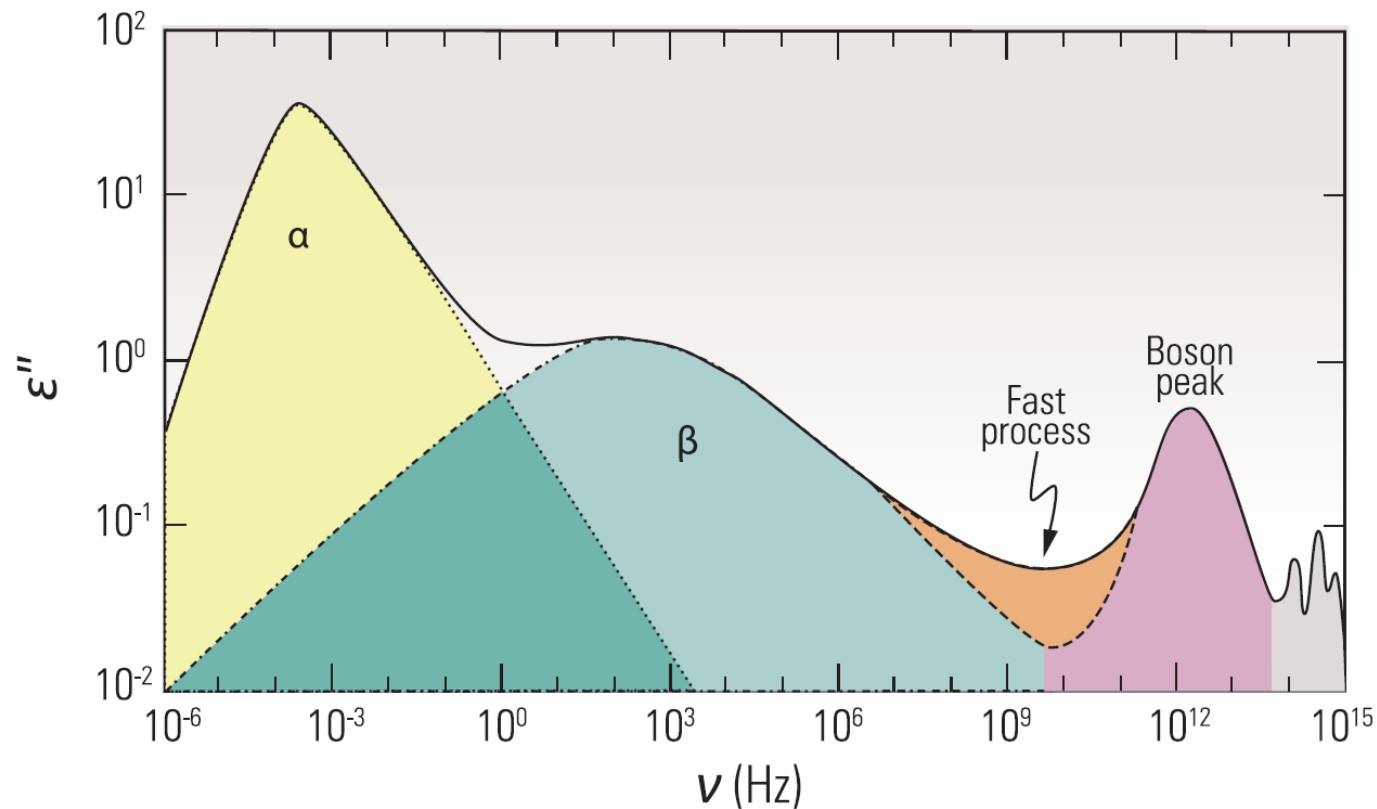# Relaxation in metallic glasses
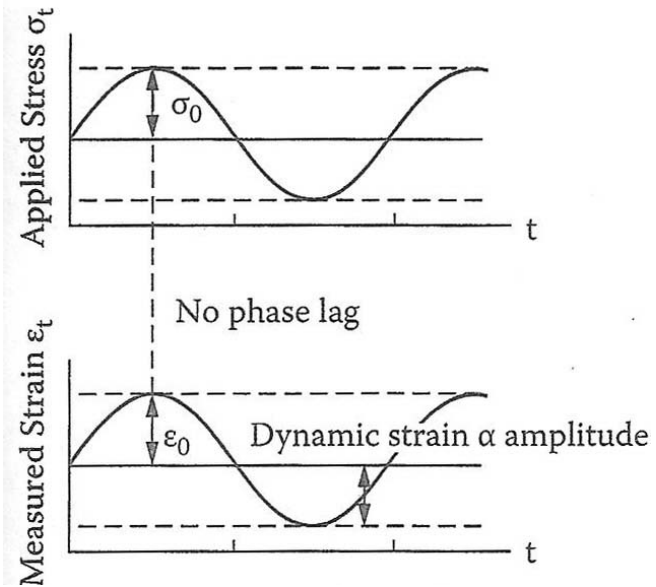
A.R.S.M

2019. 04. 22.

- In the physical sciences, relaxation usually means the return of a perturbed system into equilibrium. Each relaxation process can be categorized by a relaxation time τ.
- The activation of viscous flow reflects the complete relaxation of the system, accommodating its structure under the application of an external force
- Therefore, in structural glasses, viscosity is directly related to the primary relaxation time of the system, the so-called α-relaxation
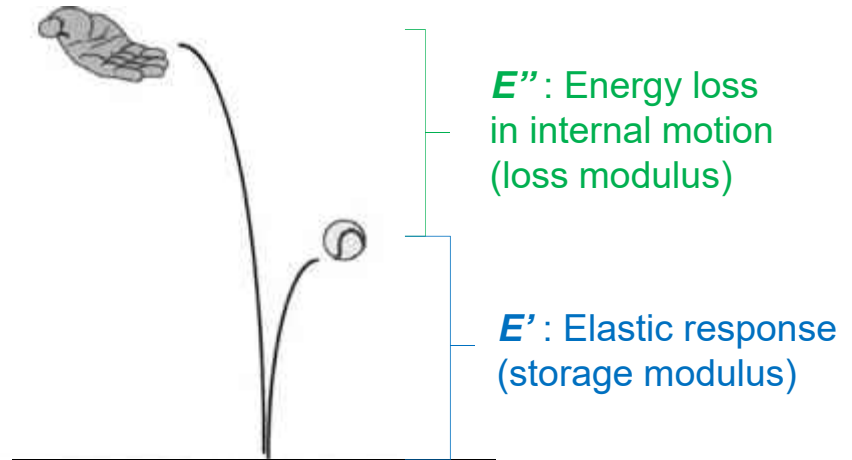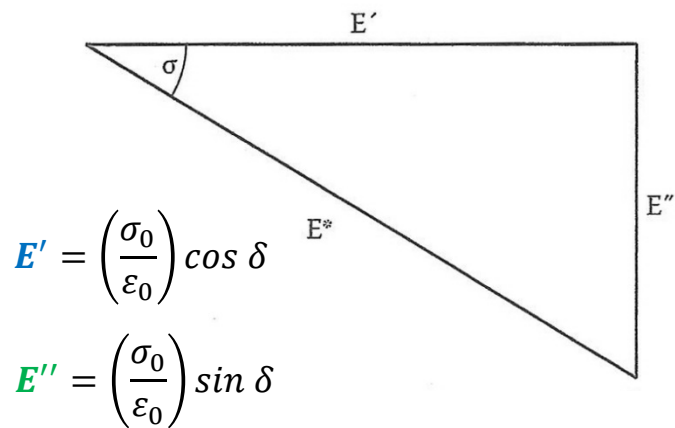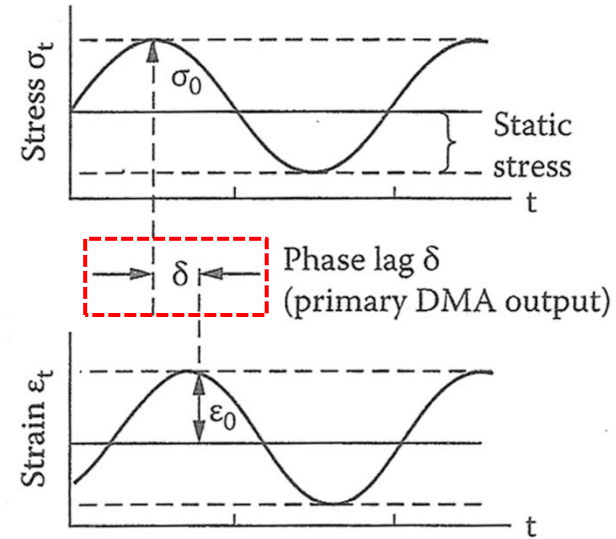
Perfectly elastic (time-independant)

