Relaxation phenomena in bulk metallic glasses: from beta relaxations to nano shear bands

Konrad Samwer,
Hai Bin Yu, Karina Avila, Walter Arnold, Jon-Olav Krisponeit, Stefan Küchemann, Sebastian Pitikaris, Bo Zhang, Antje Krüger, Marios Demetriou*, William L. Johnson*, Itamar Procaccia**

I.Physik. Institut, Univ. Göttingen
* Keck Lab., Caltech, Pasadena
** Weizmann Inst., Rehovot

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Frequency dependence of dielectric loss

P. Lunkenheimer et al., Contemp. Phys. (2000)
Mechanical Spectroscopy in Göttingen

DMA 7: 0.01-50 Hz  
DMA 8000: 300 Hz

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

DPO: 0.4-5 kHz

Ultra sound: 5-20 MHz

LASW: 5-300 MHz

AFAM: 1-2 MHz/3 GHz
Slow beta-relaxation in metallic systems

- Pd$_{77.5}$Cu$_6$Si$_{16.5}$ - Band
- $\alpha$-Relaxation und NCL (CC-Fit)

Verlustmodul $E''$ [GPa]

NCL / sub $T_g$

$\alpha$-Peak

Wing

Temperatur [K]

J.Hachenberg et al. JNCS 2006
Potential Energy Landscape

- „unhappy atoms“- T. Egami
- TL – systems – R. Pohl
- Vibrations – H. Schober
- Jumps
- Strings (β - relaxation)
- Plastic events (STZ) (α - relaxation)- A. Argon

Potential Energy \( \Phi \)

Generalized Coordinate

Stillinger, Weber
Dynamical crossover in colloidal systems

Figure 1: The shape of GNRs at $T_1$ and $T_2$. The schematic appearance of the reconfiguring region predicted by SFPC theory according to the free-energy profiles of the hexagonal phase model (see text) at $T_2$ and the crossover transition temperature $T_1^{(c)}$. The shapes are shown for both the rearranged GNR (the final state) and the partially rearranged transition state. The radius of the core, $R_{1}$, and the radius of the string, $R_{2}$, are shown in the figure.

JACOB D. STEVENSON*, JÖRG SCHMAJIAN* AND PETER G. WOLYNES**

Nature Physics, 2006
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 $\mu$m thick) centered at $z = 13.5$ $\mu$m. (D to F) Perspective view of 16-$\mu$m-thick sections showing particles with shear strain values larger than 0.025 only.
Local shear transformations in deformed and quiescent hard-sphere colloidal glasses


FIG. 6. (Color online) Evolution of strain and strain correlations in the colloidal glass during a shear experiment. The time and macroscopic strain corresponding to columns (1)–(5) are indicated in Fig. 5(c). Row (a) shows the deformation profiles. Row (b) shows the top-view reconstructions showing only those particles with individual strain $|\epsilon_{yz}| > 0.1$, colored according to their strain. On strain reversal, some of the regions of particles that acquire a high positive strain (red) return to a low-strain configuration and disappear from the reconstruction; others experience an irreversible local deformation and remain in a high-strain state at the end of the experiment. These are compensated for by other regions that deform in the opposite direction (blue) so that at the end the average strain is zero at time (5). Row (c) shows the $y$–$z$ plane cross sections of $\epsilon_{yz}$ spatial autocorrelations, showing the evolution of the fourfold pattern that is the signature of Eshelby inclusions active in the material.
AFAM: setup used by the Arnold group (IZFP Saarbrücken)
AFAM spectroscopy

Contact-resonance spectra of a SrTiO$_3$ sample and map of local elastic modulus
Bulk metallic glasses
Sample: PdCuSi, Reference samples: STO, SiO2

Map of local elastic modulus

H.Wagner et al. Nature Mat. 2011
Local elastic map & plasticity (2-D-LJ system)
M.Tsamados, J-L Barrat et al. PRE 80 (2009)

G in rigid (black) and soft (white) zones
2.5% strain (100x100 atoms)

Overlap of nonaffine displacement field
(x 300) with elastic map for 2.55% strain
Frequency distribution of local modulus with $M = 105$ GPa – amorphous PdCuSi (H. Wagner)

Frequency of the modulus

- FWHM: 28.52%
- Low modulus „soft spots“: STZ’s in the „elastic„regime
- Gaussian not good due to infinite tails – binomial or Hughes distr.

