Atomistic Modelisation of Amorphous Materials

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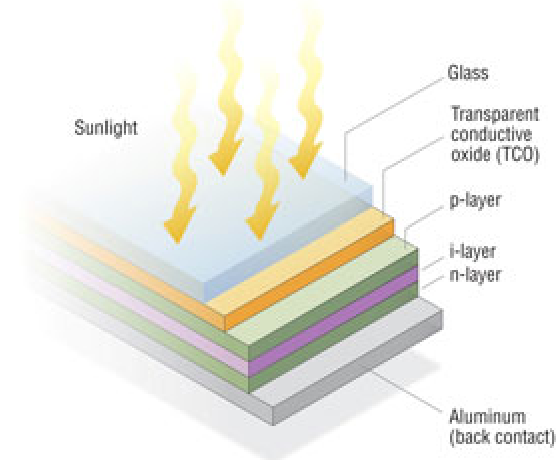
Some common amorphous systems

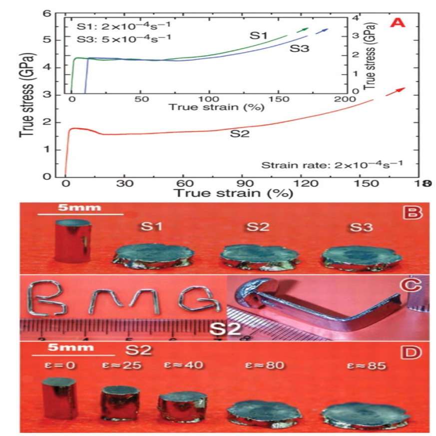
Usual silicate glasses

A-Si in cheap photovoltaic cells



Silicates + polymer films

Bulk Metallic Glasses



Many polymer glasses …
Amorphous silica in transistors ..
Monitor heat transfer,electronic conduction at small scale.