Anelastic (Viscoelastic, time-dependant)

No phase lag

Dynamic strain α amplitude

Static stress

Phase lag δ (primary DMA output)

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

$$E'' = \left(\frac{\sigma_0}{\varepsilon_0}\right) \sin \delta$$

E'' : Energy loss in internal motion (loss modulus)

E' : Elastic response (storage modulus)

Menard, K. P., *Dynamic Mechanical Analysis: A Practical Introduction, Second Edition.* CRC Press: 2008.

(a) Maximum Load

(b)

$h(t)$

$h_r + h_{p\eta}$

A

B

h_e

$h_e + h_{p0}$

C

h_t

h_r

D

1% Maximum Load

$h_{p0} + h_{p\eta}$

t

h_e

h_{p0}

h_r

$h_{p\eta}$
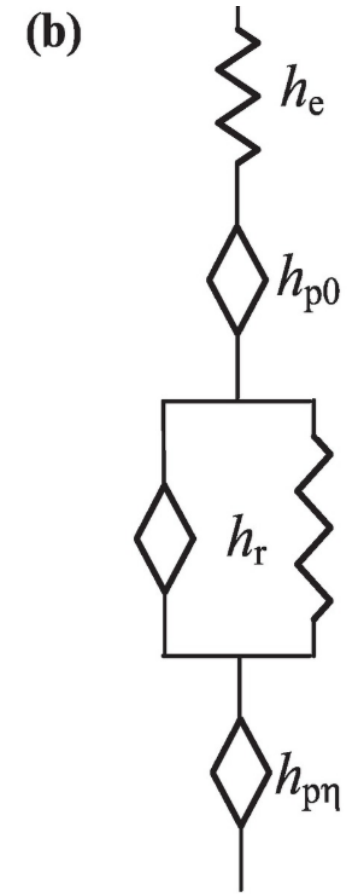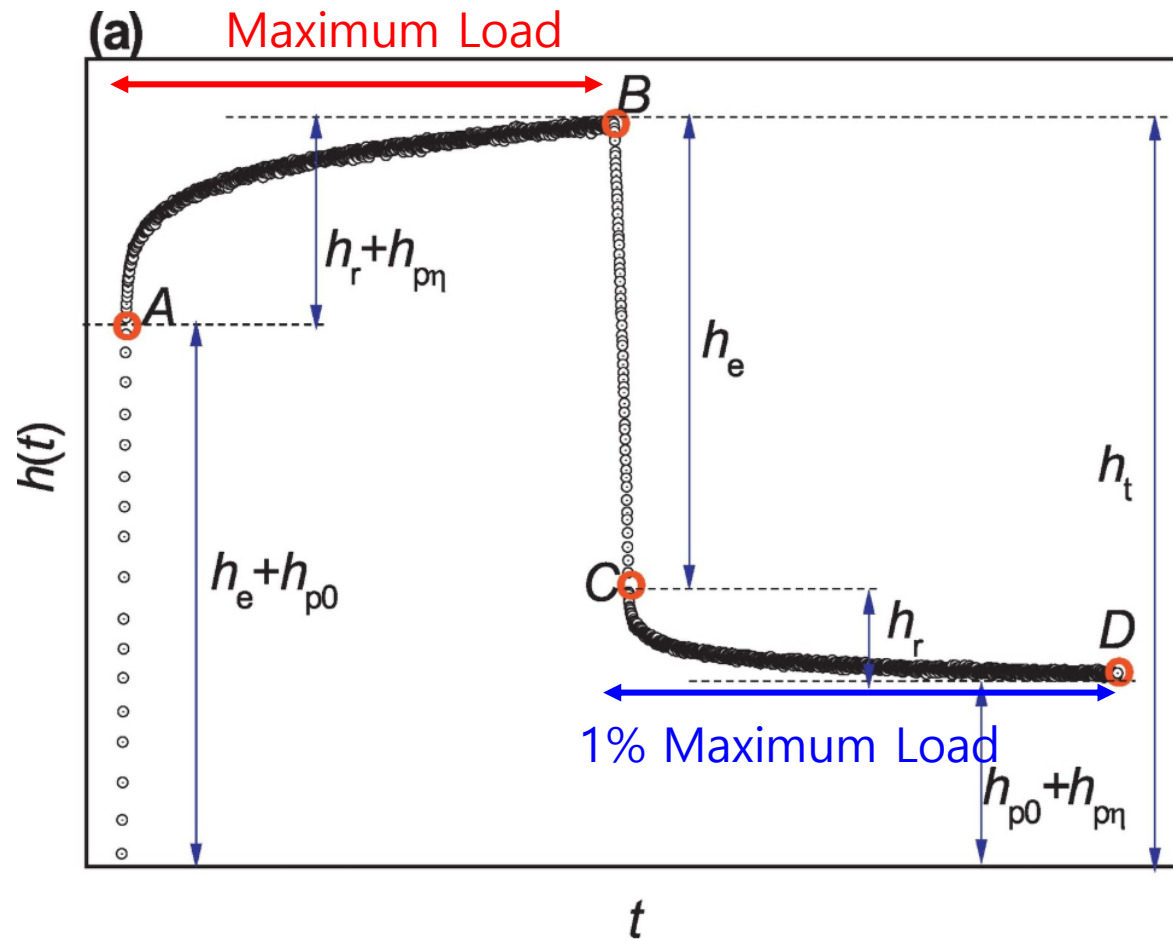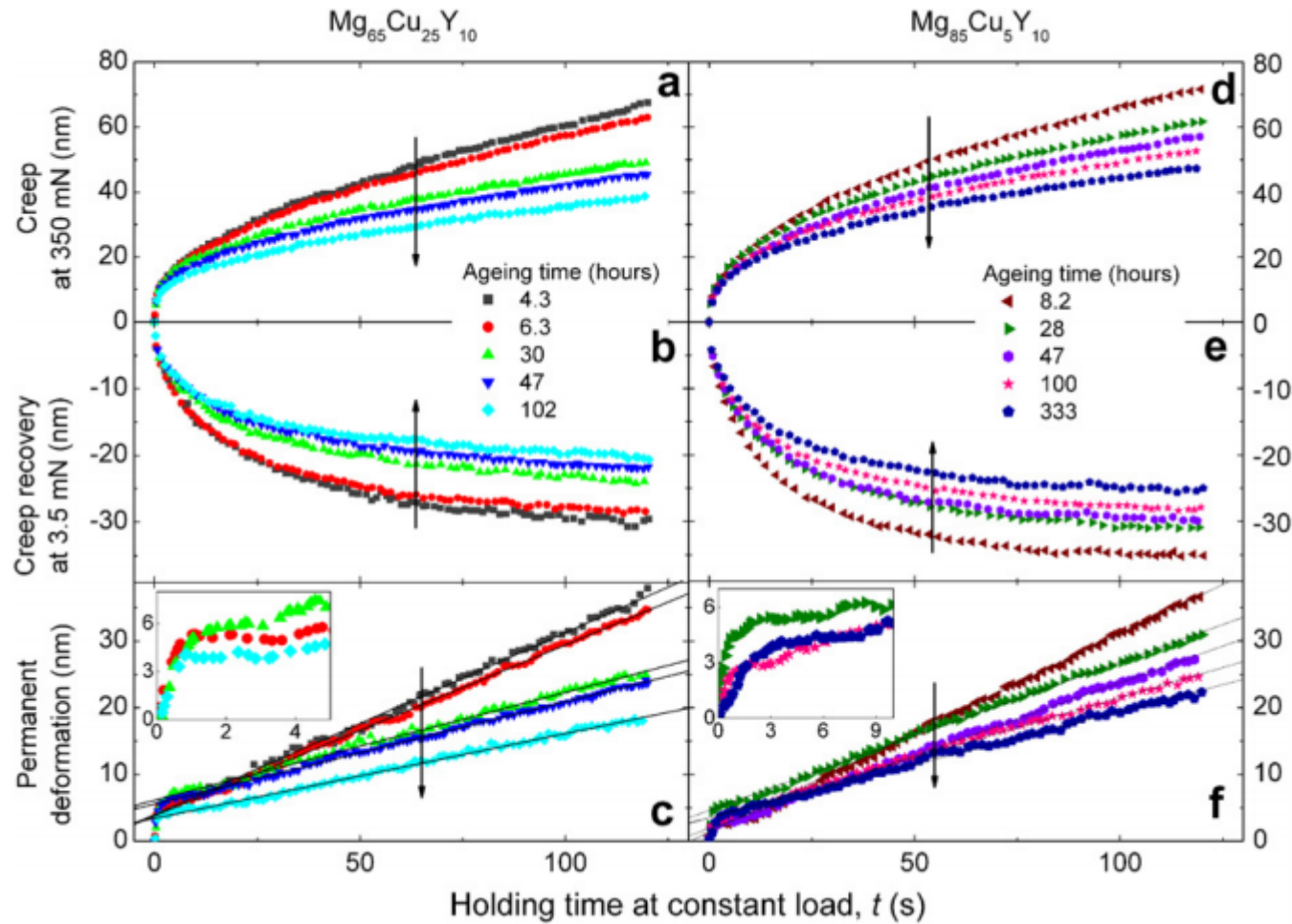
$$h(loading\ curve) = \sum_{i=1}^{n} h_i(1 - e^{-t/\tau_i}) + t/\mu_0$$

