^0_G given in Table II. T^0_G is obtained by fitting data to Eq. (1) and the fits are shown by solid lines. The data for $La_{55}Al_{25}Ni_{20}$ are shifted down by 0.17. B_2O_3 (1) refers to the sample with less than 0.1% H_2O and B_2O_3 (2) to the sample with 2.7% H_2O.

Frequency dependence of dielectric loss

Lunkenheimer – Loidl - Plot: molecular systems



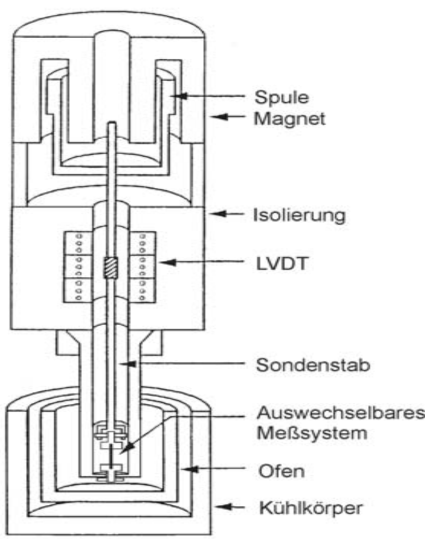
- P. Lunkenheimer et al., Contemp. Phys. 41, 15 (2000)

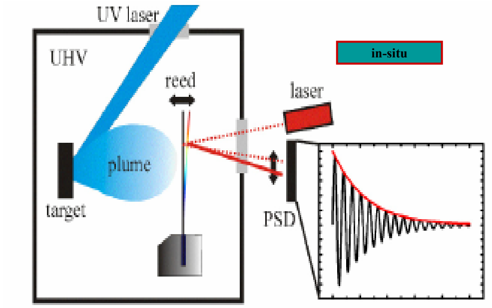
I. Mechanical Spectroscopy in Göttingen

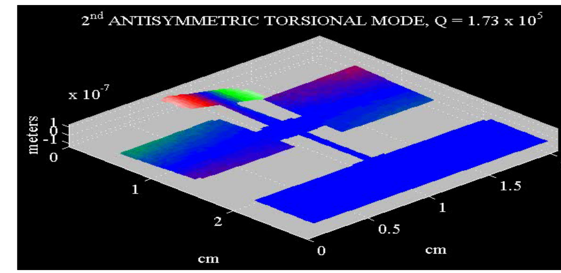
Vib. Reed : 200- 500 Hz (H.U Krebs)

