II. Hardness and Indentation Behavior

Fracture mostly initiates at the surface of glass structures

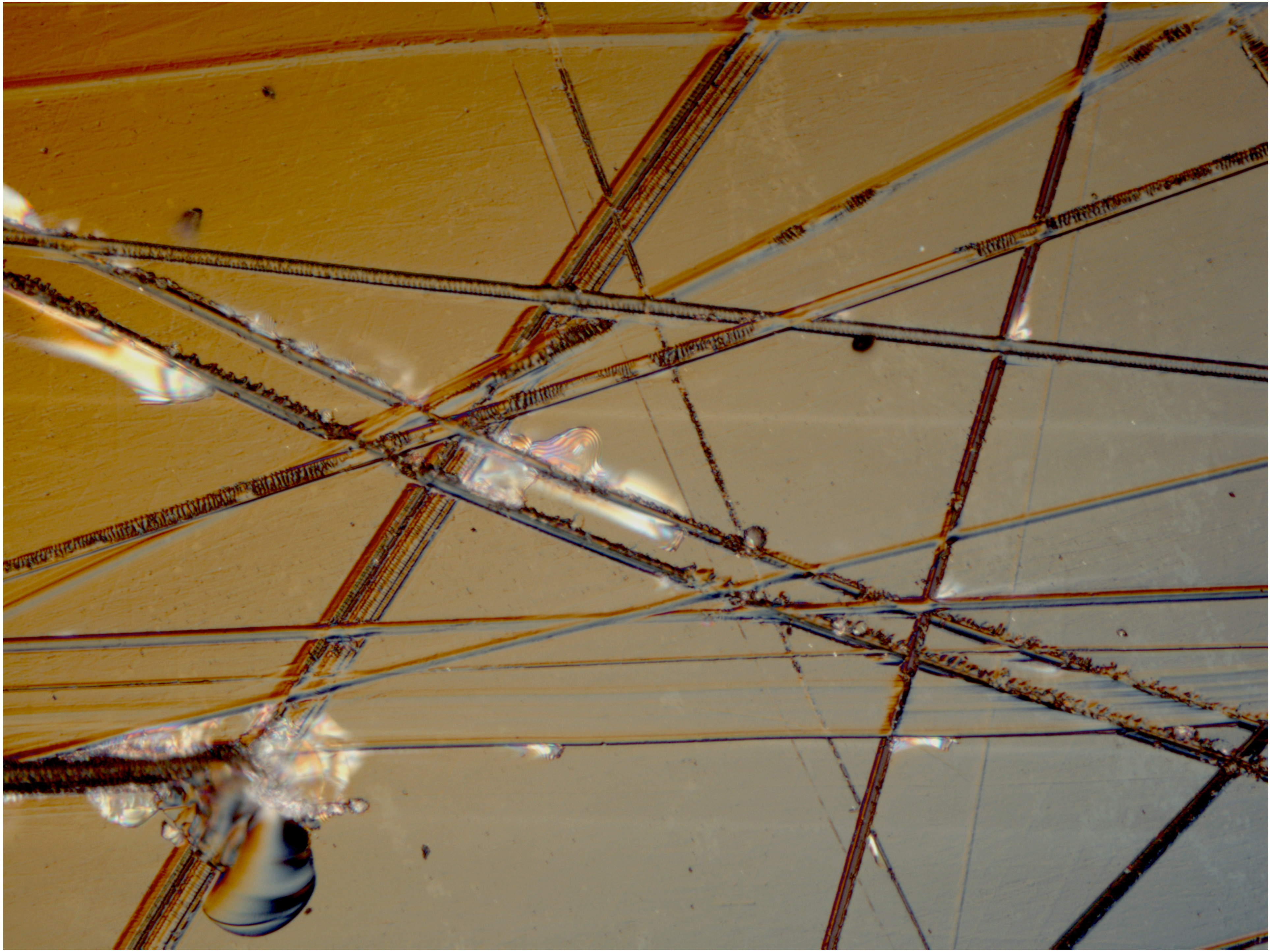
→ Understanding surface damage is a key issue in glass science

Vision au travers d'un pare-brise usé. Phénomène de diffraction. Piéton non visible

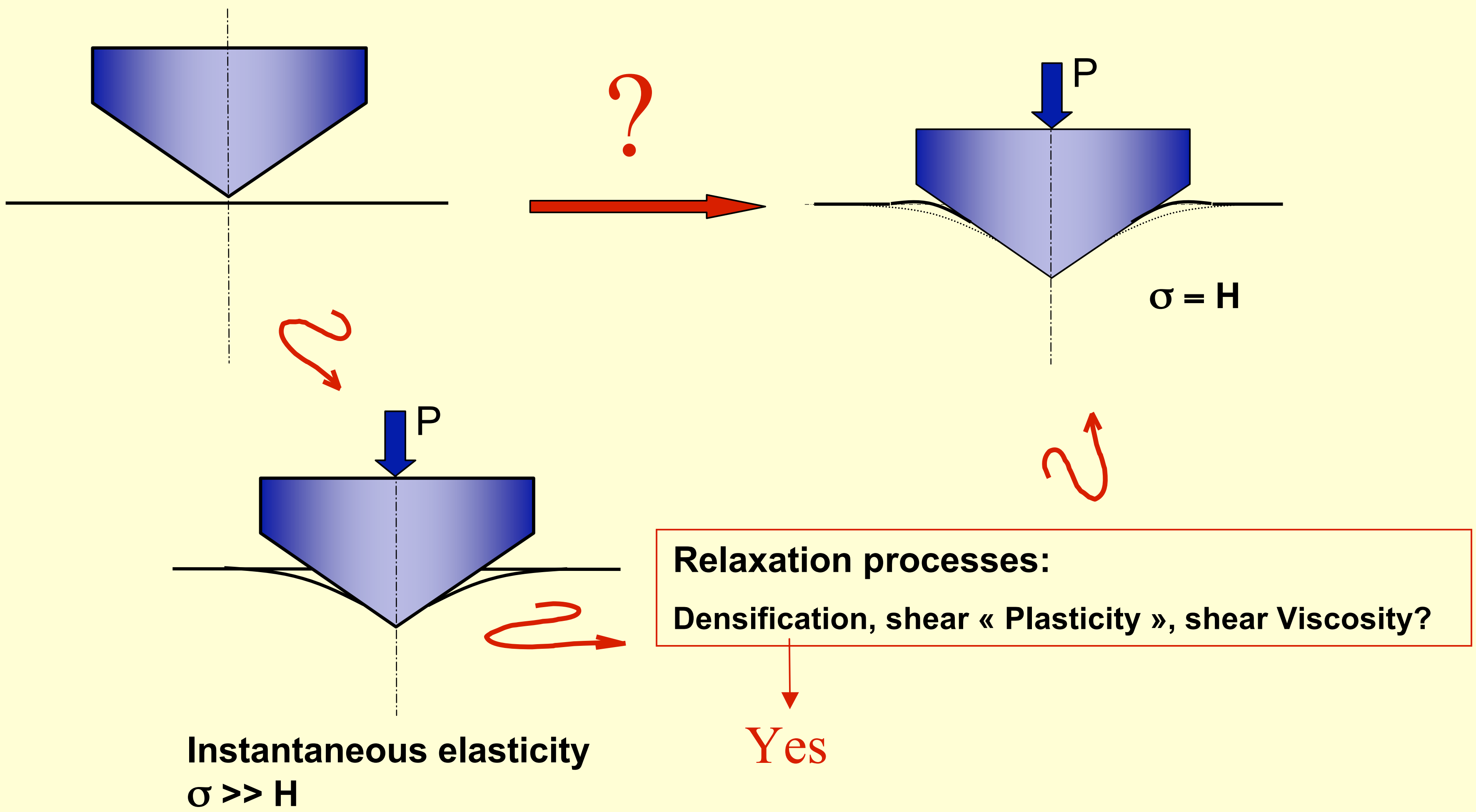
Vision au travers d'un pare-brise non usé. Image claire. Piéton visible

Surface damage alters

- *The strength*
- *The visual aspect (aesthetics)*
- *The function*



The Indentation Deformation Process



Introduction

Hardness: « Like the storming of the seas, is easily appreciated but not readily measured » (O' Neill, 1934)

Several definitions:

- **Resistance to deformation under sharp contact loading**

  ⇨ $H_{steel} > H_{rubber}$

- **Resistance to permanent deformation**

  ⇨ $H_{rubber} > H_{steel}$

In contrast with metals, for which hardness is mainly related to plastic flow, polymers and glasses behave elastic to a great extent