Visco-elastic   Visco-plastic

* glass-forming mixture chlorobenzene/cis-decalin

Arrhenius behavior

$$f = f_\infty \exp(-\frac{E_\beta}{RT})$$

Rotational diffusion (Reorientation) : Debye equation

$$D = \frac{k_B T}{8\pi\eta r^3}$$

β

α $T_g = 131 \pm 1$ K

Translational diffusion : Stokes-Einstein relation

$$D = \frac{k_B T}{6\pi\eta r}$$

Log (f_m/Hz)

$10^3/T$ (K^{-1})

Hidden flow | Macroscopic flow

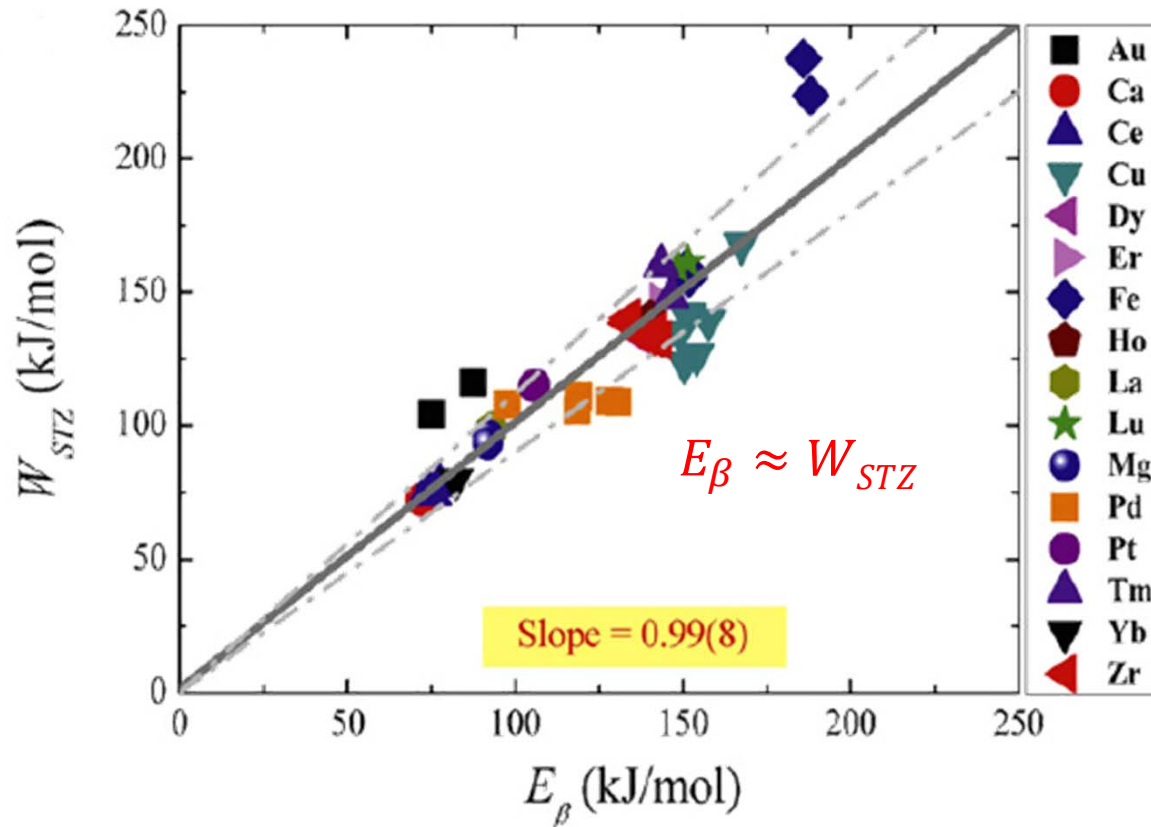T_α=481 K

E" (GPa)

α-peak

T_β=363 Kz

β-peak

T_g

Temperature (K)

- glasses and the forming of supercooled liquids have two main relaxation processes
  : **primary (α)** and **secondary (β)** relaxations.
- Relaxation in this glassy range involves decoupled, localized motion of easily mobile species; this is usually called secondary relaxations
- The α relaxation is responsible for vitrifaction, and its arrest **(near T$_g$)**
- However, as the **α** relaxation disappears below the glass transition temperature Tg, the **β** relaxation, which initiates at high temperature and continues below T$_g$, is the principal source of dynamics in the glassy state

Wang, Z., et al. "Evolution of hidden localized flow during glass-to-liquid transition in metallic glass." *Nature communications* 5 (2014): 5823.

Wang, Z., et al. "Evolution of hidden localized flow during glass-to-liquid transition in metallic glass." *Nature communications* 5 (2014): 5823.
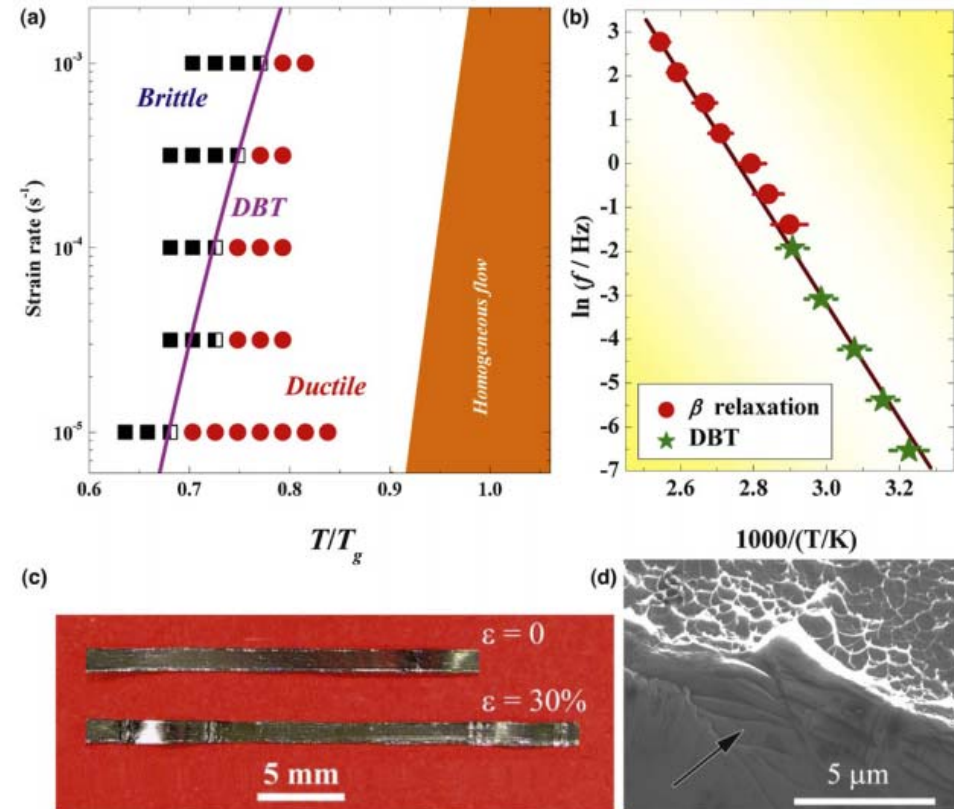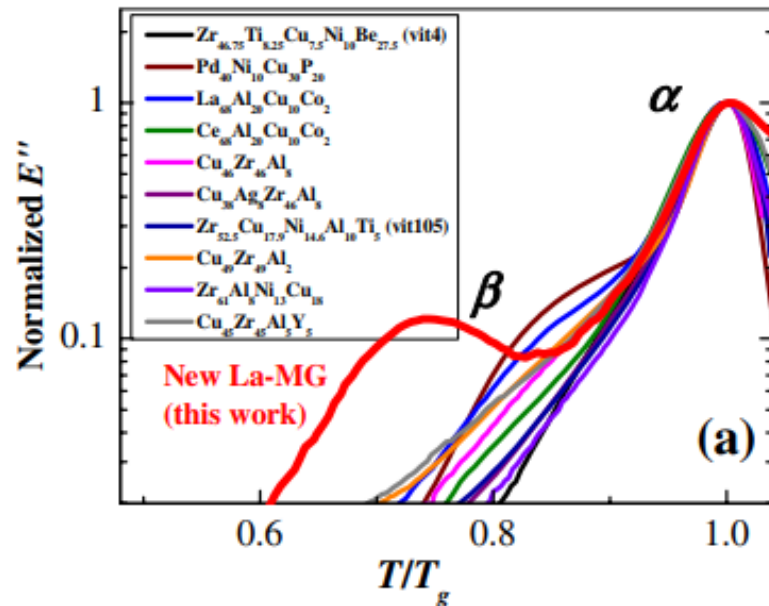
$$E_\beta \approx W_{STZ}$$