DPO: 0.4- 5 kHz

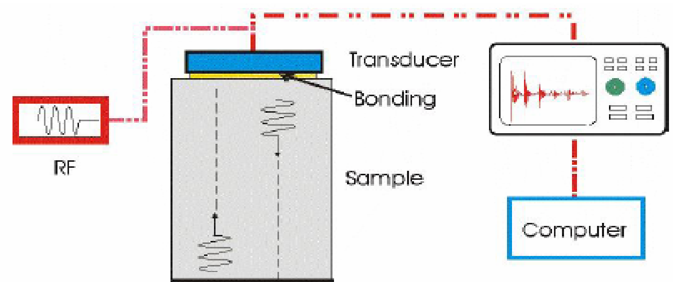
DMA: 0.01-50 Hz





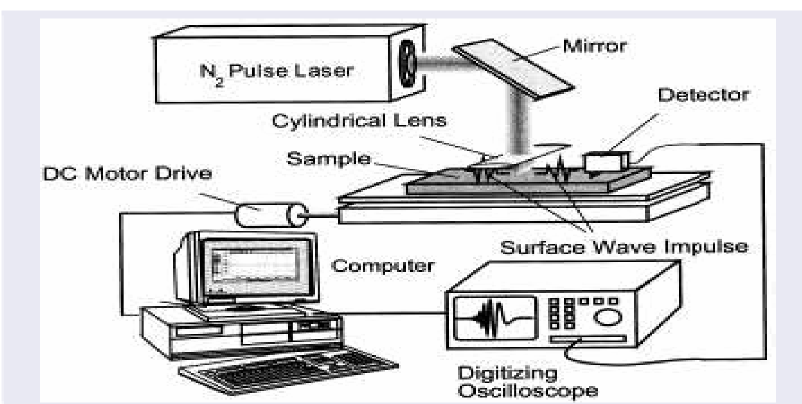


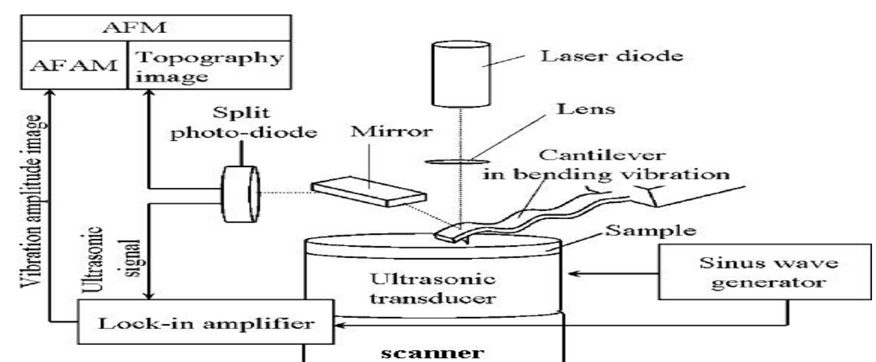
Ultra sound : 5- 20 MHz



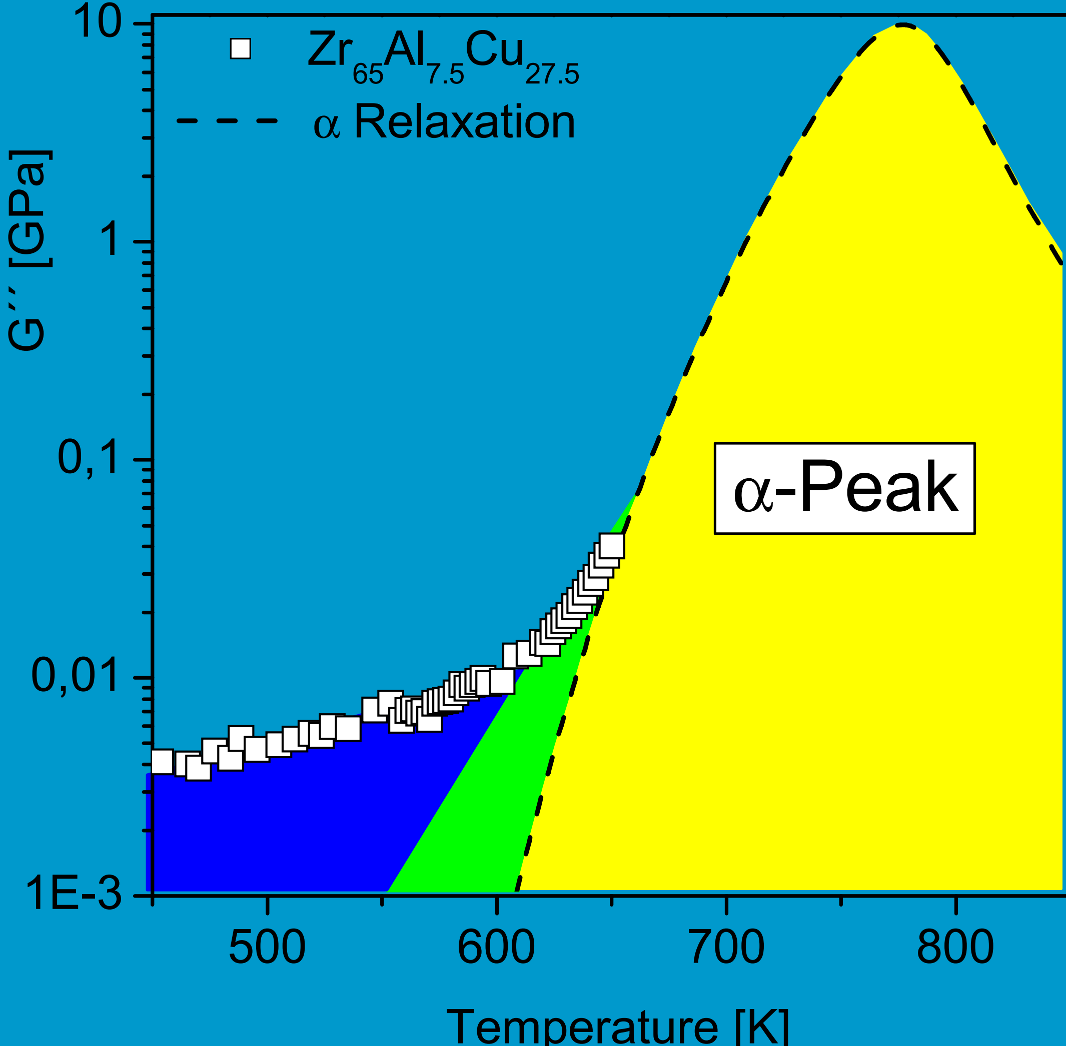
LASW : 5 - 300 MHz

AFAM: 1 - 2 MHz





$Zr_{65}Al_{7.5}Cu_{27.5}$ – Interpretation of G´´ data



α-relaxation

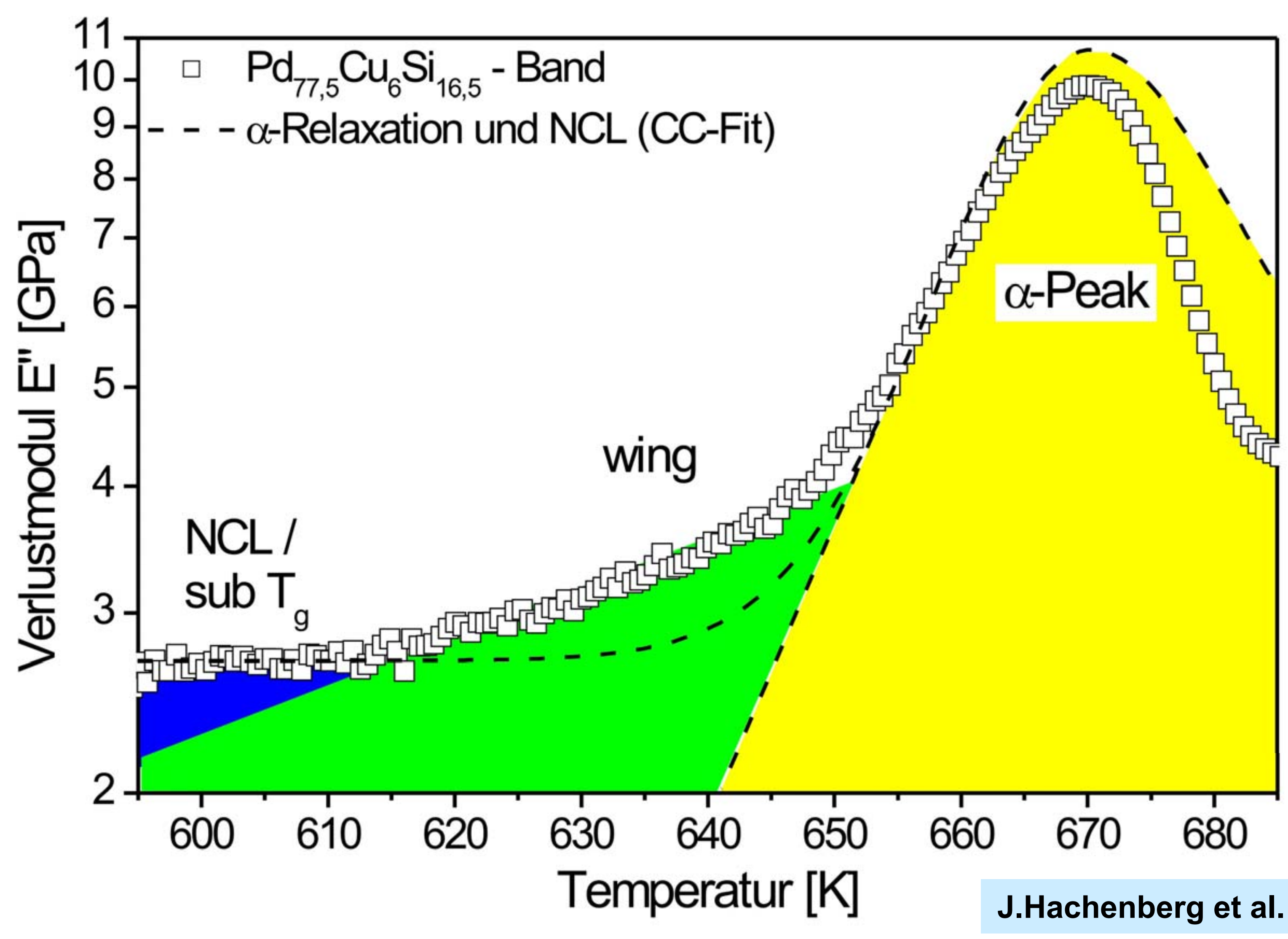
- **VFT-parameter by M. Weiß**
- **Relaxation-strength from G´**
- **HN-parameter α = 1**
- **HN-fit parameter γ**

Data deviate clearly from calculated low temperature flank

„wing“ exists in ZrAlCu!

Rösner, Samwer, Lunkenheimer, Europhys. Lett. 68 (2004) 226

Universal character of the slow beta-relaxation in metallic systems

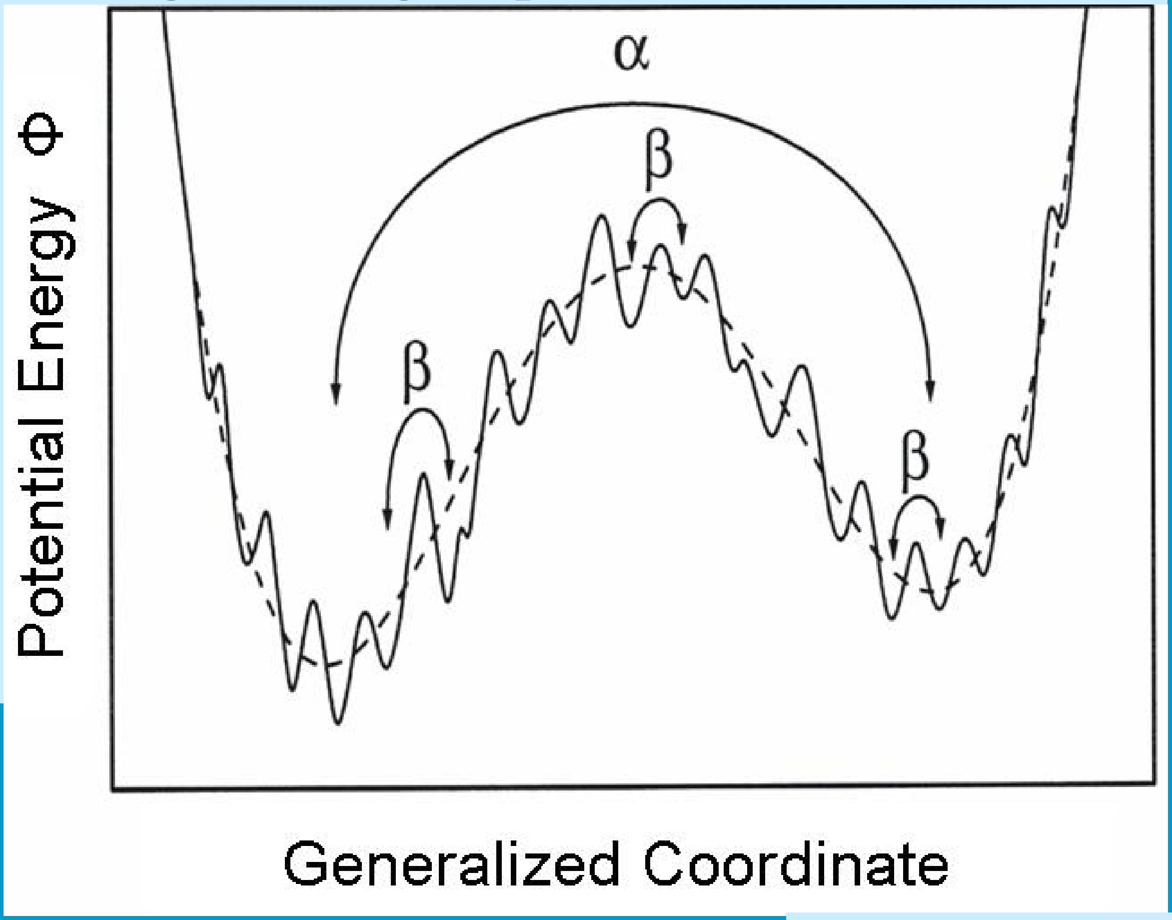


J.Hachenberg et al. JNCS 2006

Potential Energy Landscape

- Shear Transformation Zones (STZs) are clusters of atoms that reorganise during shearing –alpha-relaxations?

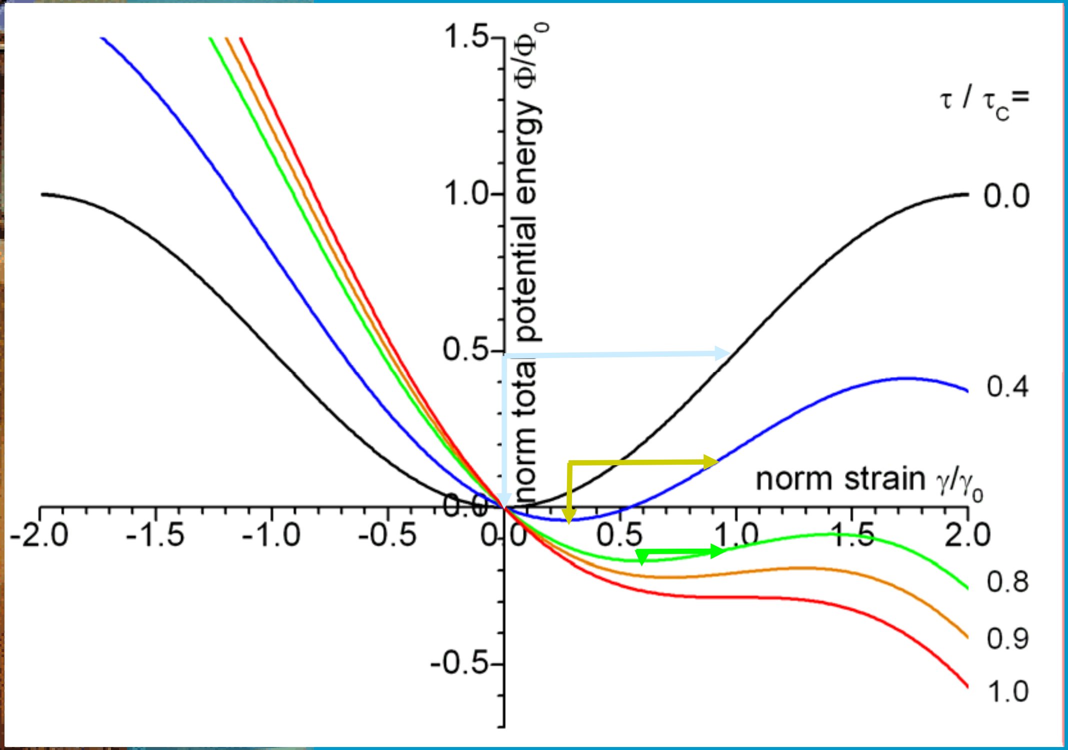
- What are beta -- string- like excitations?