Indentation mechanics

I. Rheology

I.1. The stress *(available macrscopic parameter)*

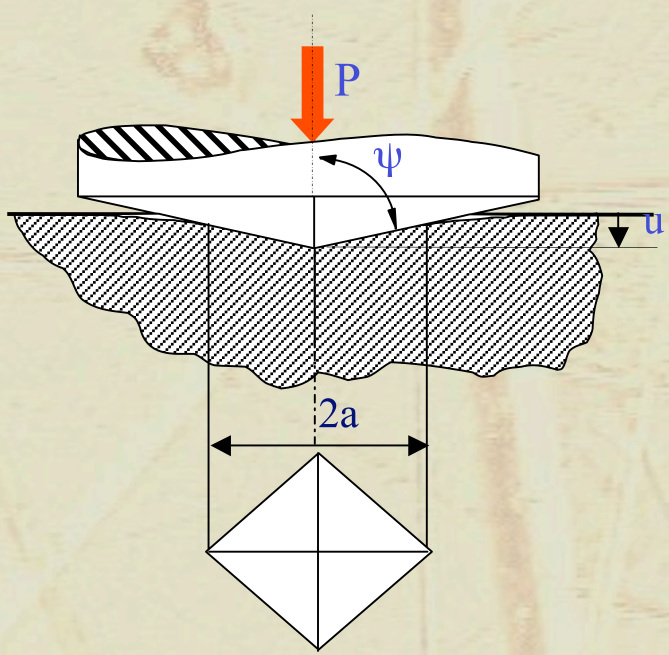
- **σ=P/contact surface: Vickers hardness**

(Hv=1,8544M/d^2, M: kg, d=2a: mm)

- **σ=P/projected contact surface: Meyer's hardness** *(Meyer, 1908)*

σ=H=P/(2a^2)

P=ka^n (Meyer's law)
n$\in$[1-2]
dH/dP$\leq$0 !



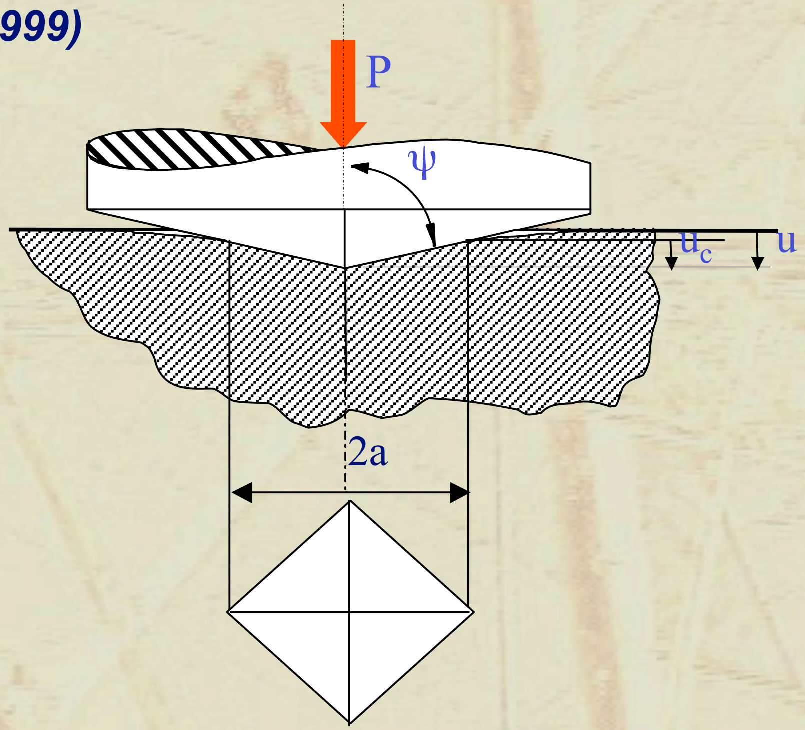
I.2. Strain

Preliminary remarks:

Small strain hypothesis: $\varepsilon_{ij}=1/2(u_{i,j}+u_{ji})$ (= $(l-l_0)/l_0$ in uniaxial loading)

For large strains: $d\varepsilon=dl/l$ et $\varepsilon=\ln(l/l_0)$ (100% in tension -50% ⇔ in compression)

- **For a ball on plane problem,** $\varepsilon \approx 0.2a/R$ (R: indenter radius) ***(Tabor, 1950)***
- **General case:** $d\varepsilon=\beta du/u$, with $\beta=\text{cotg}\ \psi$ ***(Sakai, 1999)***



$d\varepsilon=\beta\ du/u$

NB: $u=\gamma u_c=\gamma a/\tan\psi$

With $\gamma\in[1-\pi/2] = \pi/2$ in pure elasticity for a conical indenter (Love, 1939)

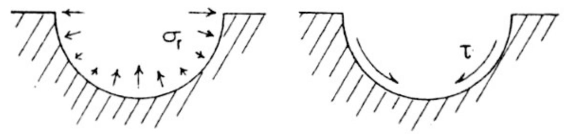
I.3. Constitutive law

- **Elasticity**

Local description:

Contact loading (Boussinesq, 1885)
+ Blister field (Yoffe, 1982)

E. H. Yoffe



Effect of blister field on a hemispherical cavity; shear stress τ and normal stress σ_r are indicated by the arrows.

Mean stress value:

$\sigma=\gamma^2/(2u^2\tan^2\psi)P$ (Vickers)
Et $d\varepsilon=\beta\ du/u$

$E=2(1-\nu^2)\tan\psi\ \sigma$ (or contact hardness) *(Stillwell – Tabor, 1961)*

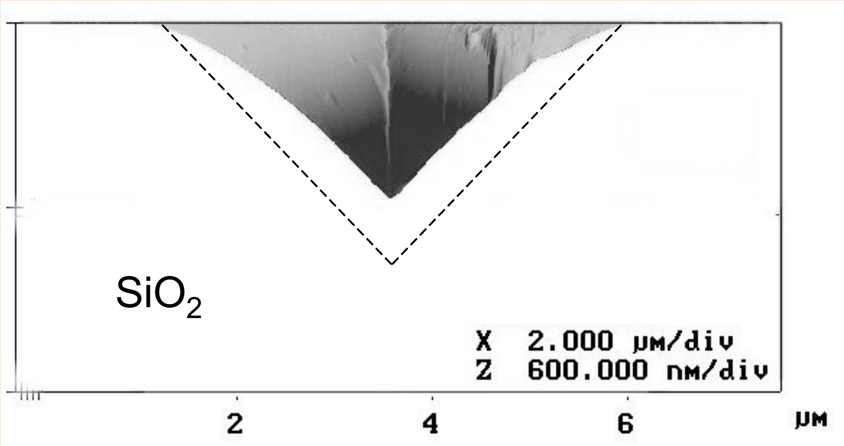
→ $P=E\tan\psi/[(1-\nu^2)\gamma^2]u_e^2$

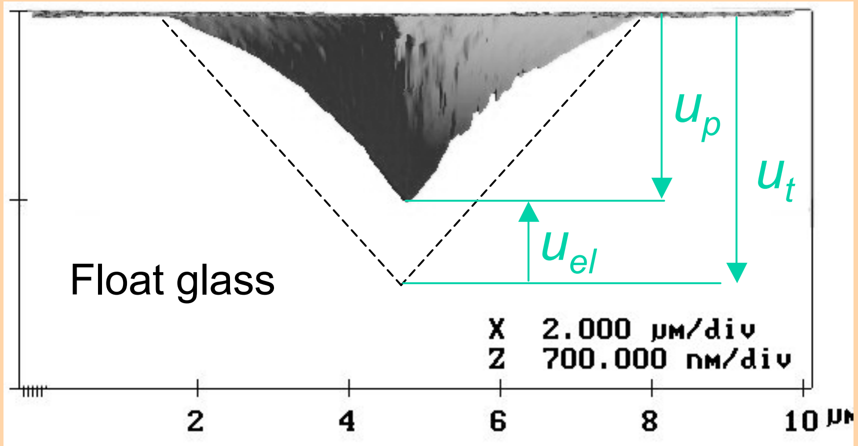
NB:where ψ is an equivalent cone angle: $\pi a^2=2a_v^2$ (ψ=70.3°)
(cone) (Vickers)