Nature Mat., 10 (2011) 439
Probability distribution of local modulus with $M = 174.5$ GPa – at least partly crystalline PdCuSi (H. Wagner)

Polycrystalline material with grain size orientation distribution = Modulus distribution

Note: HWHH a factor 100 smaller compared to glass and soft parts are missing in Gauss distribution (first to crystallize)

Map of local elastic modulus

Frequency of the modulus

$\text{FWHM: 0.22\%}$
Loss distribution of amorphous and x-talline PdCuSi

FWHM (a-PdCuSi) $\sim 0.33 \times 10^{-2}$

FWHM (x-tal PdCuSi) $\sim 0.017 \times 10^{-2}$
Frequency distribution of local modulus and loss–amorphous SiO$_2$ -a strong glass forming system

H.Wagner et al. accepted by JAP 2014
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Universal character of the slow beta-relaxation in metallic systems

Prof Wei Hua Wang Group, Beijing, China

Type A and type B-Glasses (Roessler): for metallic systems depending on "molecule-like" metallic glass types.

„Molecule -like“ metallic glasses: Chemical influence on $\beta$ relaxations

Creep-recovery experiment for glassy PdCuSi below Tg to test the β - relaxation

M.Schwabe et al., EJPE, 2011
Loss landscape for the secondary - JG- β - relaxation versus temperature and stress
Activation volume for the secondary- JG- β relaxation for glassy PdCuSi

\[ V = k_B T \left( \frac{\partial \ln \text{delay - time}}{\partial \sigma} \right) \]

String volume only 0.4 nm\(^3\) ~ 20-30 atoms– factor 20 less than STZ size and decreasing length scale with increasing temperature

see also MW Chen, H.Schober, F. Faupel et al.
Size of plastic events (STZ) – α - relaxation

Computer simulations:

Experiments on bulk samples:
(strain rate sensitivity)

STZ – size ~ 120 Atoms

STZ size ~ 560 Atoms

See experimental results from D. Pan, MW Chen et al. PNAS 2008 and Y.H.Liu et al. PRL(2011) :
Correlation length ~ 2.5nm (Phase)
β-excitation or string acts as an elastic quadrupol!!

H. Schober (from Miracle MRS Bull. 2007)
String with Eshelby stress field (not correct scale)
Activation energy for beta relaxation and small atom diffusion

Hai Bin Yu et al. PRL 2012
Activation energy for beta relaxation and small atom diffusion

Sliding event for diffusion (here shown only in 1D)

H. B. Yu et al. PRL 2012
MD simulation (2-D) for beta relaxation without and with pinning centers

Fig. 5: (Color online) Left panel: a graphic representation of the cooperative motion that is associated with the $\beta$-wing. Note the chains of particles that have moved coherently during a time span of four time units. The particles that move more than 40\% of the typical inter-particle distance are marked in dark blue. Right panel: similar graphic representation of the suppression of the majority of the cooperative motion that is responsible for the $\beta$-wing by the addition of 2.5\% pinned particles. In contrast to the previous figure, here one needs to look at cumulated motions for 15 time units to see the remnant correlated motion.