Stillinger,Weber

II. Cooperative shear model

Extended Frenkel's periodic elastic energy density model



$$\phi = \phi_0 \sin^2\left(\frac{\pi}{4} \cdot \frac{\gamma}{\gamma_C}\right) - \tau \cdot \gamma$$

$$G = \left.\frac{d^2\phi}{d\gamma^2}\right|_{\gamma=\min(\gamma)} = \frac{\pi^2}{8} \cdot \frac{\phi_0}{\gamma_C^2}$$

$$T = 0K$$

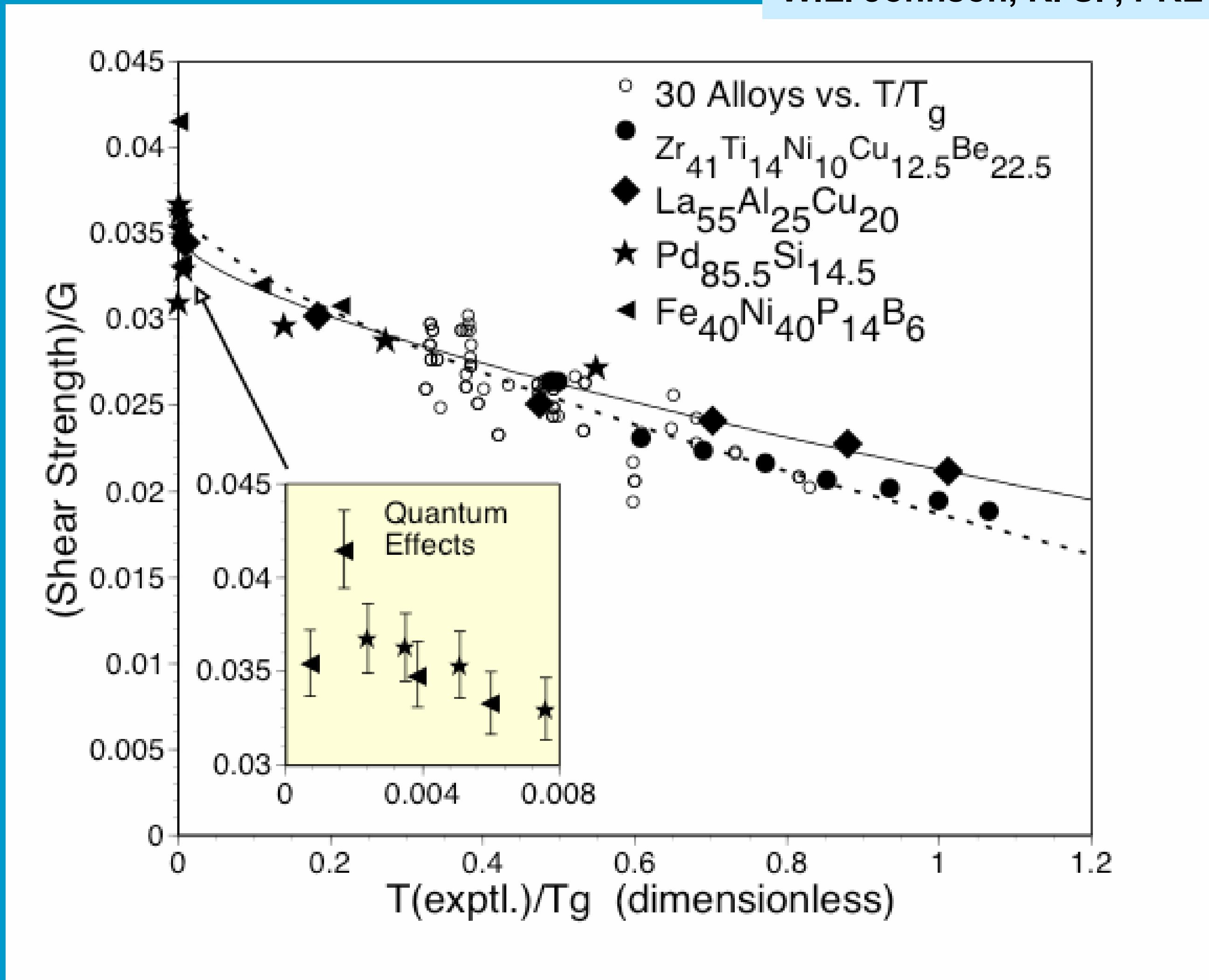
$$W_0 = \varsigma \, \Omega \, \phi_0$$

$$\frac{W}{G \cdot (\delta\gamma)^2} = R = const$$

W.L. Johnson, K. Samwer, PRL (2005)

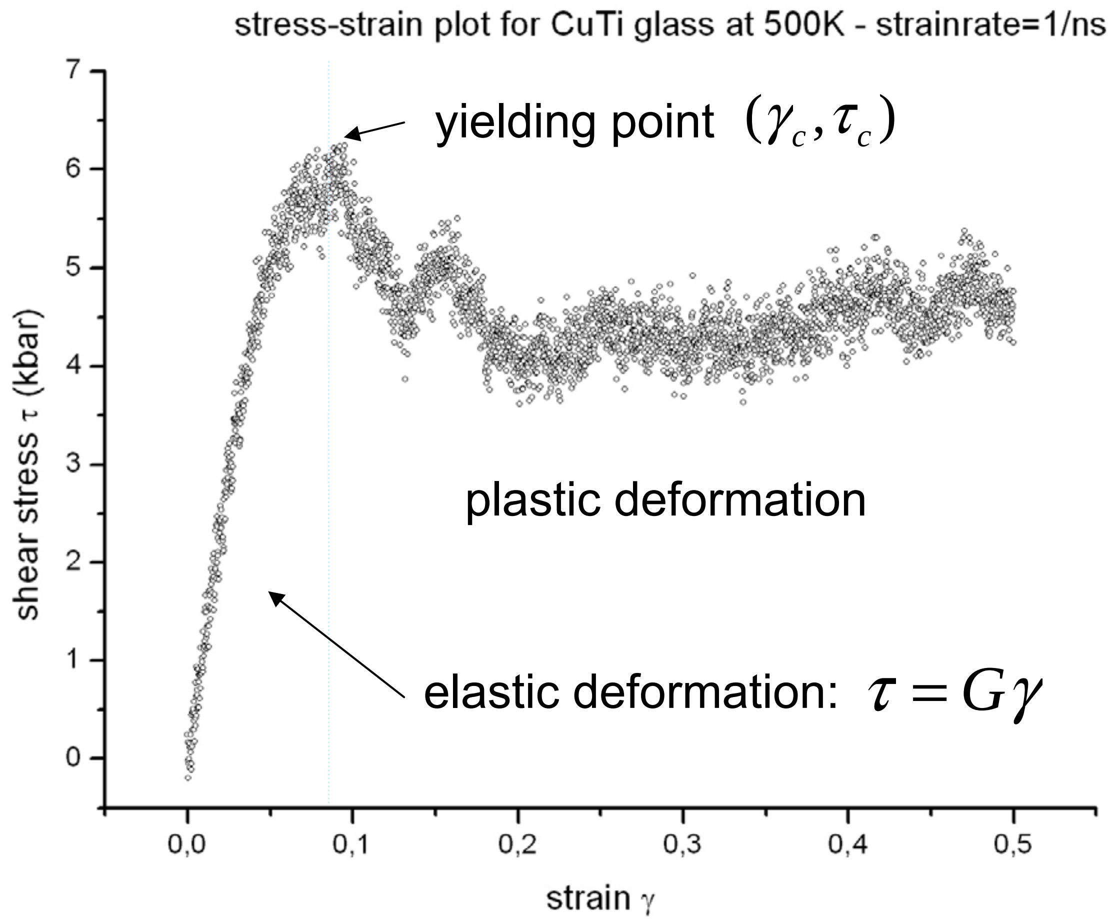
Shear strength versus temperature for 30 metallic glasses

W.L. Johnson, K. S. , PRL (2005)



Experimental shear strain at yielding ($\tau Y/G$) vs. t = T/Tg. Small open circles show results at room temperature on 30 alloys of varying Tg. Solid circles show the T-dependence of $\tau Y/G$ for Vitreloy 1 ($Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$). Filled diamonds, stars, and triangles show flow stress data down to cryogenic temperatures for bulk $La_{55}Al_{25}Cu_{20}$ (ref.43), and melt spun ribbons of $Pd_{85.5}Si_{14.5}$ and $Fe_{40}Ni_{40}P_{14}B_6$

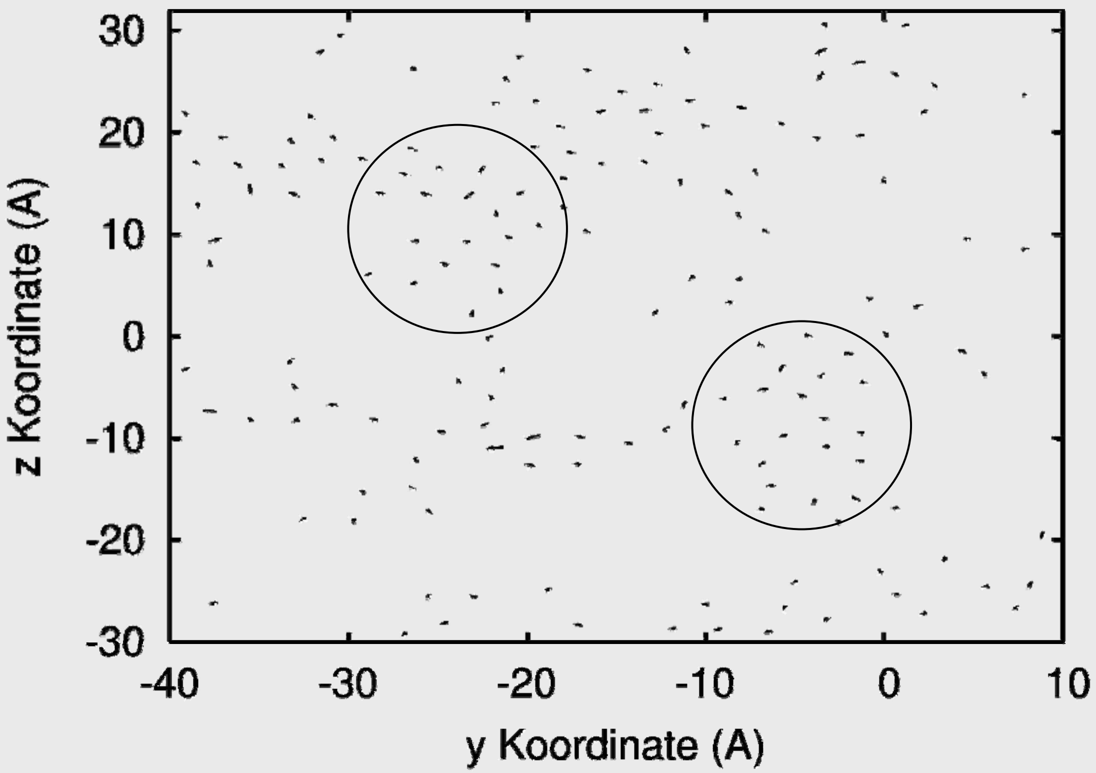
III. MD-Simulations: Stress-strain behavior