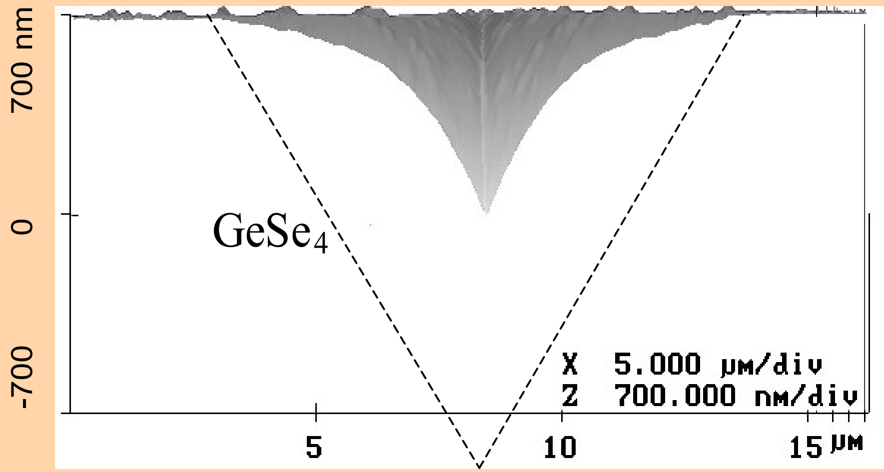
a – The elastic contribution

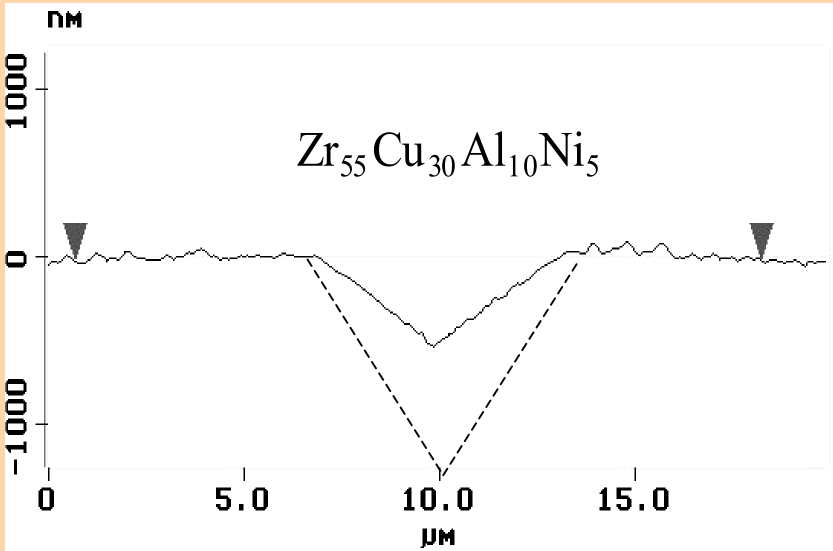
Elastic recovery

---------- *Indenter position at maximum penetration depth*









$E=P(1-\nu^2)\gamma^2/(\sqrt{2}\pi \tan\psi \, uu_e)$ *(Sneddon, 1965 - Loubet, 1986)*

I.3. Constitutive law

- **Plasticity**

σ (=P/(2a^2)) **= χY with** $\chi\in$[3-3,5] *(Ishlinsky, 1944)*

$$P=(2\beta Y\tan^2\psi/\gamma^2)u_p^2$$

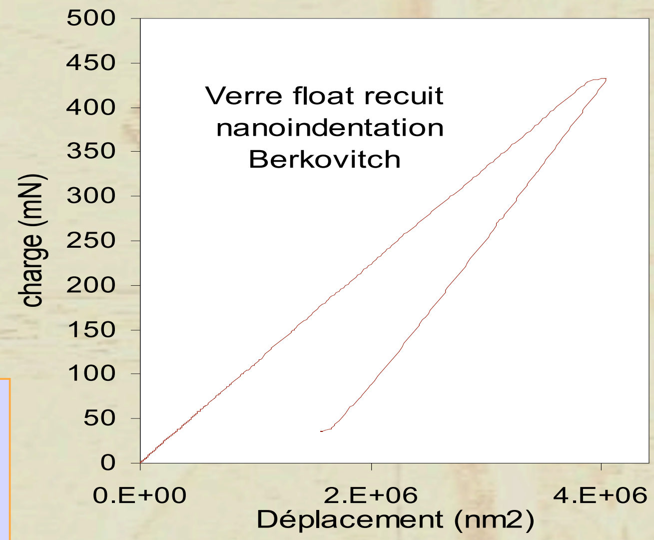
- **Elasto-Plasticity**

$$u=u_e+u_p$$
$$P=K_{ep}u^2$$
With $K_{ep}=[(K_e)^{-1/2}+(K_p)^{-1/2}]^{-2}$

$P= \sqrt{2}\pi\ E\ \tan\psi/((1-\nu^2)\gamma^2)uu_e$ *(Sneddon, 1965 - Loubet, 1986)*

$P=E\ \tan\psi/((1-\nu^2)\gamma^2)(2u-u_e)u_e$ *(Lawn, 1981)*

NB: The elastic recovery oes not affect the hardness measurement



I.3. Constitutive laws

- **Viscosity**

Recall:

$\sigma_{ij}=(-p+\lambda d\varepsilon_{kk}/dt)\delta_{ij}+2\eta d\varepsilon_{ij}/dt$ **(Newtonian viscosity)**

η: dynamical viscosity coefficient (Pa.s)

Stokes law (1885):

$P=6\eta R du/dt$ (sphere with radius R in a viscous fluid))

For a cone: $P \alpha \eta u du/dt$ (α: proportionnal)

⇒ $u^2 \alpha P/\eta t$

And $H \alpha P/u^2$ ⇒ $H \alpha \eta/t$

$H=4\eta/(\pi t \tan\psi)$ (Yang, 1997)

Elasticity (Hooke) - Viscosity (Newton) analogy: $H=\eta/((1-\nu)t \tan\psi)$ (Sakai, 1999)

Non-linear viscosity: $d\varepsilon/dt \alpha \sigma^n$ ⇒ $\eta \alpha (d\varepsilon/dt)^{(1-n)/n}$ and $H \alpha t^{-1/n}\exp[\Delta G_a/(nRT)]$ (Guin, 2002)

I.3. Constitutive laws

- **Viscoelasticity**

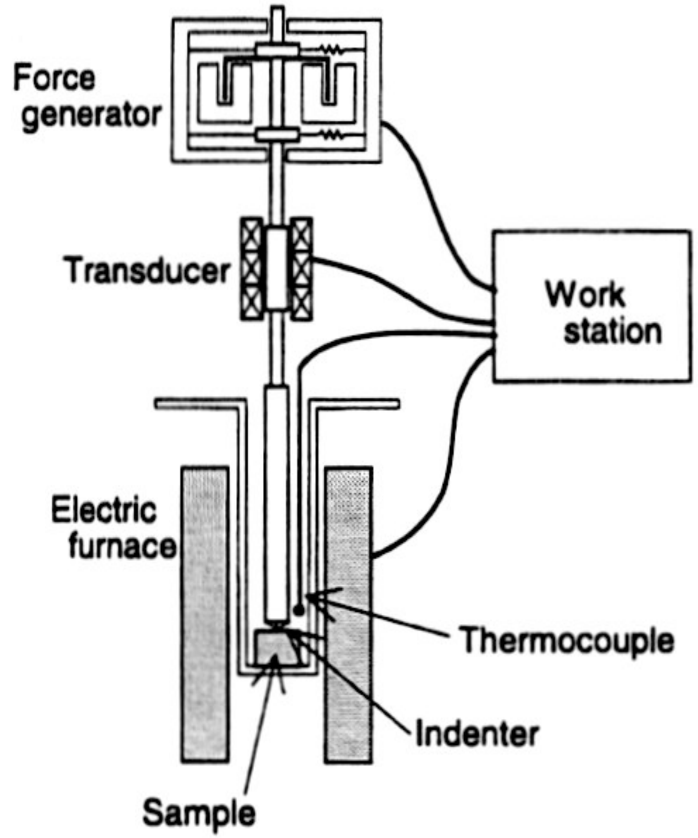
Using known elastcity solution transposed to pure Newtonian viscosity problems by means of the Boltzmann superposition principle
(Lee & Radok, 1960) (Ting, 1966) (Shimizu, 1999)

$H = 1/[2\tan\psi\ (1-\nu^2)J(t)]$

Constant load, with $J(t)=\varepsilon(t)/\sigma_o$: creep compliance

$H = G(t)/[2\tan\psi\ (1-\nu^2)]$

For imposed constant displacement, where $G(t)=\sigma(t)/\varepsilon_o$: relaxation modulus

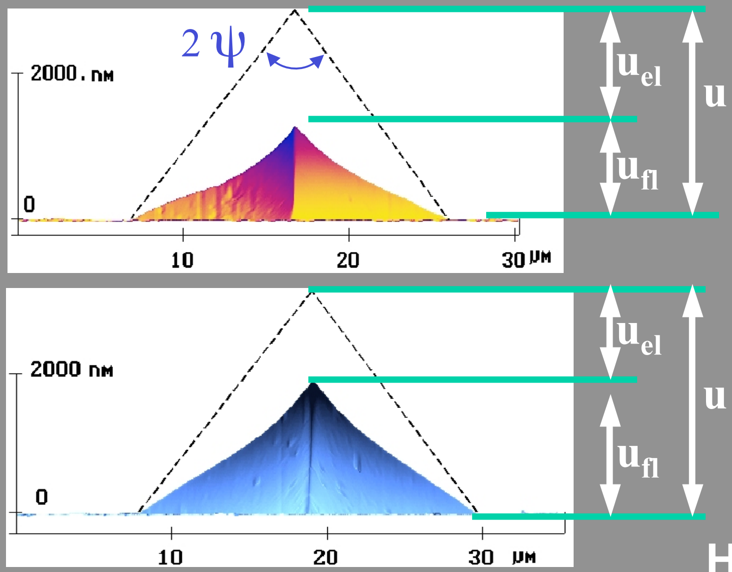


Schematic setup for constant-load creep test.