Y. Cohen, I. Procaccia, K. S. et al. EPL 100 (2012) 36003
Suppression of beta relaxation (wing) due to pinning centers (5%)

Y. Cohen, I. Procaccia, K. S. et al., EPL 100 (2012) 36003
Crackling or Barkhausen noise (minimal resolution 15 nm)

PdCuSi

not during recovery (like pop in’s)
MD-simulation: Stress-strain behavior

stress-strain plot for CuTi glass at 500K - strainrate=1/ns

yielding point \((\gamma_c, \tau_c)\)

plastic deformation

elastic deformation: \(\tau = G\gamma\)

MD-Simulation below critical yield strain - local STZ


(a) $\gamma_i = 3.9\%$

(b) $\gamma_i = 4.9\%$

(c) $\gamma_i = 5.9\%$

(d) $\gamma_i = 6.9\%$
Fixed stress boundary condition: Results for $\varepsilon=0$:

- Stress strain curve (ductile)
- Critical point
- Avalanche size distribution:
  \[ S_{\text{max}} \sim (F-F_c)^{-2} \]

K. Dahmen, Nature 2010
Distribution of waiting time $s$ for avalanches

$T = 330^\circ C$
Scaling of waiting time distribution with applied stress at fixed temperature

\[ D(s, F) \sim 1/s^\tau g[s \cdot (F_c - F)^{1/\sigma}] \]

with universal scaling exponents \( \tau = 1.5, \sigma = 0.5 \) and scaling function \( g(x) \sim A \exp(-Bx) \),
Binning analysis for different time length s: single events versus coordinated avalanches?

$t \sim 0.8$ from A. Lemaitre for plast. deformation

Nature Comm. 5 (2014) 3616
Nano-shear bands

- $\Delta l \sim 15\text{nm}$ slip length of a $50\mu\text{m}$ thick sample under 45 degree assuming a STZ size of $3.5\text{nm}$ (1000 atoms) and critical strain of 2% ($\sim 0.07\text{nm}$):
  - $20000 \text{ STZ} \times 0.07\text{nm} = 1.14 \times 10^3 \text{ nm} \sim 1\mu\text{m}$ offset of a macroscopic shear band
  - $15\text{nm}$ offset about 1.5% $\sim 300 \text{ STZ}$
- Seen as offset in AFM and TEM work
- Upper limit – could be even smaller
\( Kc = 0.85 \text{ N/m} \) (determined from thermal tuning)

-Free resonance \( f_0 = 23.9 \text{ kHz} \)
-Static Force \( F = 17 \text{ nN} \)

Shear offset = 16 nm

Hai Bin Yu, unpublished
AFAM on shear bands

- The region near shear bands seems with low resonance frequency.
- However, the height is large.
A single shear band in a metallic glass: Local core and wide soft zone


1Institute for Materials Physics, University of Göttingen, Friedrich-Hund Platz 1, 37077 Göttingen, Germany
21st Physics Institute, University of Göttingen, Friedrich-Hund Platz 1, 37077 Göttingen, Germany
3Department of Materials and Materials Technology, Saarland University, Campus D2 2, 66123 Saarbrücken, Germany
FIG. 4: (Color Online). Left panel: The nonaffine displacement field associated with a plastic instability that results in a shear band. Right panel: the displacement field associated with 7 Eshelby inclusions on a line with equal orientation. Note that in the left panel the quadrupoles are not precisely on a line as a result of the finite boundary conditions and the randomness. In the right panel the series of 7 Eshelby inclusions, each given by Eq. 8 and separated by a distance of 13.158, using the best fit parameters of Fig. 2, have been superimposed to generate the displacement field shown.
Summary

• beta relaxations are the fundamental excitations in a disordered system
• In BMG they form strings ($0.4 \text{ nm}^3 \sim 20$-30 atoms: factor 20 less than STZ size)
• beta relaxations line up for diffusion of the small atoms far below the glass transition
• above 2.5% pinning center the beta relaxations are stopped
• Crackling noise analysis show powerlaw statistics common for small avalanches
• avalanches or nano shear bands form out of 300 STZ (1-D)

For a review on beta relaxations see: HB Yu, WH Wang and K.S. Materials Today 2013