M. Zink, K. Samwer, W. L. Johnson, S. G. Mayr , Phys. Rev. B 74 (2006) 012201

Heterogeneous deformations at 10K

Plastic displacement field of atoms: cross section



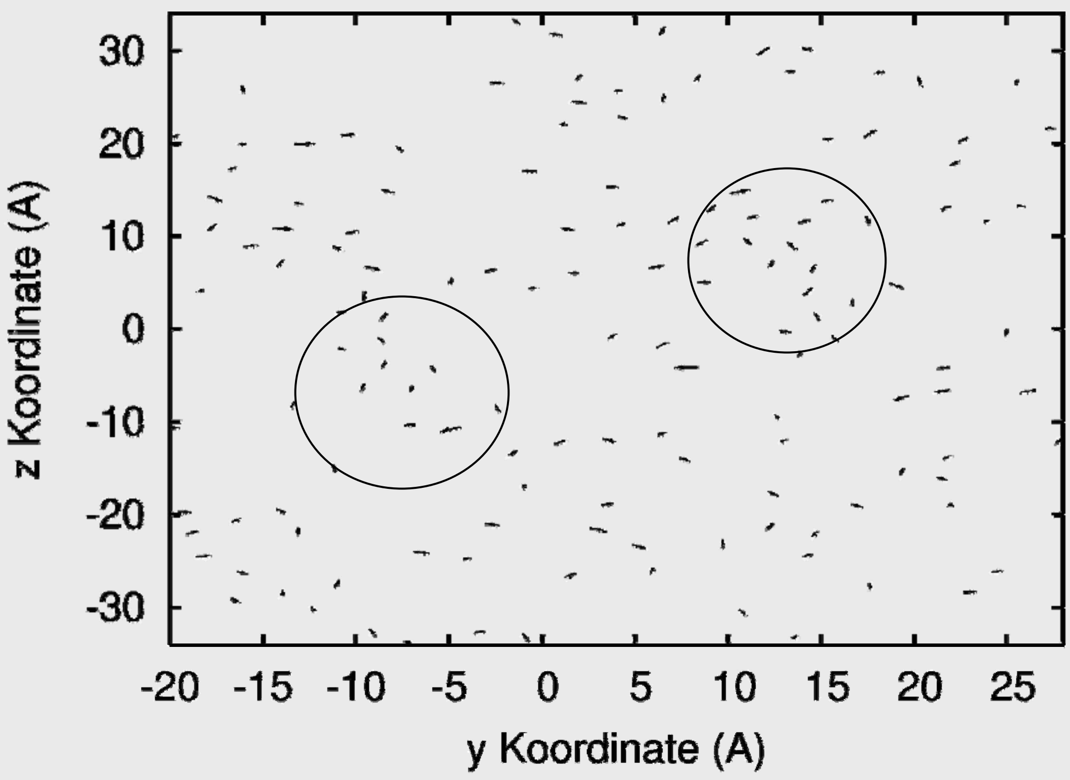
4% strain
shear rate = 1/ns

Cutoff to eliminate thermal vibrations: 0.2 Å

Irreversible deformations occur in regions of ≈10 – 15 Å diameter
~ 150 atoms in metallic systems

Heterogeneous deformations at 500K

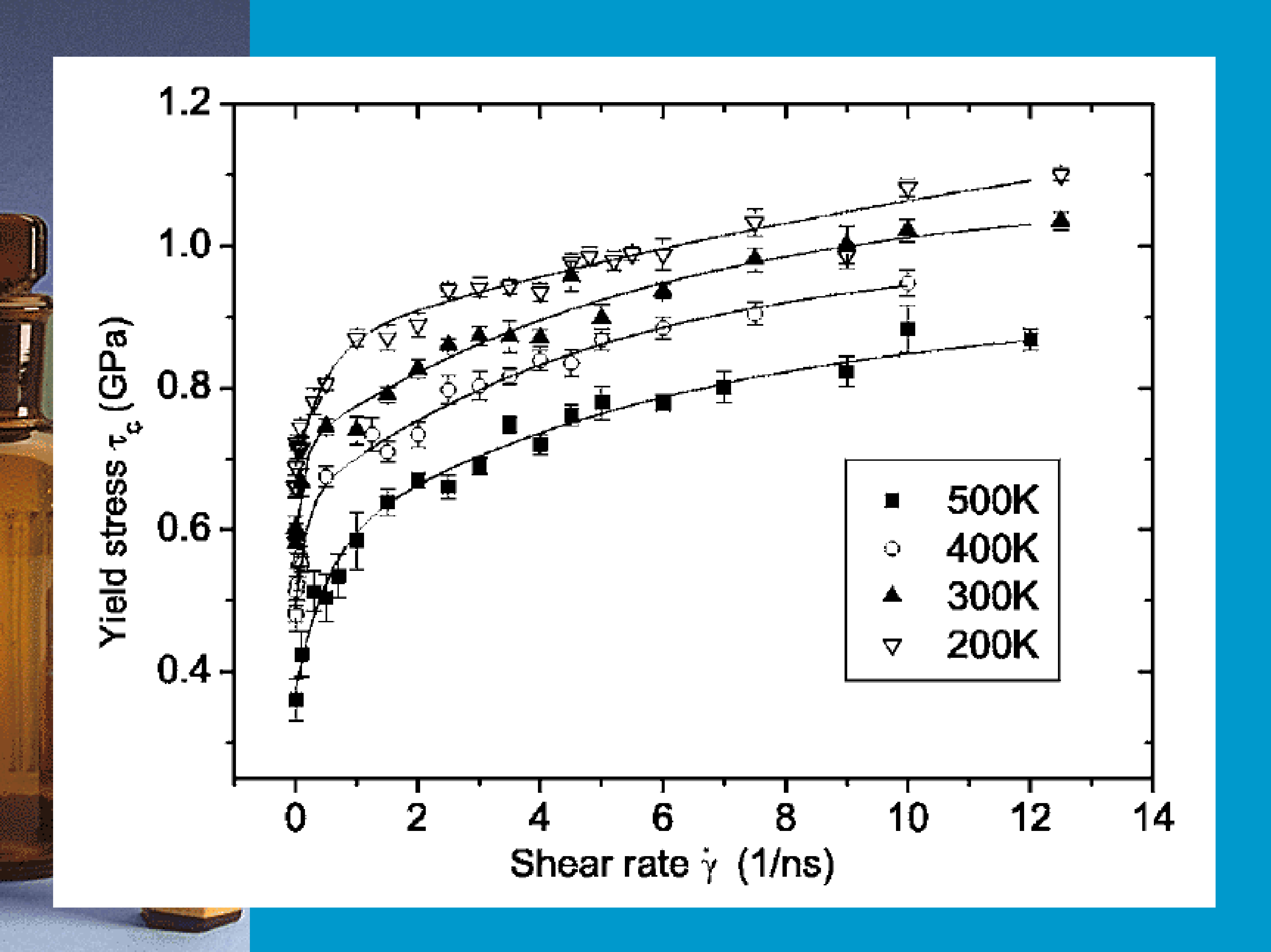
Plastic displacement field of atoms: cross section



4% strain
shear rate = 1/ns

Cutoff to eliminate thermal vibrations: 0.45 Å

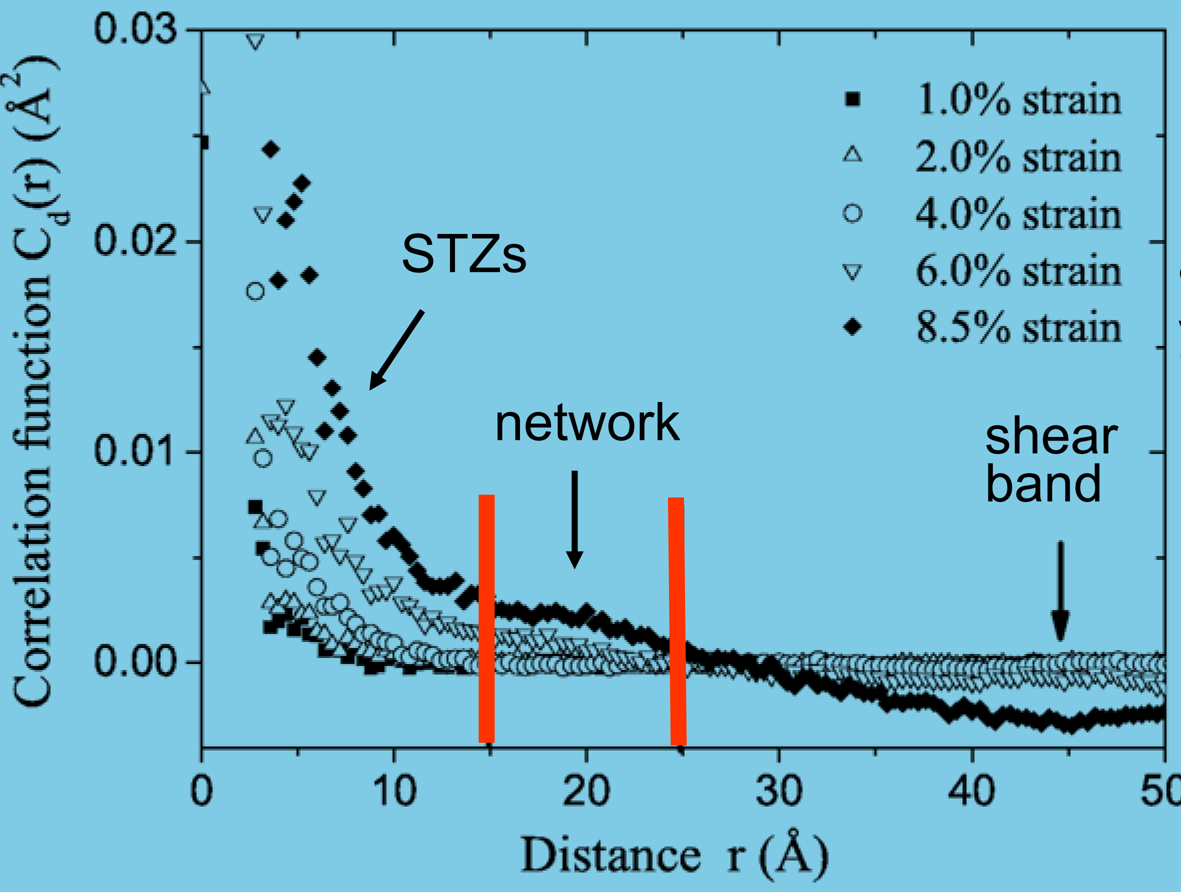
Identify highly deforming regions (10 - 15 Å diameter) with shear transformation zones (STZs)


1.2
1.0
0.8
0.6
0.4
Yield stress τ_c (GPa)
0
2
4
6
8
10
12
14
Shear rate $\dot{\gamma}$ (1/ns)
500K
400K
300K
200K

Network of STZs and shear bands at high strains

Displacement correlation function:

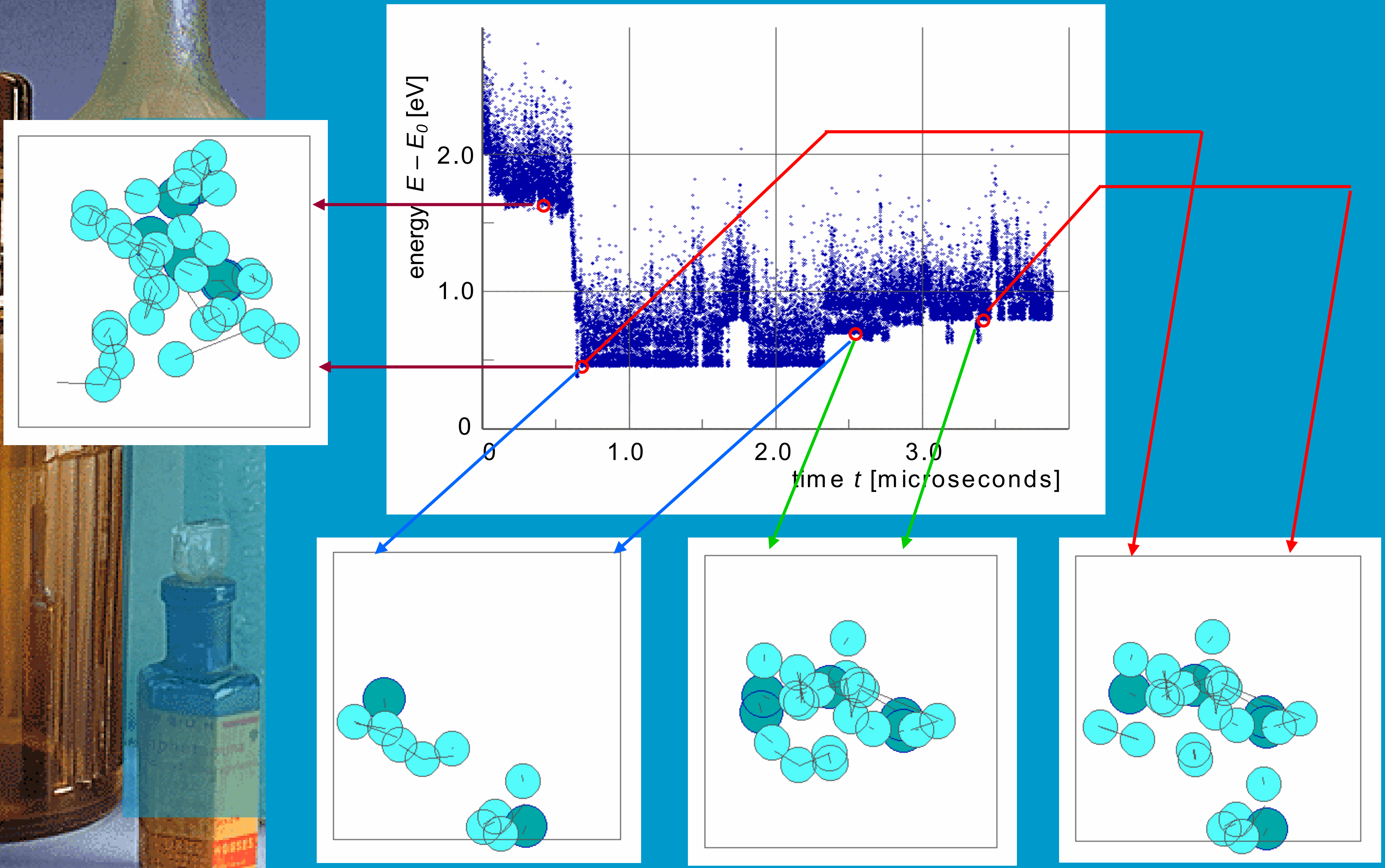
$$C_d(r) = \left\langle d(\vec{R}+\vec{r})\cdot d(\vec{R})\right\rangle_{\vec{R},|\vec{r}|=r} - \left\langle d(\vec{R}+\vec{r})\right\rangle_{\vec{R},|\vec{r}|=r} \cdot \left\langle d(\vec{R})\right\rangle_{\vec{R},|\vec{r}|=r}$$



shear rate: 1/nsec

8.5% = yielding point

Displacement differences between two inherent structure configurations at 700 K:



H.Teichler, Göttingen,2005

Local shear process as origin for NCL and Boson peak?

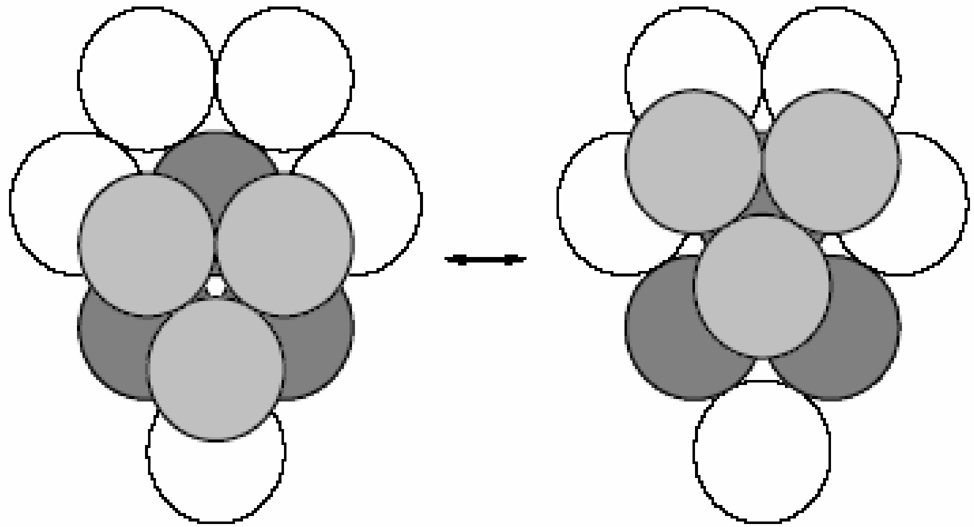
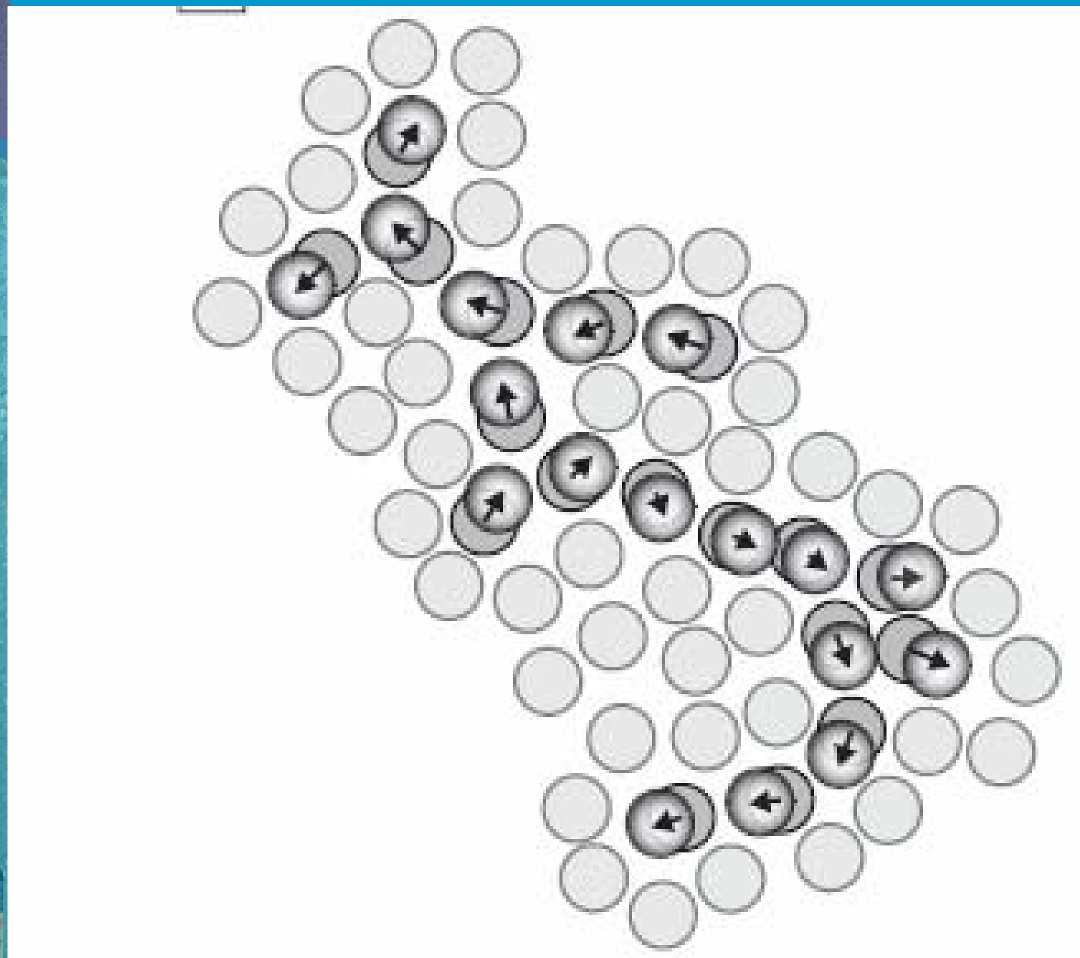


FIG. 1: The gliding-triangle rearrangement of six closely packed spherical atoms.

(U.Buchenau and H.Schober,cond.mat 4/3/ 2008)

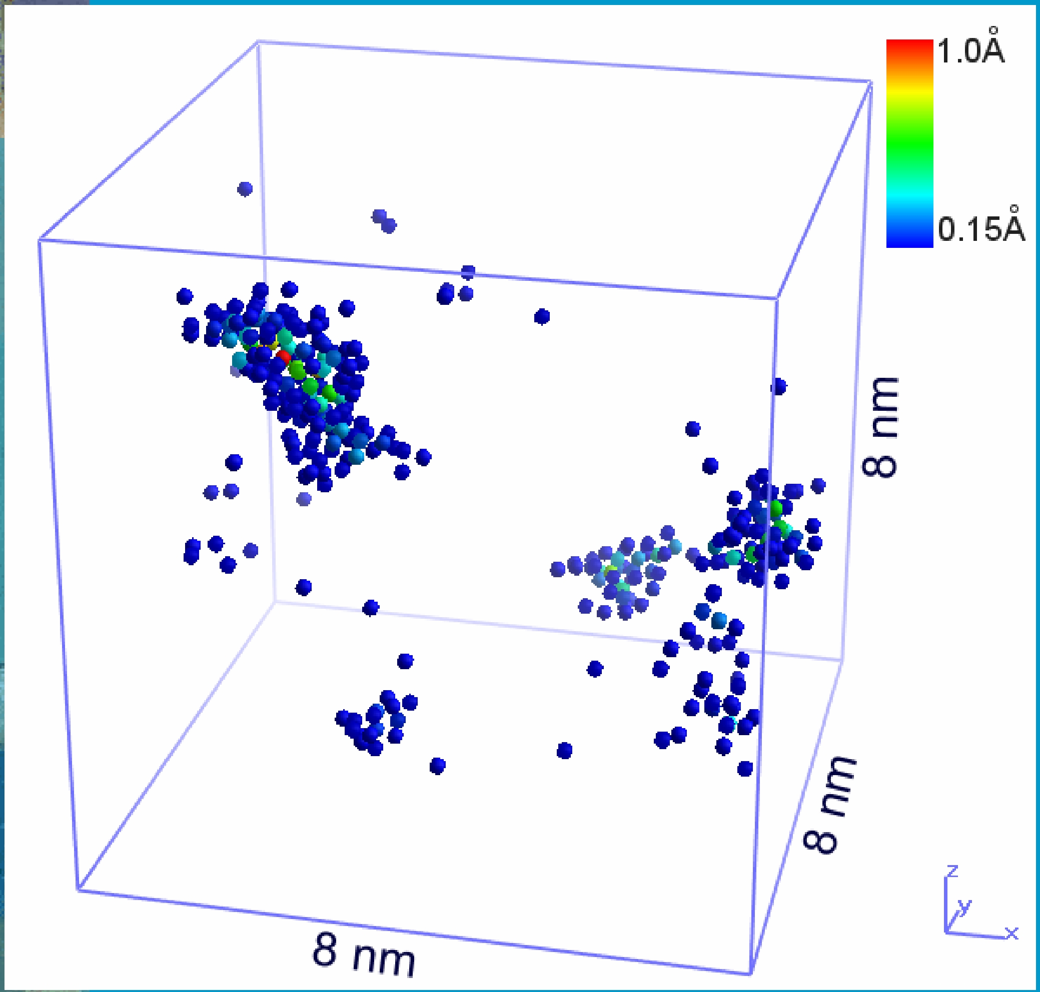
β-excitation or string acts as an elastic quadrupol ?