Slope = 0.99(8)
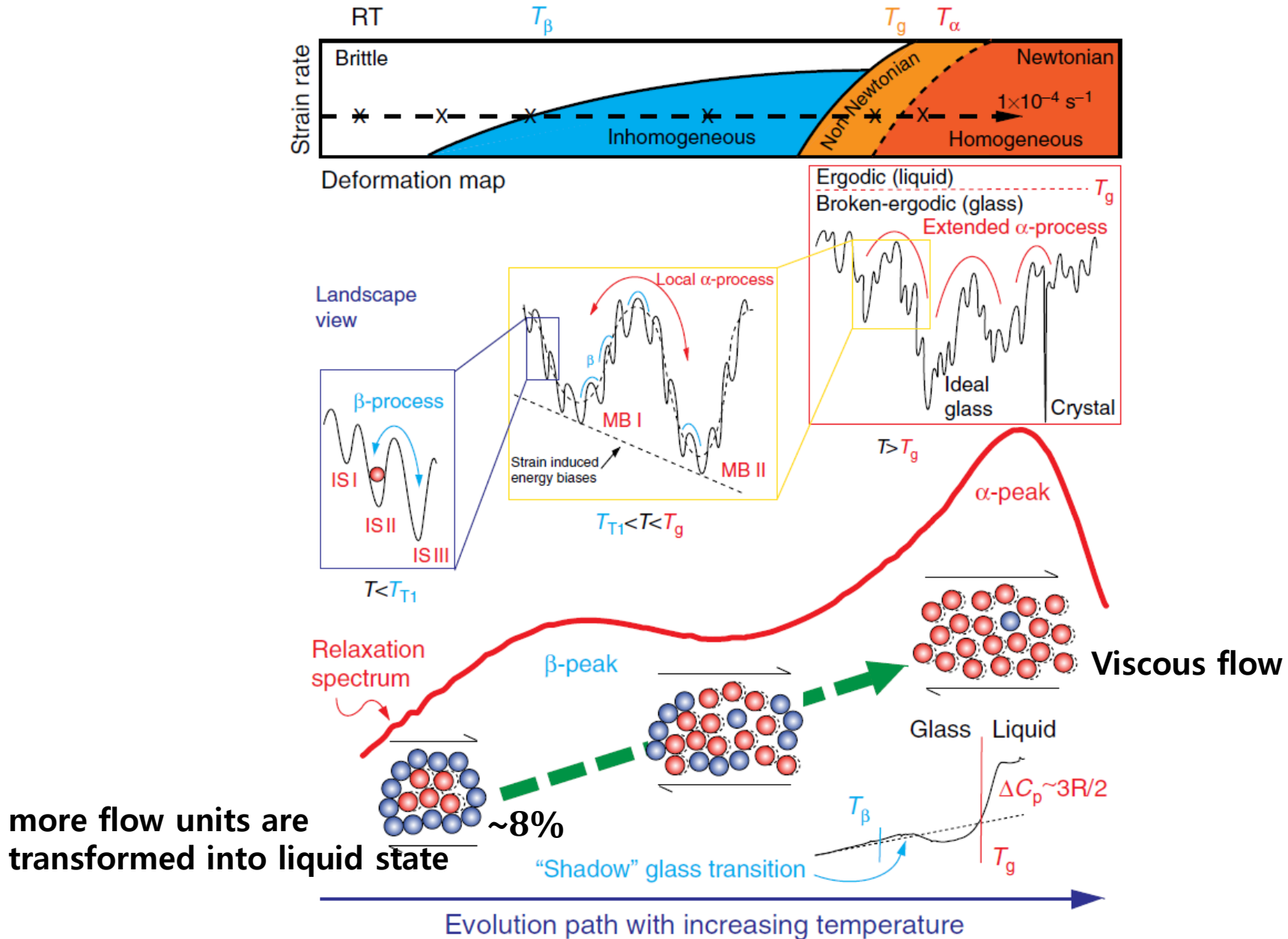
$$W_{STZ} = \left(\frac{8}{\pi^2}\right) G\gamma_c^2 \zeta\Omega$$

Clearly, this relation connects two fundamental issues in glassy physics
: the deformation mechanisms and relaxation dynamics.

Yu, H. B., et al. *Physical Review B* 81.22 (2010): 220201.

La68.5Ni16Al14Co1.5 MG

- One can expect that MGs with pronounced b relaxations at relatively low temperatures might be macroscopically ductile
- The pronounced beta relaxations of the MG indicate that the MG has abundant potential STZs, and global tensile plasticity can then be triggered when the high density potential STZs are activated to reach the percolation limit by external stresses
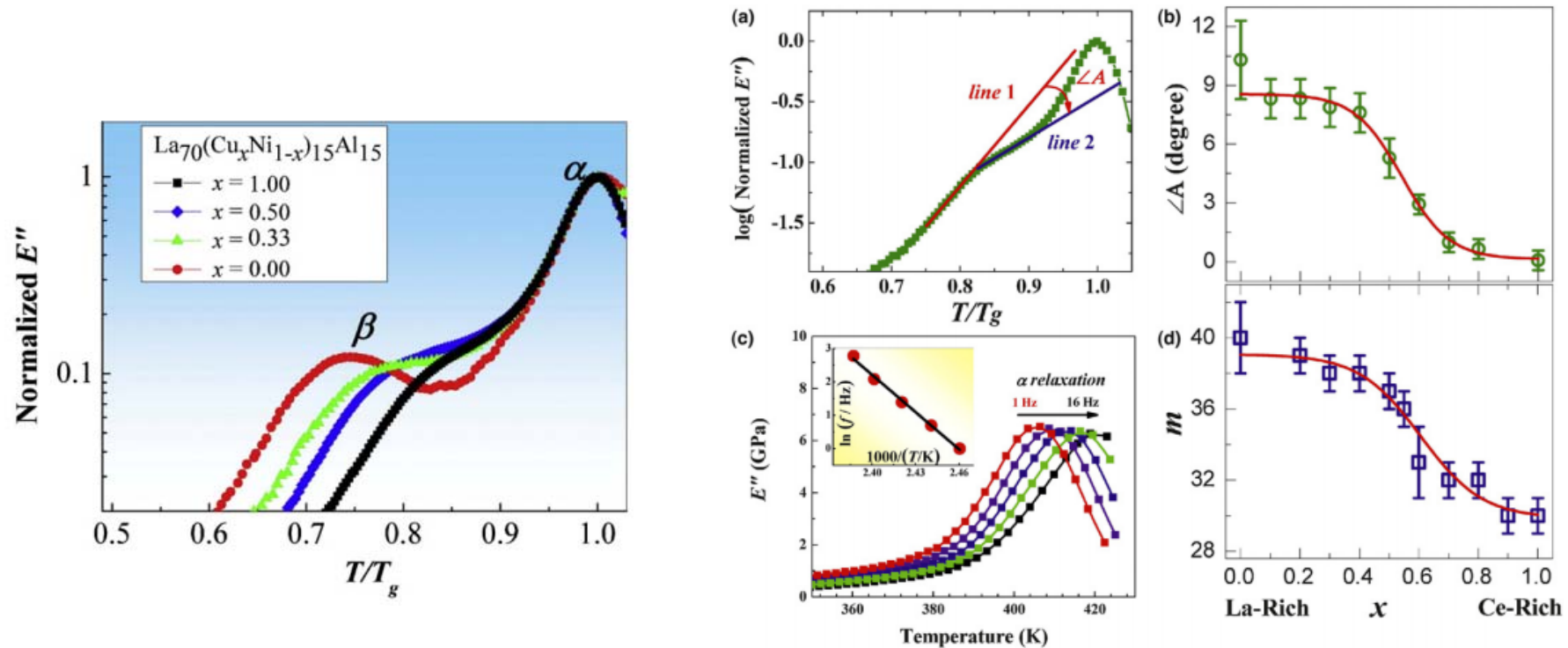
In addition, the behavior of the b relaxation in MGs is sensitive to chemical compositions . For example, as shown in Fig. 2b, the replacement of a small amount of Ni by Cu in a La70Ni15Al15 MG results in a dramatic change in the appearance of the beta relaxations