Indentation creep

$$u = u_e + u_{fl}$$

elastic component — viscous component



selenium 2.94 N, 5 et 50 s

u_{fl} can be derived either from the elasticity results
or by solving the standard Navier-Stokes equations:

Hooke-Newton analogy
$$u_{fl}(t) = \left[\frac{\gamma^2(1-\nu)P}{\eta \tan\psi} t\right]^{1/2}$$

Navier-Stokes
$$u'_{fl}(t) = \left[\frac{\gamma^2 \pi P}{4\eta \tan\psi} t\right]^{1/2}$$

(Yang and Li, 1997)

With $\gamma \in [0,9-1.6]$

$H = \gamma^2/(u^2 \tan^2\psi)P$ (Vickers) →

$$H(t) = \frac{4}{\pi \tan\psi} \frac{\eta}{t}$$

II.2 Critical load for cracking

Indentation=flaw

$K_{Ic} \alpha \sigma\sqrt{a}$

$\rightarrow P_c \alpha \sigma a^2 \alpha K_{Ic} a^{3/2}$

$\sigma \alpha P/a^2$

$P_c = K_{Ic}(\pi a)^{3/2} \tan\psi$ *(Lawn, 1975)*

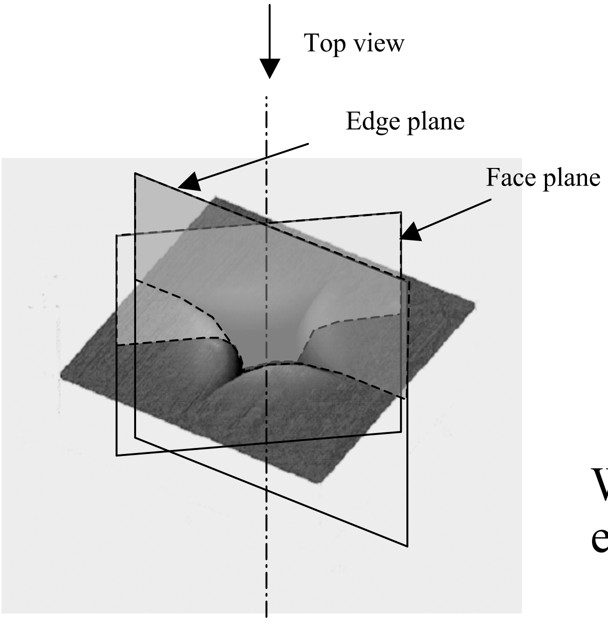
Typically: ψ=68°, K_{Ic}=1 MPa and H=5 GPa → a=2 μm

With $H=P/(2a^2)$, one obtains:

$P_c = 2.2.10^4 K_{Ic}^4/H^3$ *(Lawn, 1977)*

$P_c = 885\ K_{Ic}^4/H^3$ *(Hagan, 1979)*

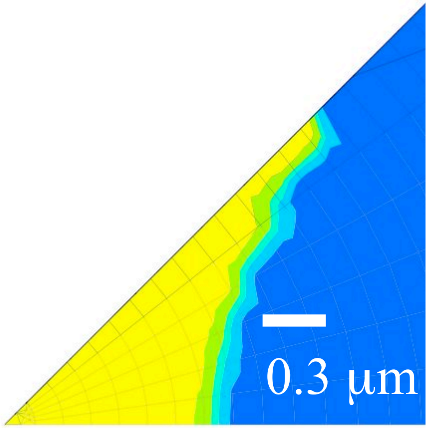
- Simulation of the Vickers indentation (F=100 mN)



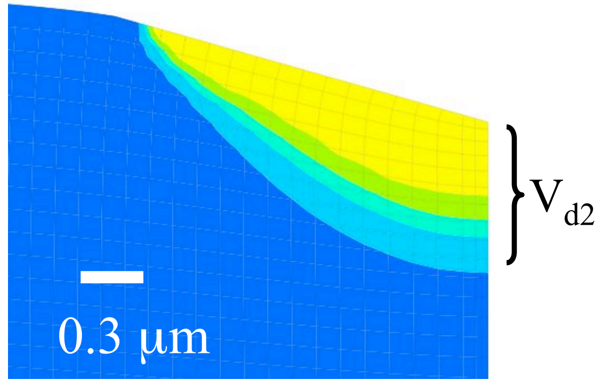
Schematic drawing of the different views

$$P = (1+\nu)F/(3\pi r^2)$$

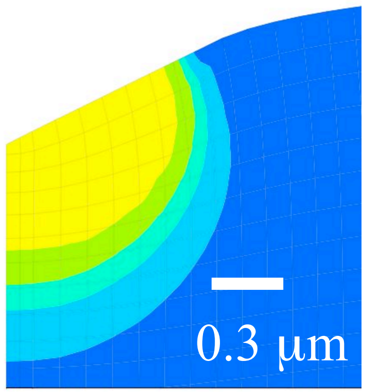
$$\frac{\Delta\rho}{\rho_o} = \alpha\left[\frac{1}{1+\beta\exp(-P/Po)} - \frac{1}{1+\beta}\right]$$



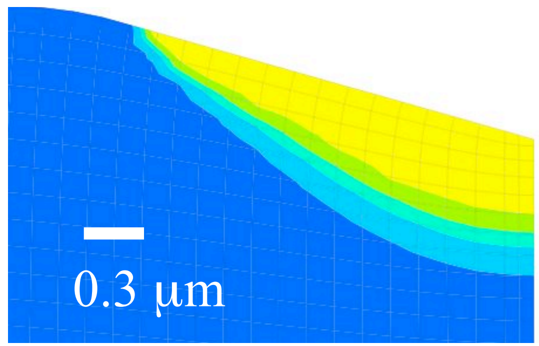
WG, top view of the elementary unit of symmetry



WG, densification gradient in an edge plane



WG, face view of the densification gradient

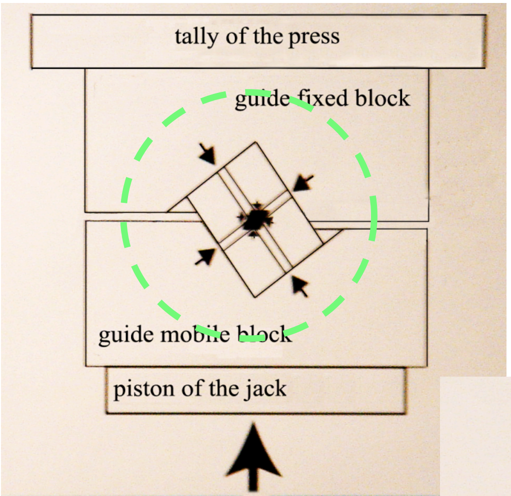


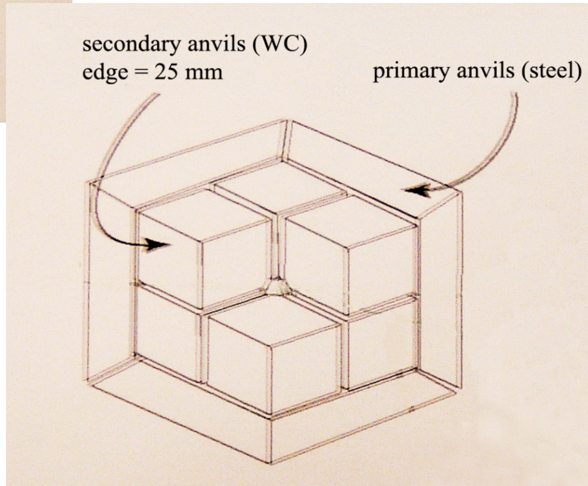
a-SiO2, densification gradient in an edge plane