see video:
β-mode for a
free 7 atom cluster

H. Schober1993 (from Miracle MRS Bull. 2007

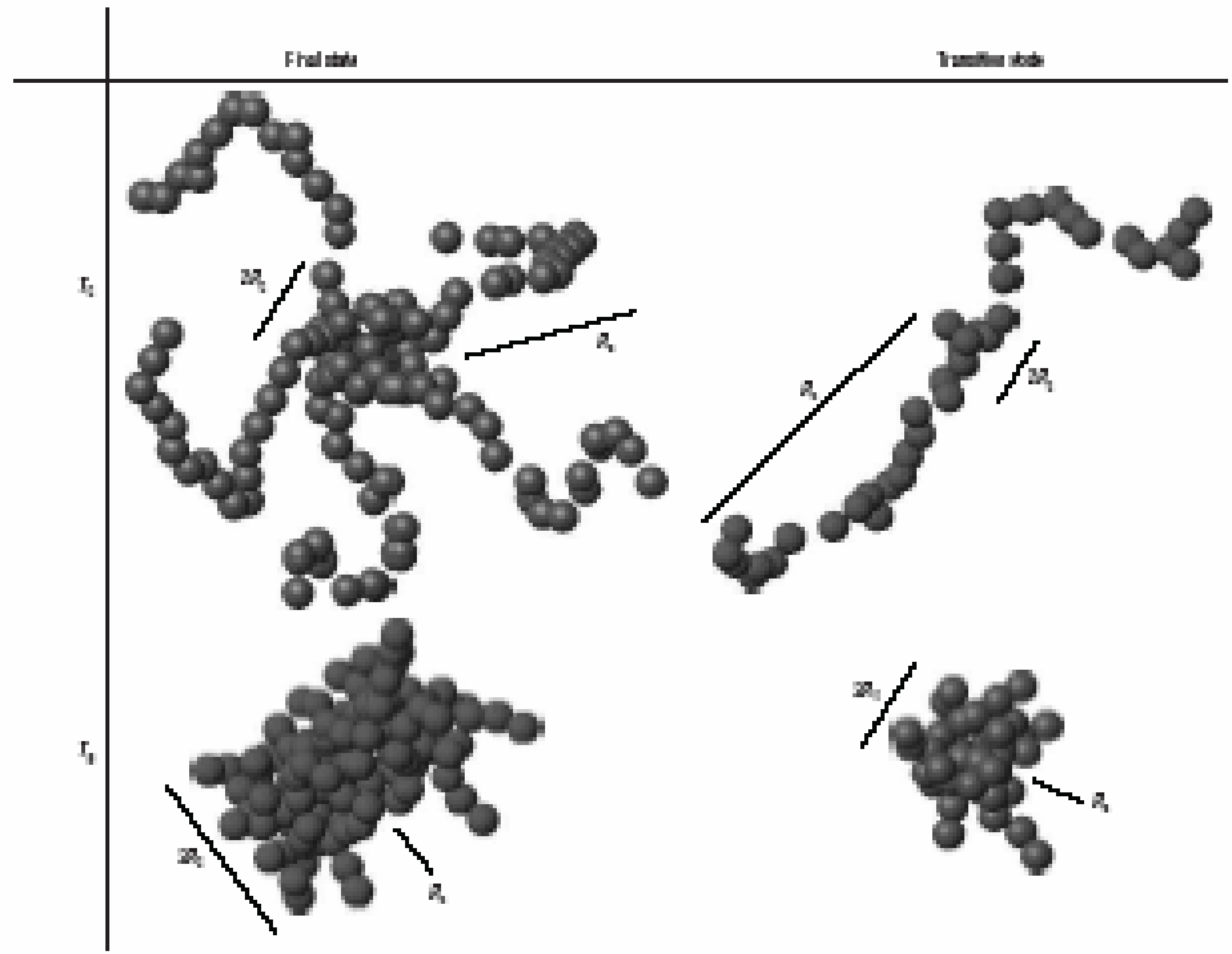
Shear transformation zone under 5% strain in MD CuTi- Simulation



T=10 K
Quenchrate 5K/nsec
Strainrate 10%/nsec
Cutoff 0.015 nm
Displacement :
see colour code

M.Neudecker, S.G.Mayr,Scripta Mat. 2009

Dynamical crossover in colloidal systems



JACOB D. STEVENSON[1]*, JÖRG SCHMALIAN[2] AND PETER G. WOLYNES[1]*

Nature Physics,2006

STZ's and network forming in colloidal systems – P.Schall, D.Weitz and F.Spaepen

Science 2007

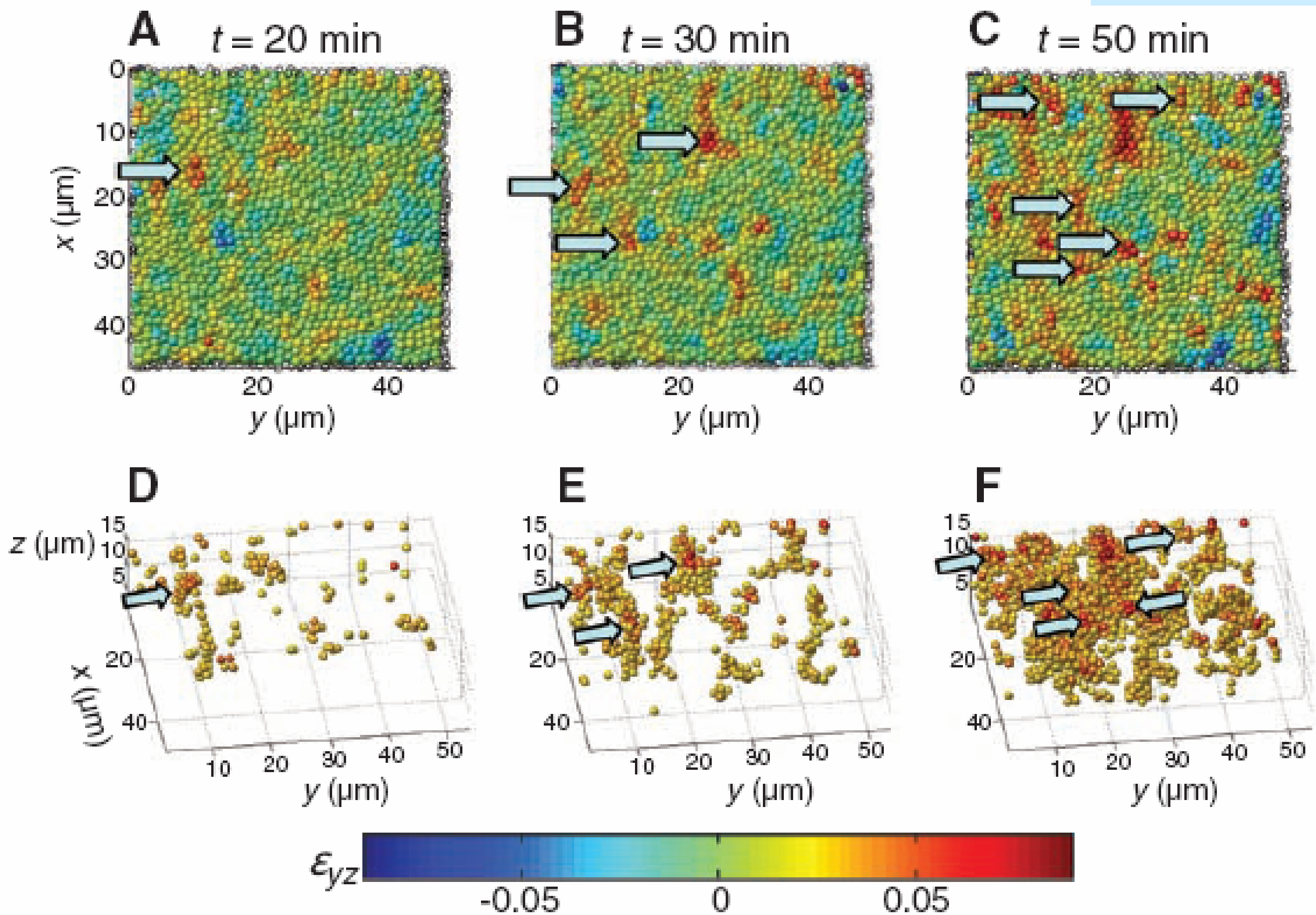


Fig. 4. Strain evolution during shear. Distribution of the cumulative shear strain after 20, 30, and 50 min of shear. For each frame, arrows indicate shear transformation zones that have been formed in the time interval before the frame shown. Shear transformation zones appear to form a connected network at $t = 50$ min. (**A** to **C**) *x-y* sections (5 μm thick) centered at $z = 13.5$ μm. (**D** to **F**) Perspective view of 16-μm-thick sections showing particles with shear strain values larger than 0.025 only.