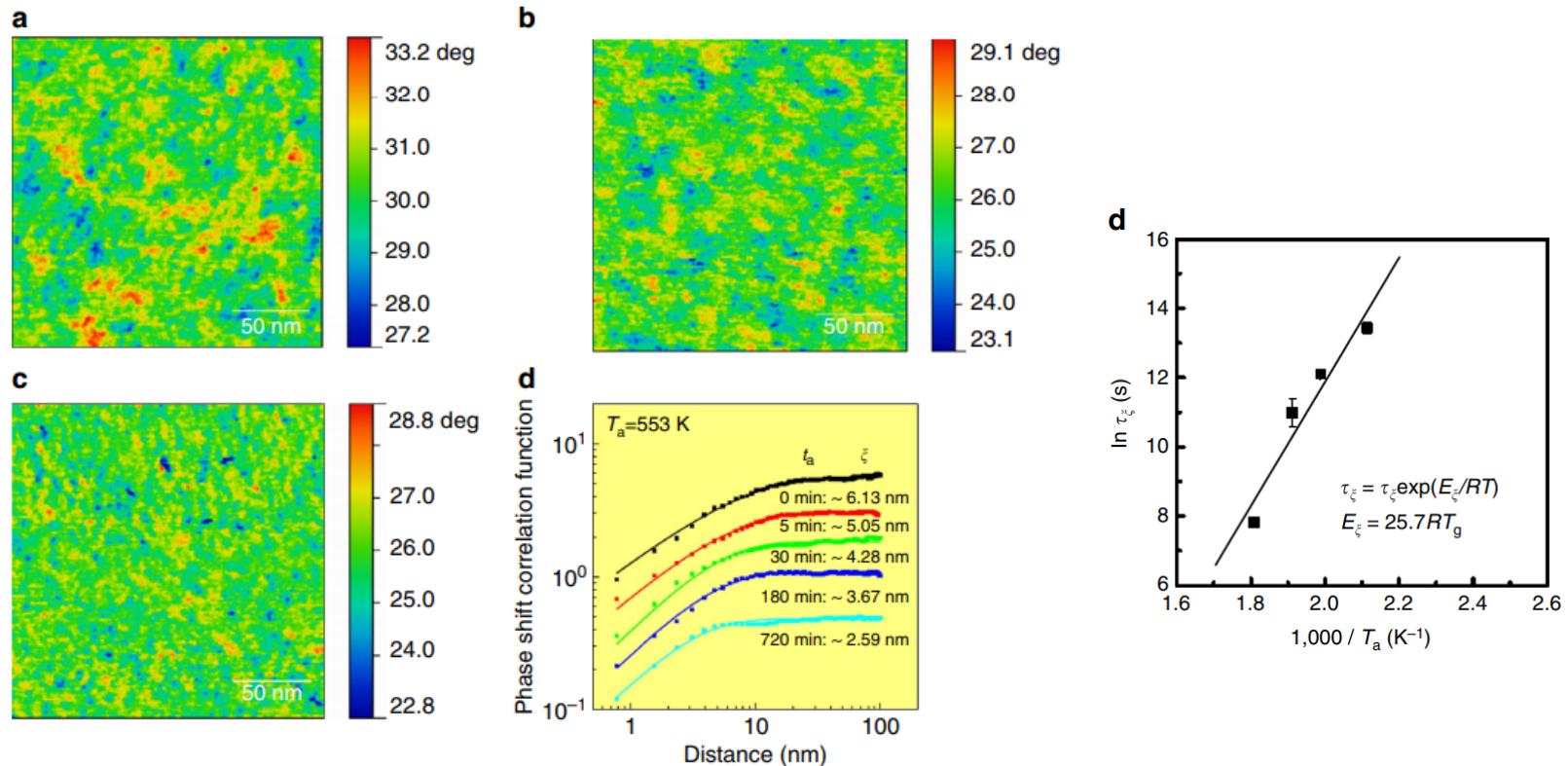**amplitude-modulation dynamic atomic force microscopy**

Figure 3 | Evolution of spatial heterogeneity during sub-T_g relaxation at $T_a = 553$ K. Phase shift images of (**a**) the hyper-quenched metallic glass, (**b**) the metallic glass relaxed at 553 K for 5 min and (**c**) relaxed at 553 K for 720 min. (**d**) Correlation function curves of the samples annealed at 553 K for different durations. The correlation lengths of spatial heterogeneity in phase shift images can be determined by the correlation function curves. Note that the curves were shifted vertically for clear identification.
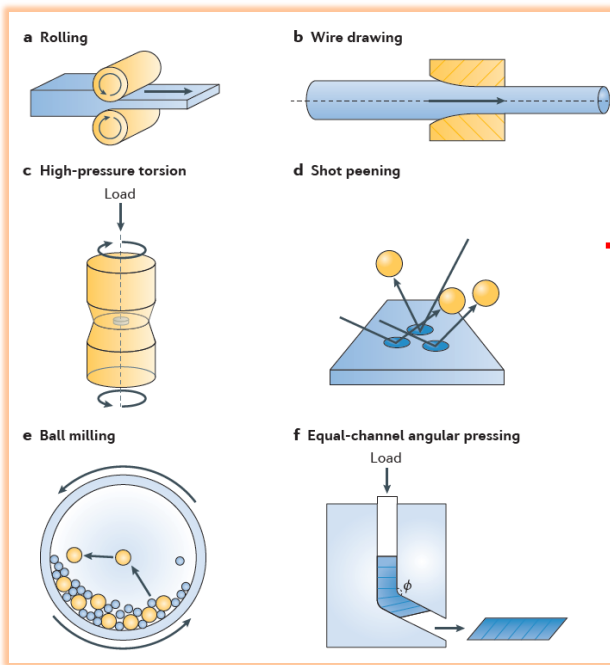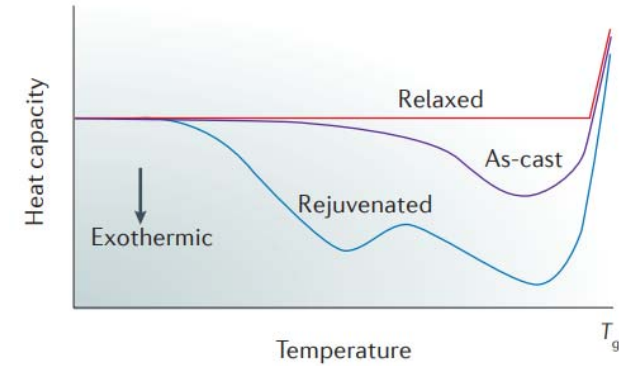
Evolution of spatial heterogeneity in a hyper-quenched metallic glass during sub-Tg b-relaxation is reported.