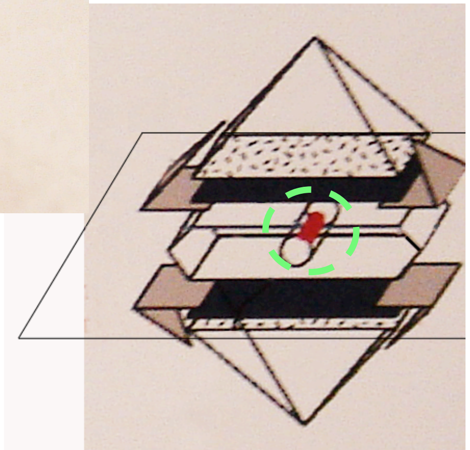
High pressure set-up

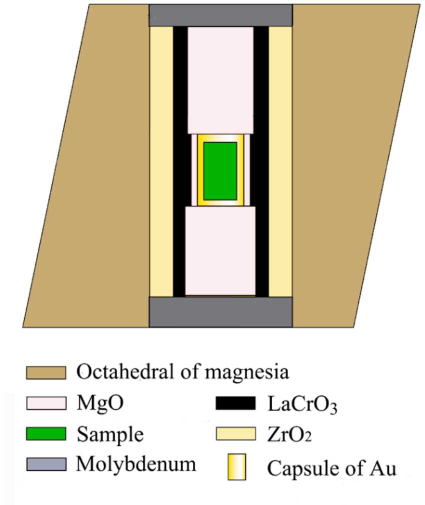
T = 293 K
P = 3 ~ 25 GPa
t = 1 ~ 720 min