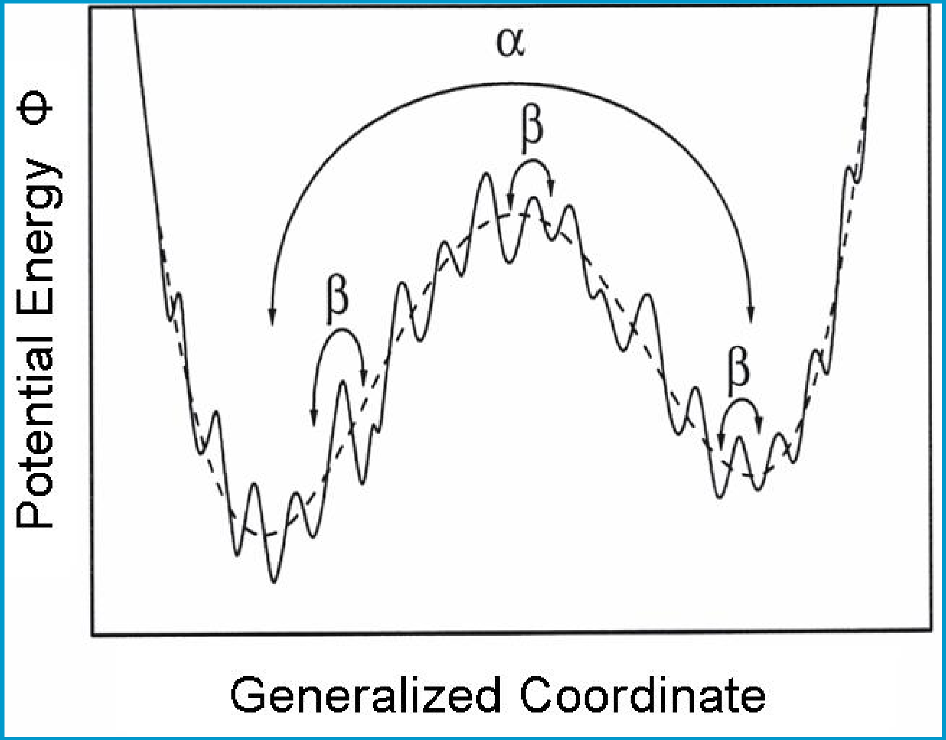
Potential Energy Landscape

- Shear Transformation Zones (STZs) are clusters of atoms that reorganise during shearing –alpha-relaxations?

- What is beta?

string- like

excitations?



Stillinger,Weber

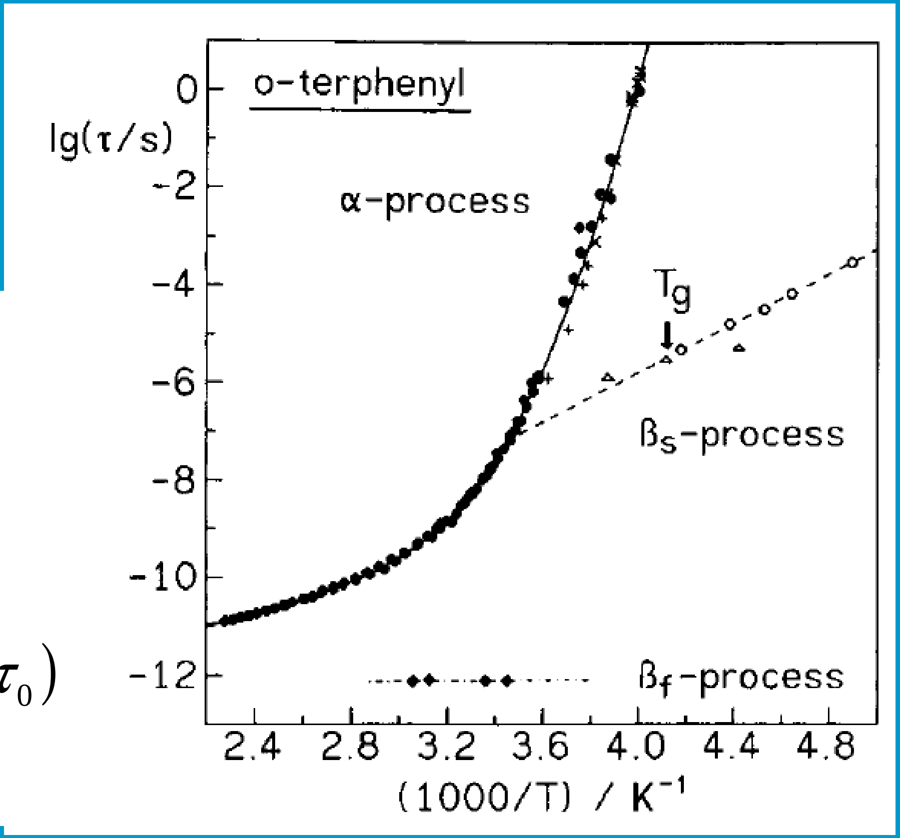
IV. Alpha- beta-merging in molecular systems

Frequency dependence of the alpha and beta relaxations

$$\omega\tau = 1$$

$$\tau(T) = \tau_0 \exp\left(\frac{E_A}{k_B T}\right)$$

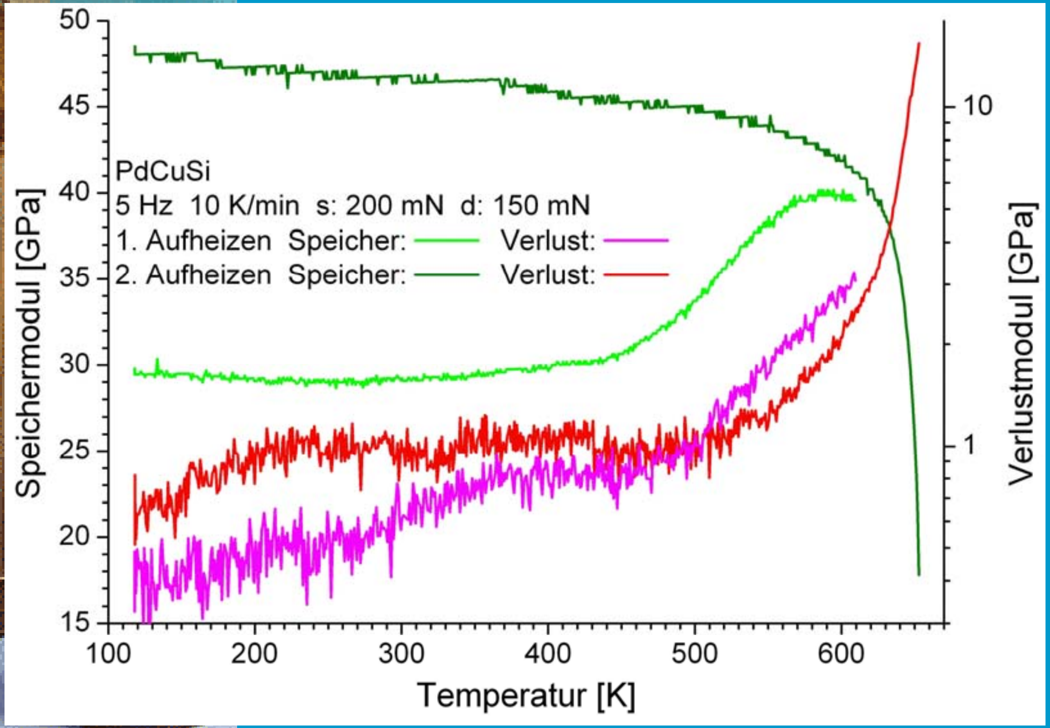
$$\log_{10}(\tau) = \underbrace{E_A \cdot \frac{\overbrace{\log_{10}(e)}^{const}}{1000\ \mathrm{K} \cdot k_B}}_{Steigung} \frac{1000\ \mathrm{K}}{T} + \log_{10}(\tau_0)$$



M. D. Ediger, C. A. Angell, S. R. Nagel, J. Phys. Chem. **100**, 13200 (1996)

Heating rate dependence of beta- relaxation in metallic glasses

- β- relaxation clearly seen in:
  - As quenched samples (frozen into high minimum in PEL)
  - High heating rates (no smeared out relaxation due to averaging)
- Aging effect: Increase of storage modulus prior to increase of phase angle (at first heating of as quenched samples)



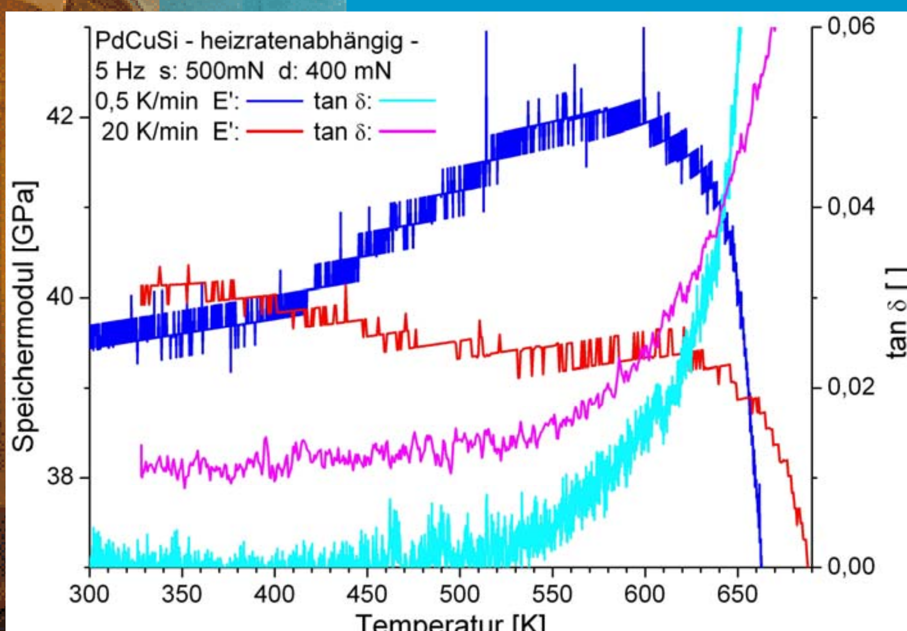
Relaxations change Phase angle (normal case)

- Decoupled transitions

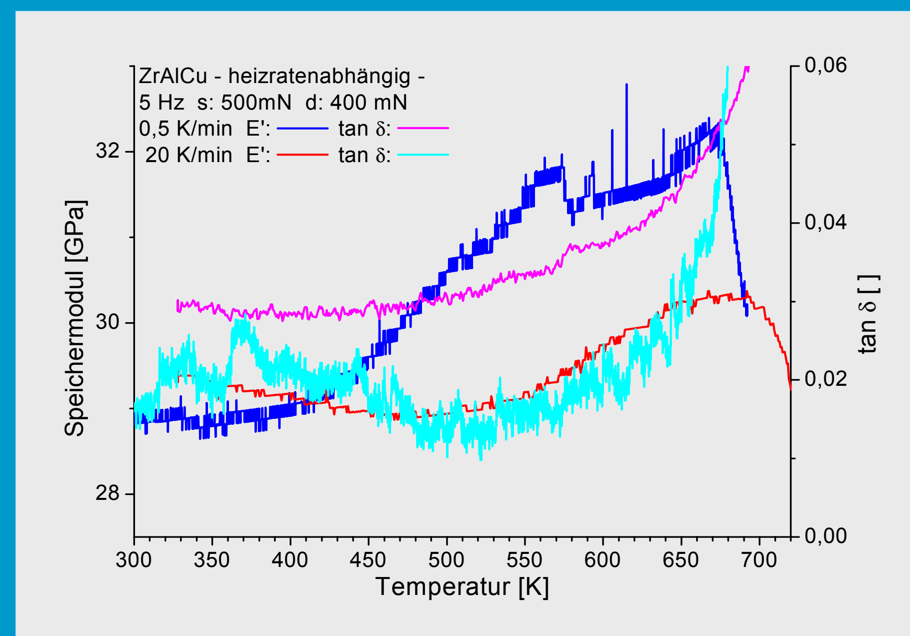
$$E' = \frac{\sigma_0}{\varepsilon_0} \cdot \cos(\delta)$$

β -relaxation and aging due to same effect!