The characteristic relaxation times and activation energy of the spatial heterogeneity dynamics are in well accordance with those of b-relaxation, evidencing the intrinsic correlation between local structure evolution and sub-Tg b-relaxation
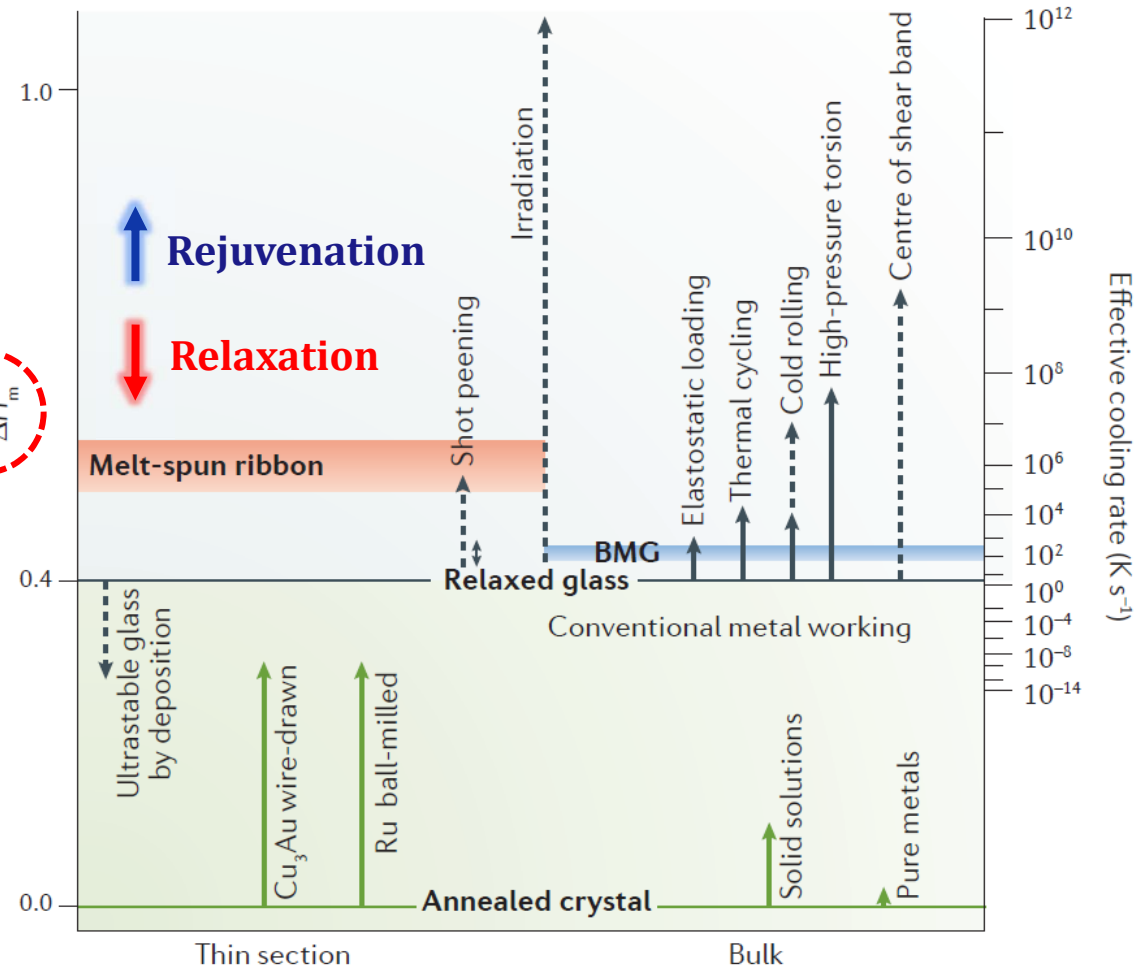
< Relative enthalpies of deformed metallic glass at RT>