Multi-anvil press

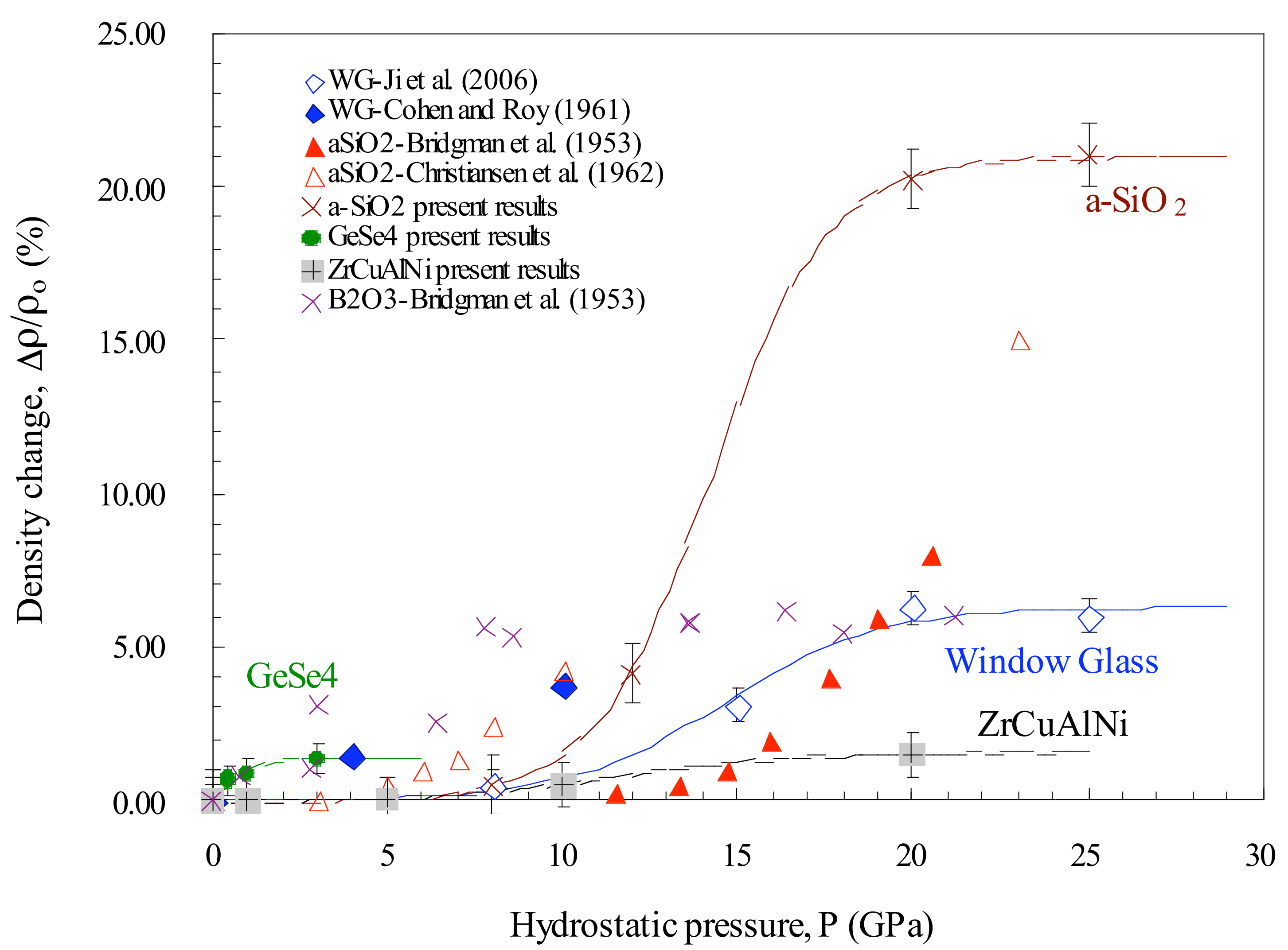




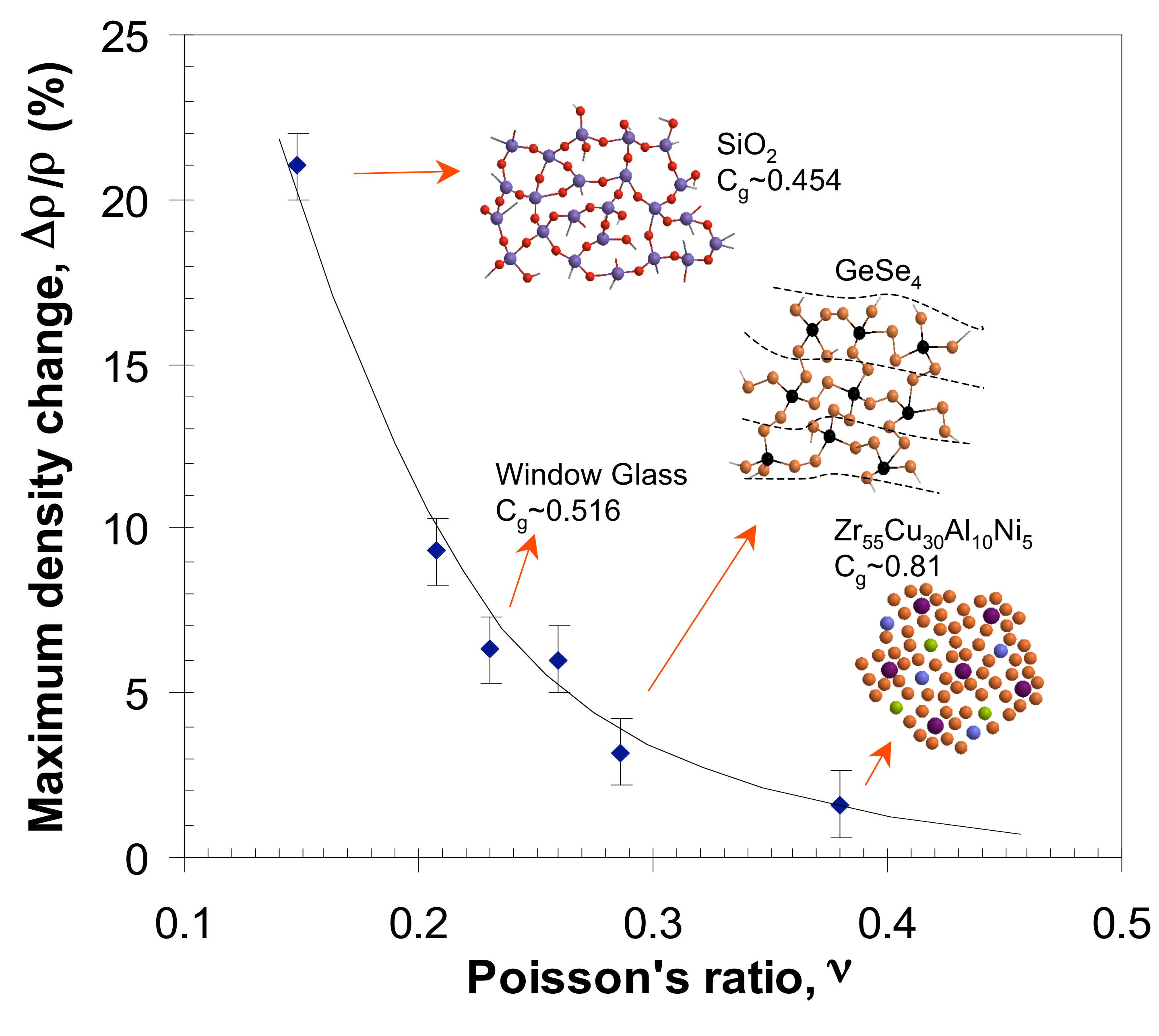




The Densification contribution



H. Ji, V. Keryvin, T. Rouxel and T. Hammouda, Scripta Mat., 55 1159-1162 (2006).



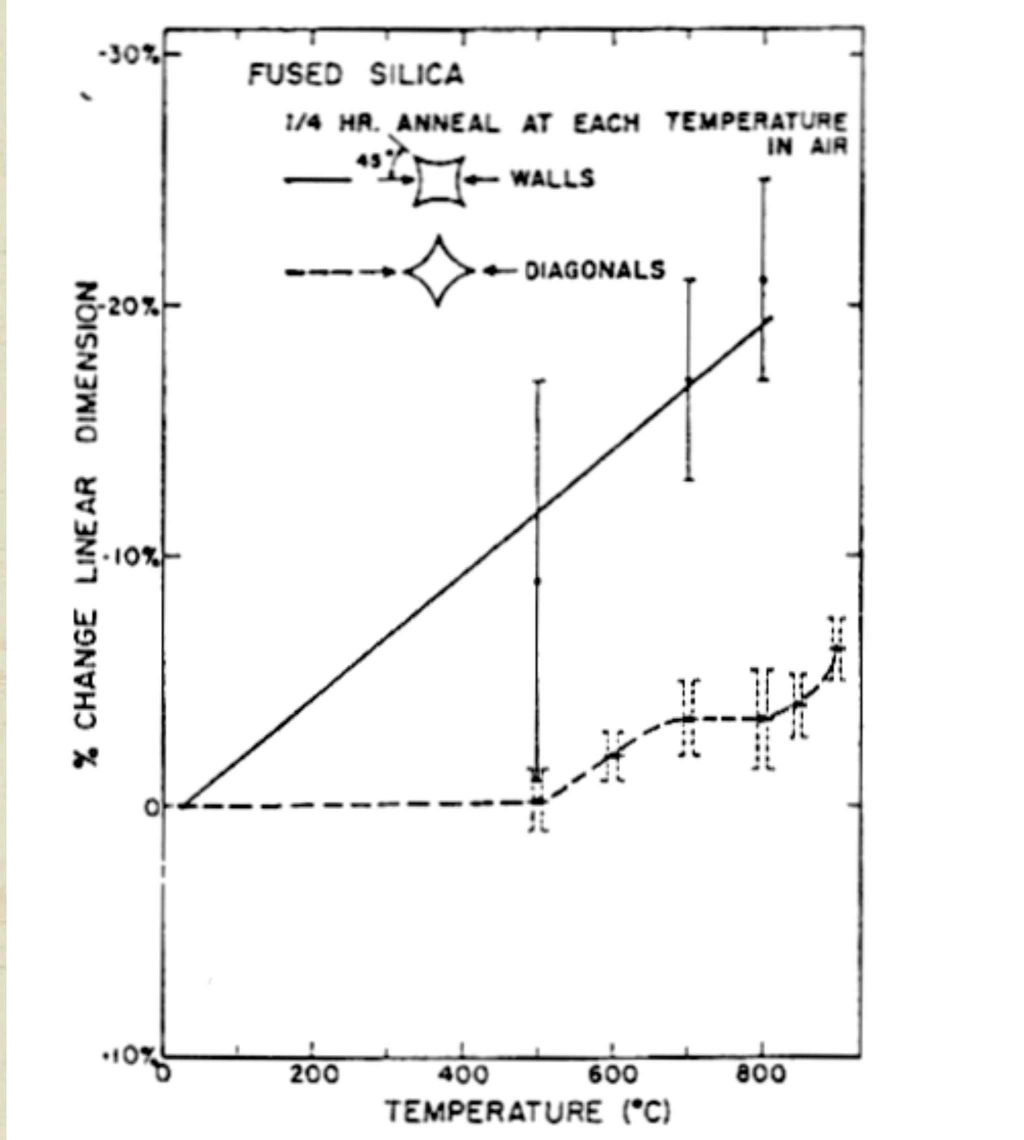
Maximum density change, Δρ/ρ (%)
25
20
15
10
5
0
0.1
0.2
0.3
0.4
0.5
Poisson's ratio, ν
SiO$_2$
C_g~0.454
GeSe$_4$
Window Glass
C_g~0.516
Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$
C_g~0.81

Quantitative evaluation of the amount of densification

Bi-refringence effects (Ernsberger (1968), Peter (1970), Arora (1979))

Deformation recovery after annealing (Neely (1968), Yoshida (2001))

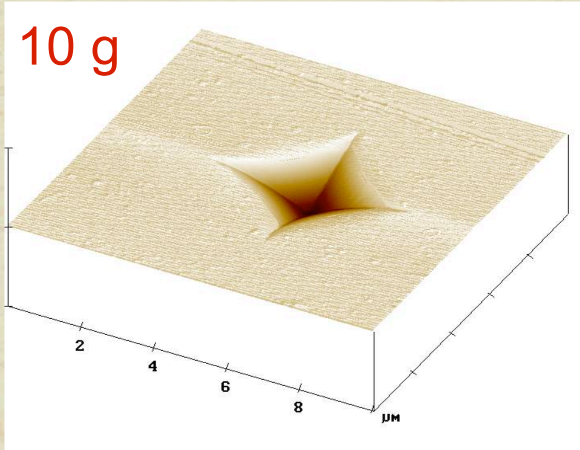
(Neely and Mackenzie, 1968)

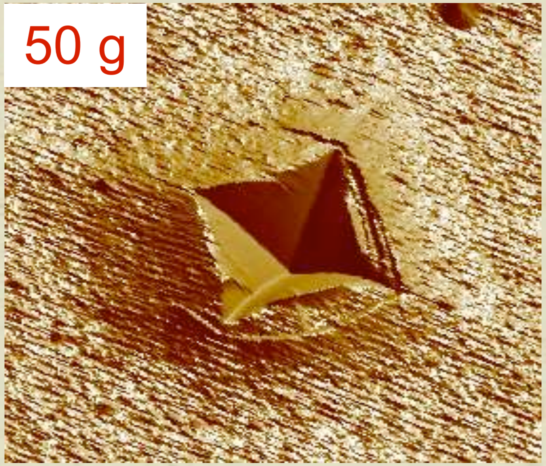


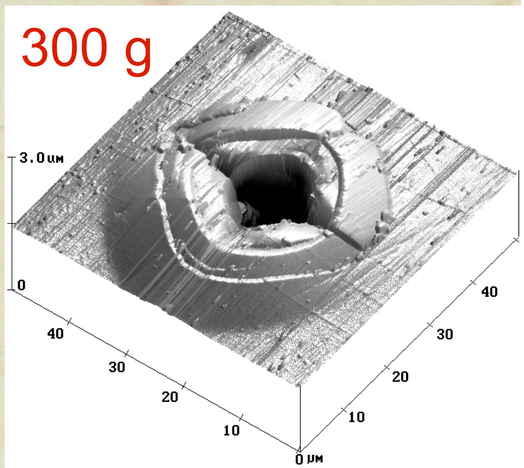
The Densification contribution: experimental evidence from Vickers indentation