Time –Temperature - Superposition principle not fulfilled
Interpretation only correct if β has a different heating rate dependence than α.



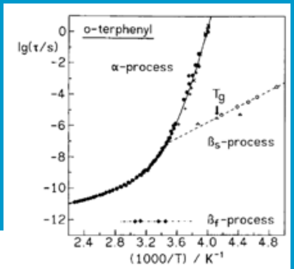
PdCuSi



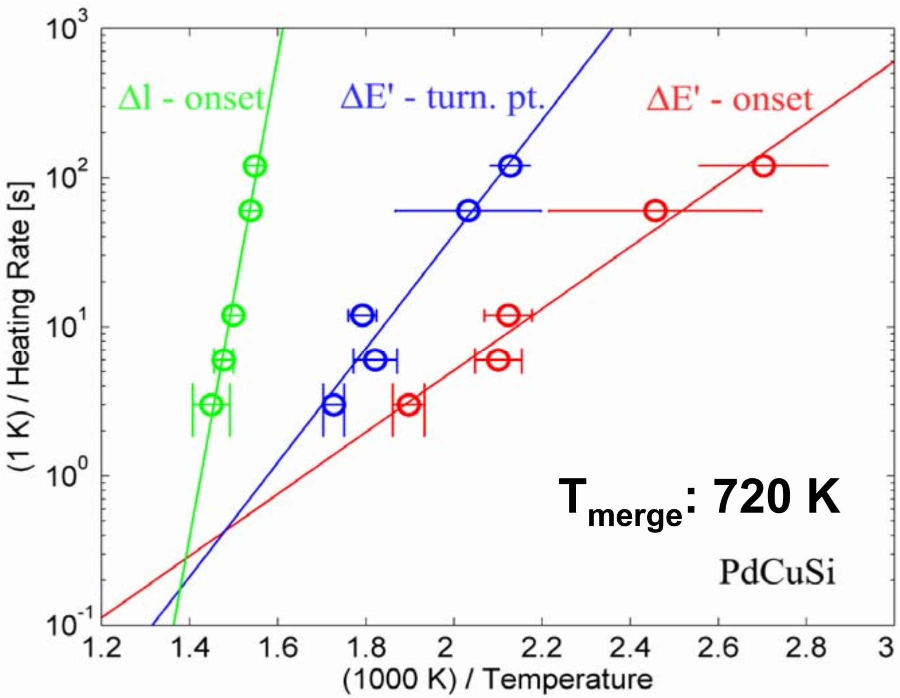
ZrAlCu

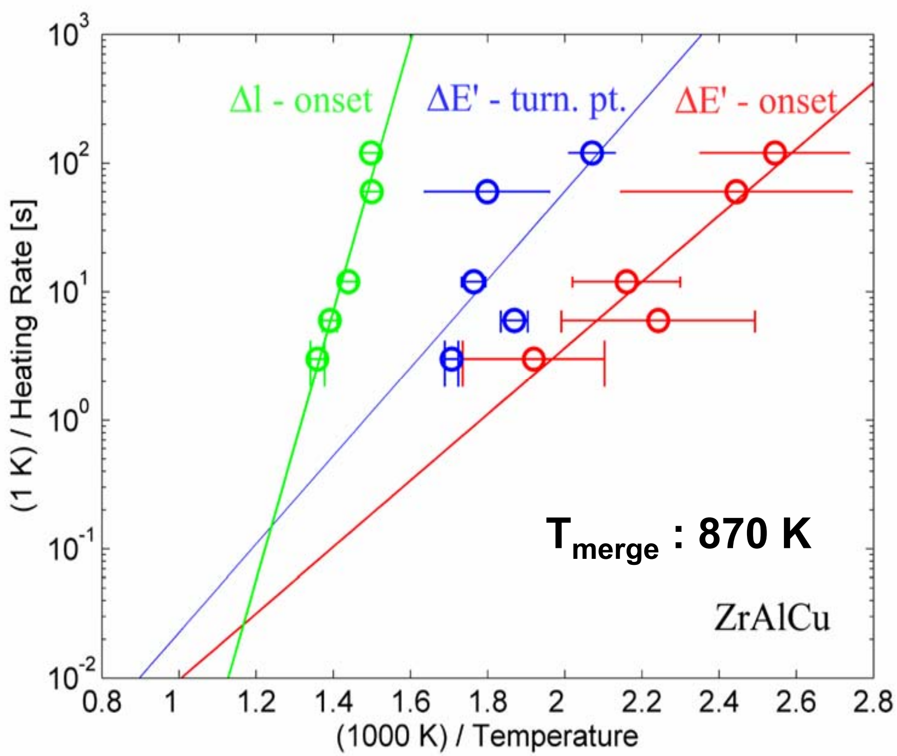
Heating rate dependence :

- Rate dependence at constant frequency



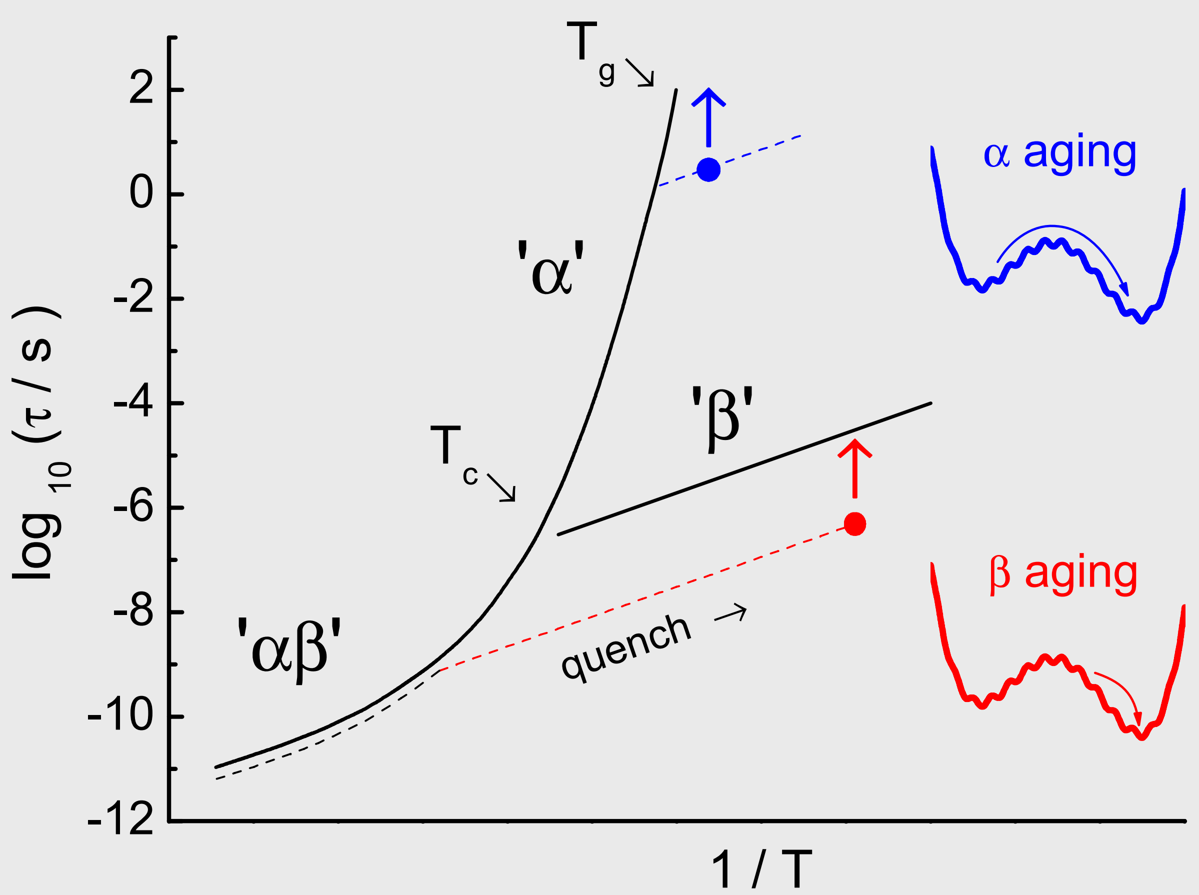
$$\omega_H \tau = 1 \quad \& \quad \omega_H \propto R \quad \Rightarrow \quad \log_{10}\left(\frac{1\ \mathrm{K}}{R}\right) = \underbrace{E_A \cdot \frac{\overbrace{\log_{10}(e)}^{const}}{1000\ \mathrm{K}\cdot k_B}}_{Steigung} \frac{1000\ \mathrm{K}}{T} + const$$





Note: full excitation of beta- modes only above glass transition – near MCT-Tc:
=> no backstress anymore- no local correlations - free to cavitate??

Merging of the α – and β- process in metallic glasses



J.Hachenberg et al. APL,2008

Conclusions

- cooperative shear model due to shear modulus G
- RMD-simulations for stress-strain curve exhibit α – and β- events
- local mechanical spectroscopy via AFAM verifies broad local distribution of modulus
- merging of α- and β- modes near Tc of MCT?
- Soft spots crystallize first ?

Outlook

Quantitative model for STZ vs. β -relaxation ? Only β!
Also good for nucleation and amorphisation-melting ?!