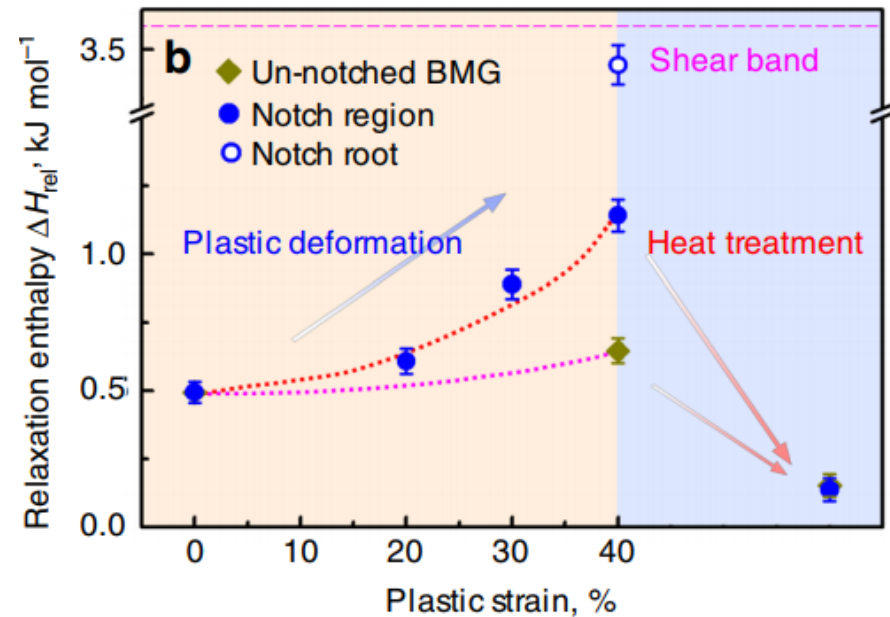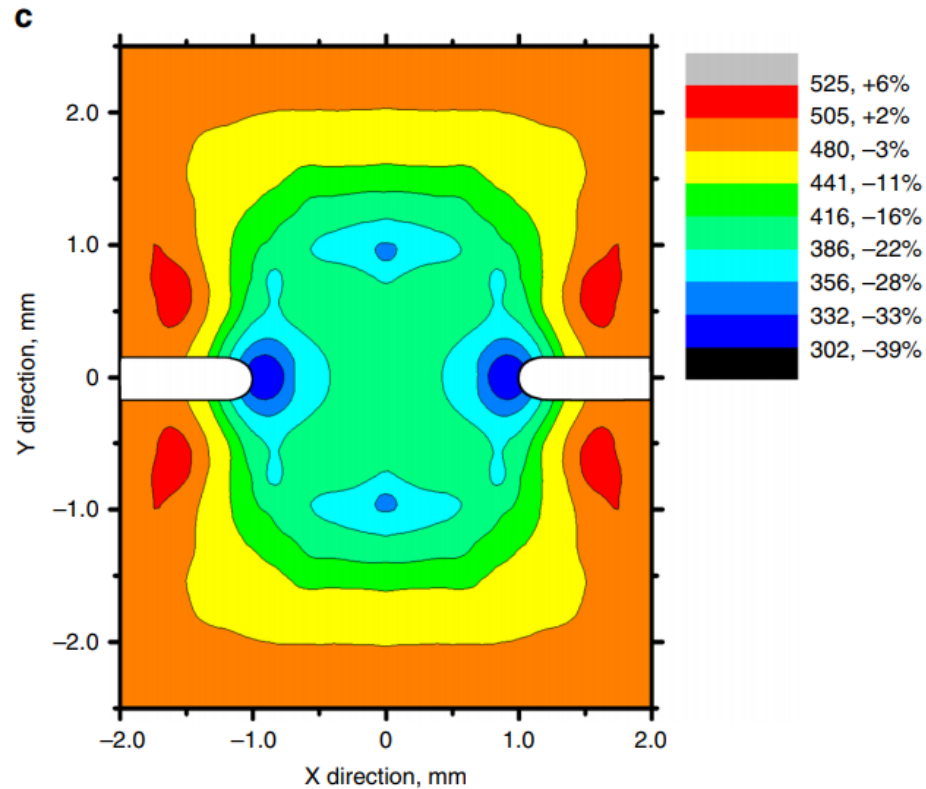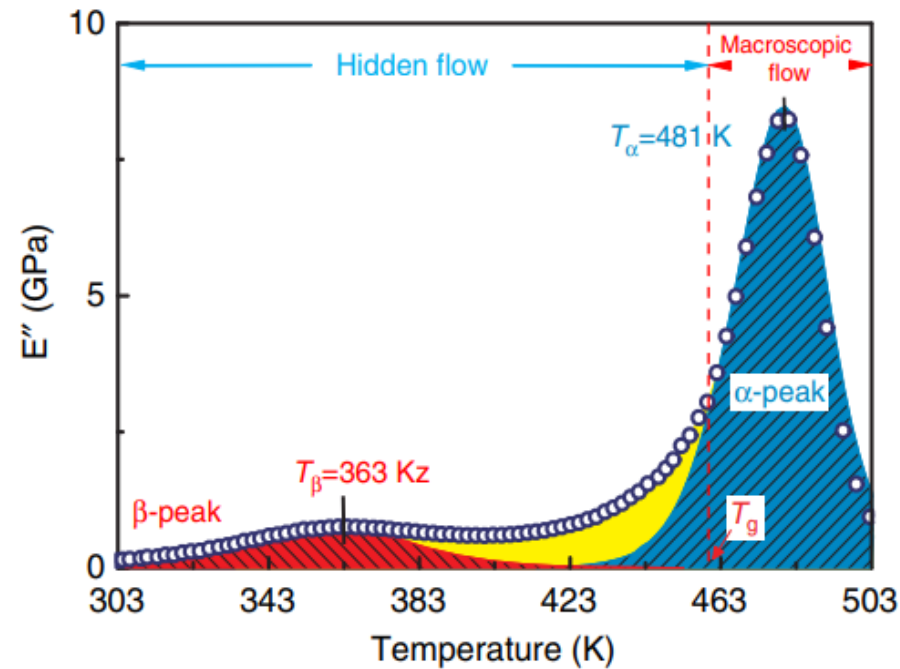
- While it improves the plasticity of the glass, this degree of rejuvenation has not yet eliminated the shear banding instability, a goal that remains for future work.