Load must be lower than 50 g

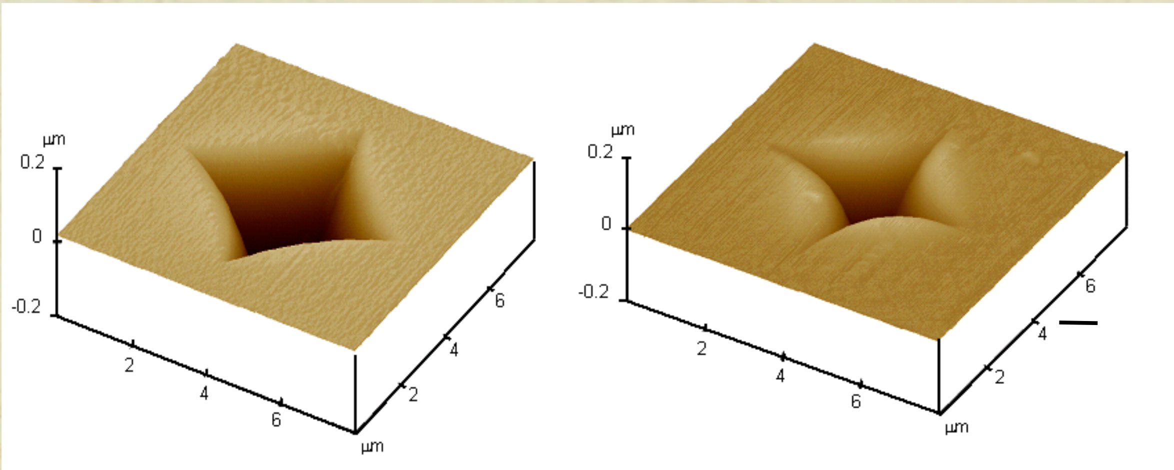
Vitreous silica







Float glass

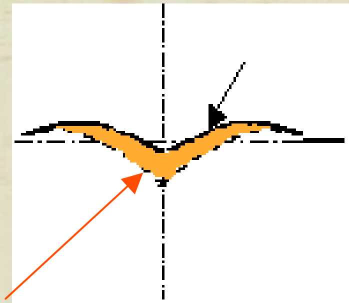


Before annealing

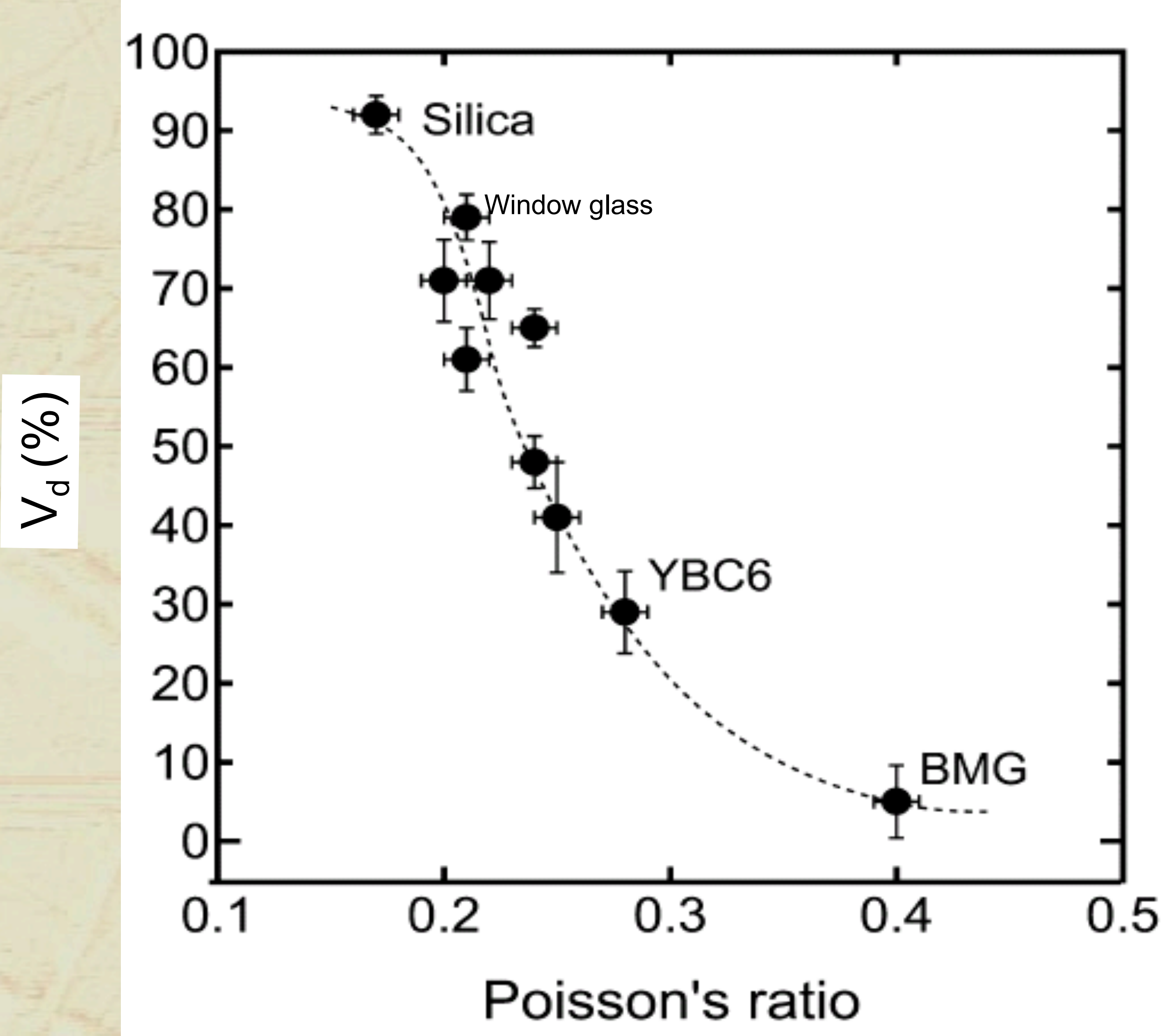
After annealing at 0.9 Tg (478 °C) for 2 hours

Method: AFM topometry

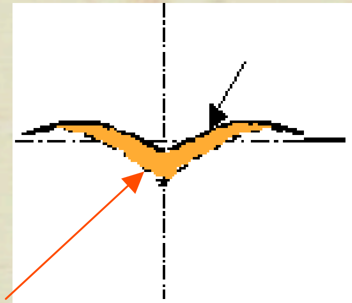
After annealing



$V_d=(V_i^+-V_{io}^+)-(V_{io}^--V_i^-)$



After annealing



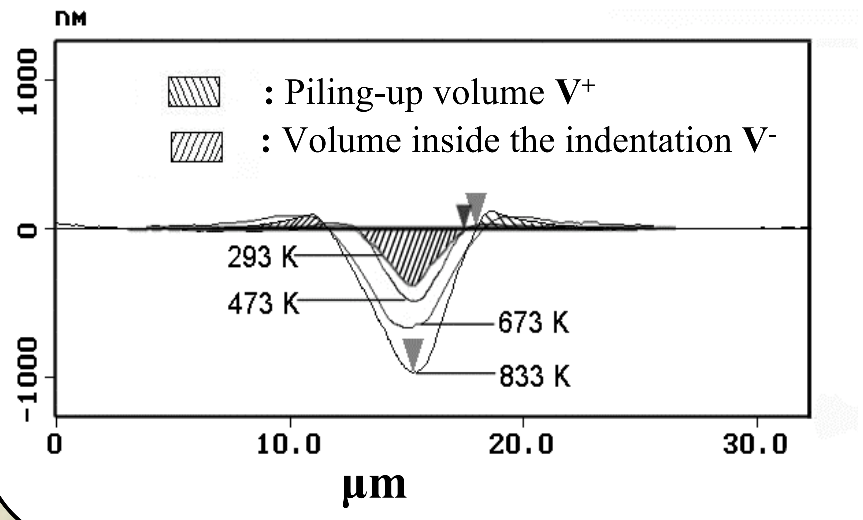
$V_d=(V_i^+-V_{io}^+)-(V_{io}^--V_i^-)$

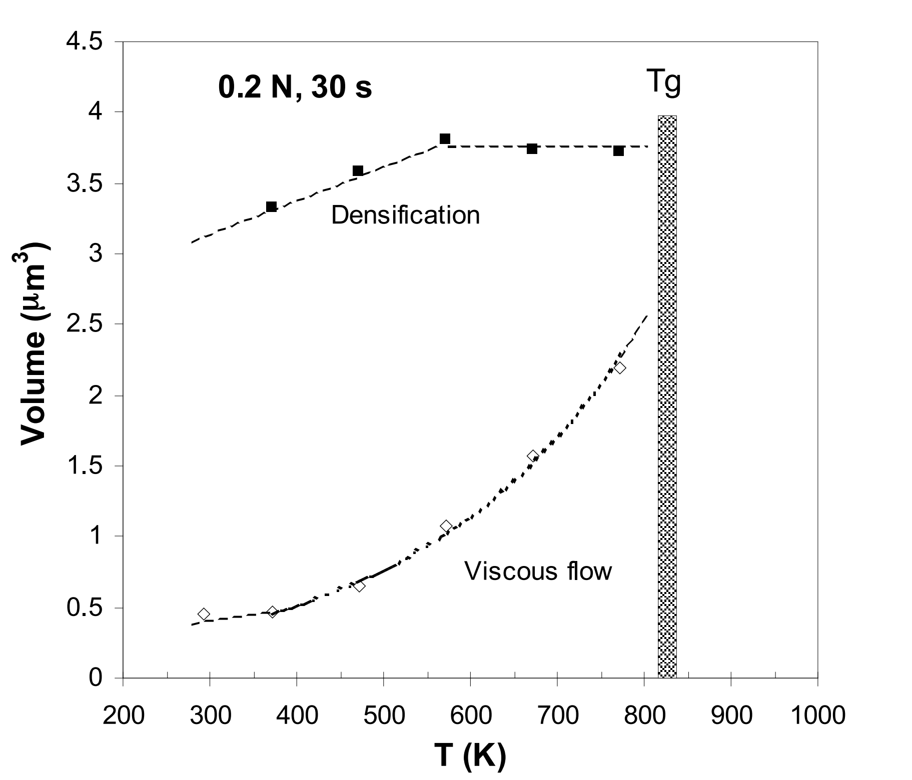
V_d (%): Densification contribution to the permanent indentation deformation

S. Yoshida, J-C. Sangleboeuf and T. Rouxel, J. Mat. Res., 20 3404-3412 (2005).

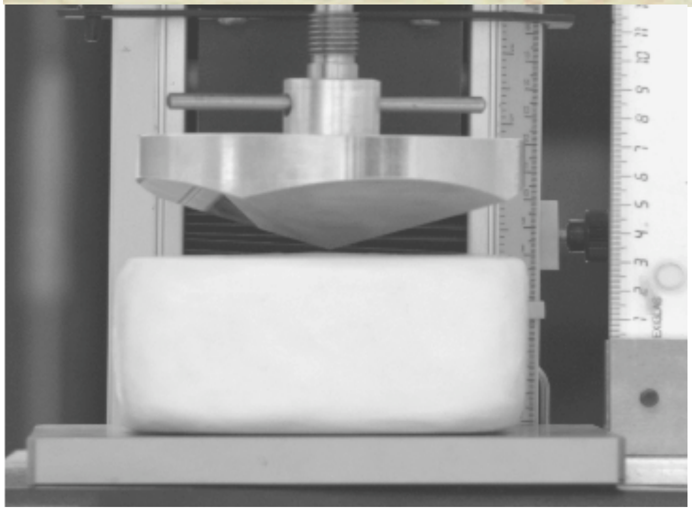
Viscous flow versus Densification

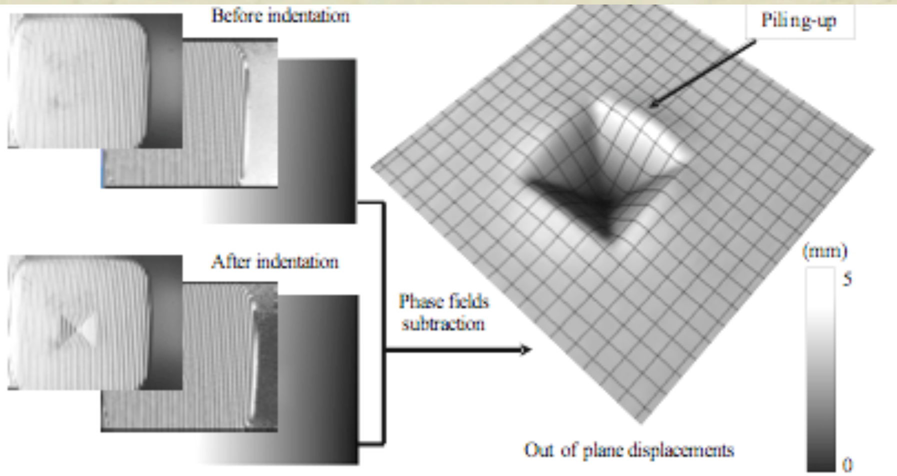
Temperature effect





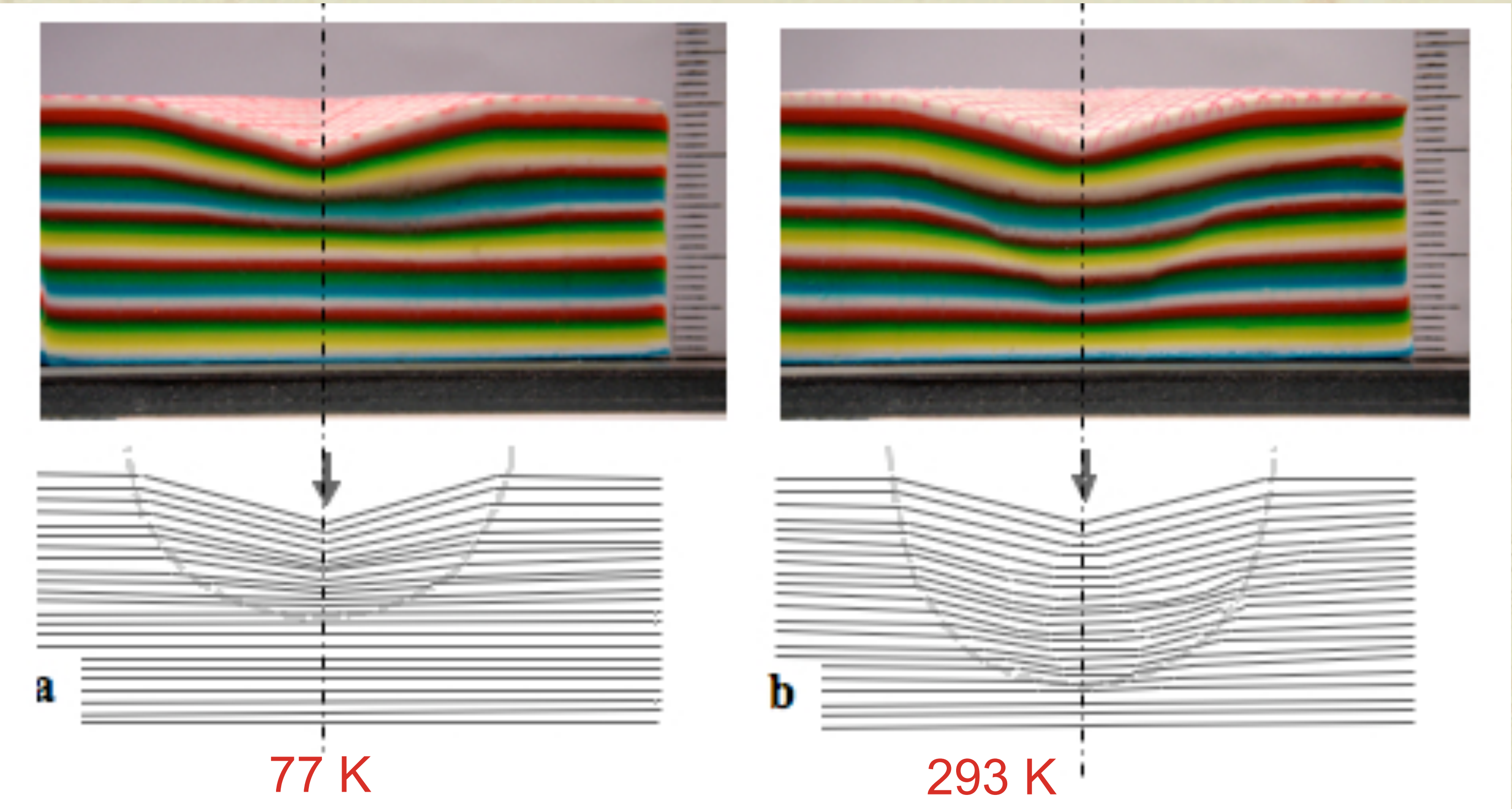
The shear flow contribution increases with temperature





Plasticine as a model material

The two different mechanisms:



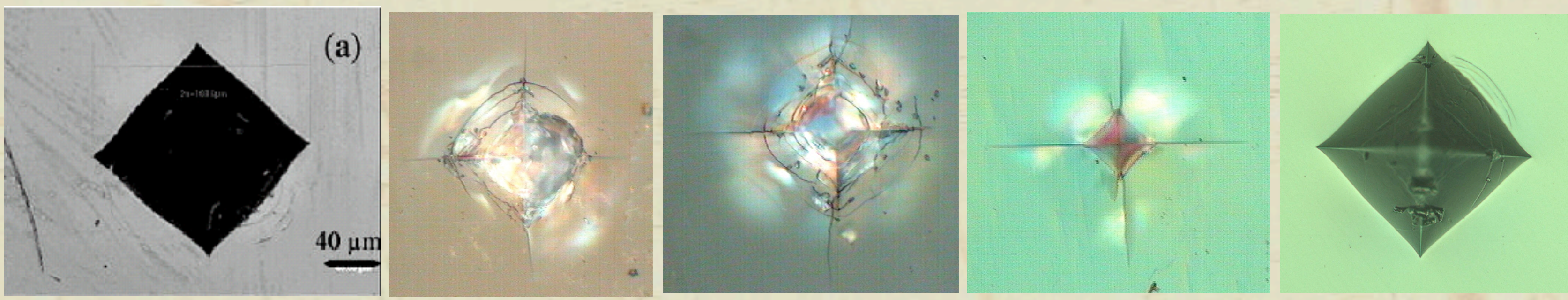
Densification:	*Volume conservative shear flow:*
Low temperature	*High temperature (≥T_g)*
High T_g glasses	*Low T_g glasses*
Low Poisson's ratio glasses	*High Poisson's ratio glasses*

Conclusion 2: INDENTATION BEHAVIOR

1) Densification can represent up to 90% of the indentation volume in silica and 80% in window glass but is almost neligible in ZrCuAlNi BMG

2) The shear-flow contribution increases with respect to the densification one as temperature increases

3) One can have an idea of the predominant indentation deformation mechanism and indentation cracking resistance from the value of Poisson's ratio



SiOC	SiO_2	Borofloat	Window glass	ZrCuAlNi
(20 kg!)	(1 kg)	(1 kg)	(1 kg)	(10 kg)
0.11	**0.16**	**0.18**	**0.21**	**0.38**

ν ↗