Pan, J., et al. *Nature communications* 9.1 (2018): 560.

- In the physical sciences, relaxation usually means the return of a perturbed system into equilibrium. Each relaxation process can be categorized by a relaxation time τ.
- the **β** relaxation, which initiates at high temperature and continues below T_g, is the principal source of dynamics in the glassy state
- Understanding of structural origin of b-relaxation gives the microscopic connection between structure and dynamics of metallic glasses
  → Important in designing novel metallic glasses with improved properties

Thank you for kind attention
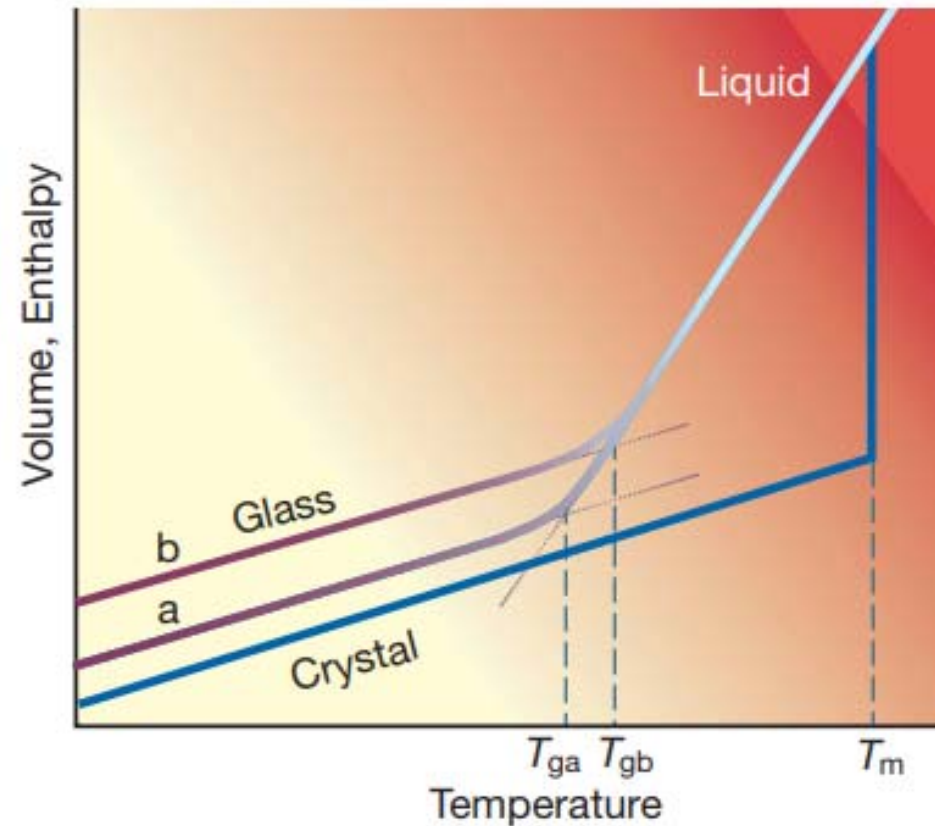
- Upon cooling below the freezing point Tm, molecular motion slows down. If the liquid is cooled sufficiently fast, crystallization can be avoided

- Eventually molecules will rearrange so slowly that they cannot adequately sample configurations in the available time allowed by the cooling rate

- The slower a liquid is cooled, the longer the time available for configurational sampling at each temperature, and hence the colder it can become before falling out of liquid-state equilibrium