Preparation

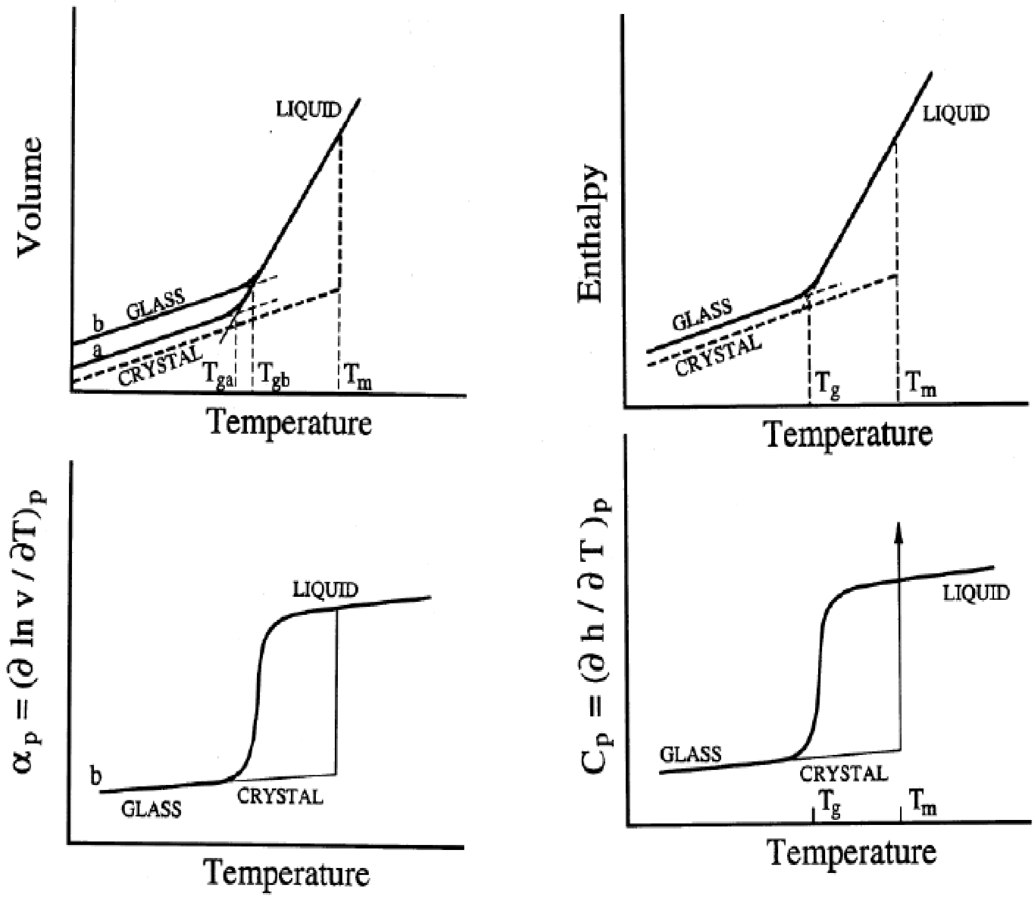
*) Melt and Quench

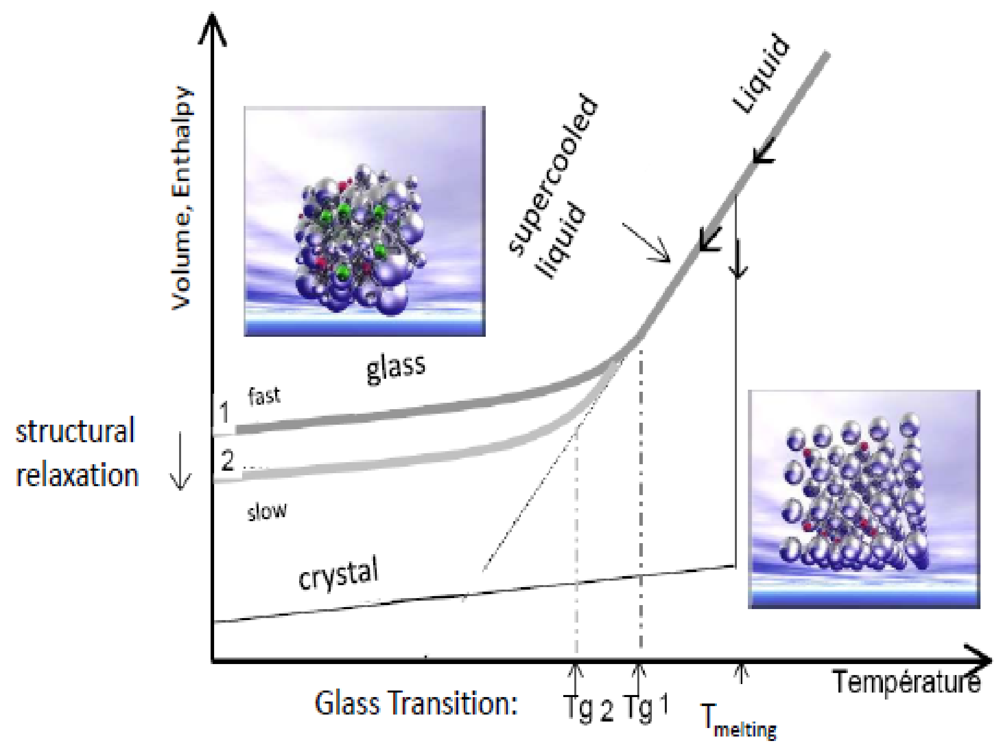
*) Chemical Vapor Deposition

*) Ion implantation

*) local melt and quench by laser

General characteristics : (1) Glass transition





General characteristics : (1) Glass transition

Mesures de Viscosité

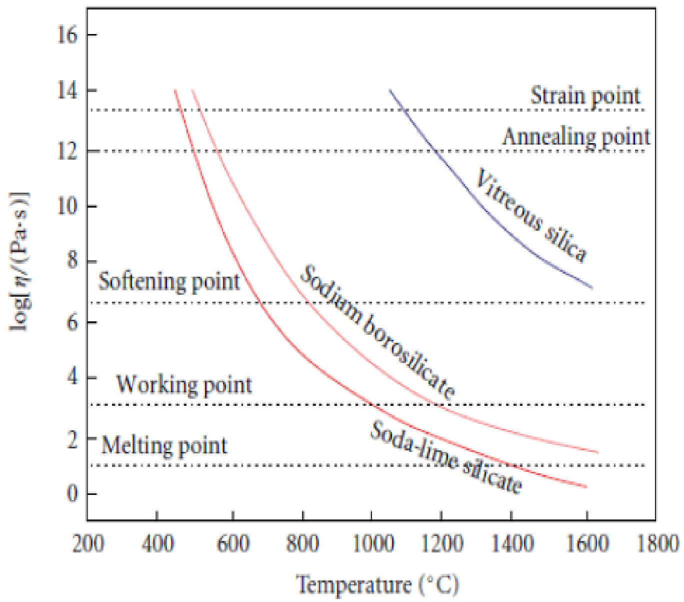
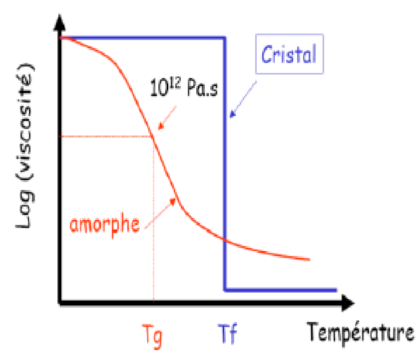
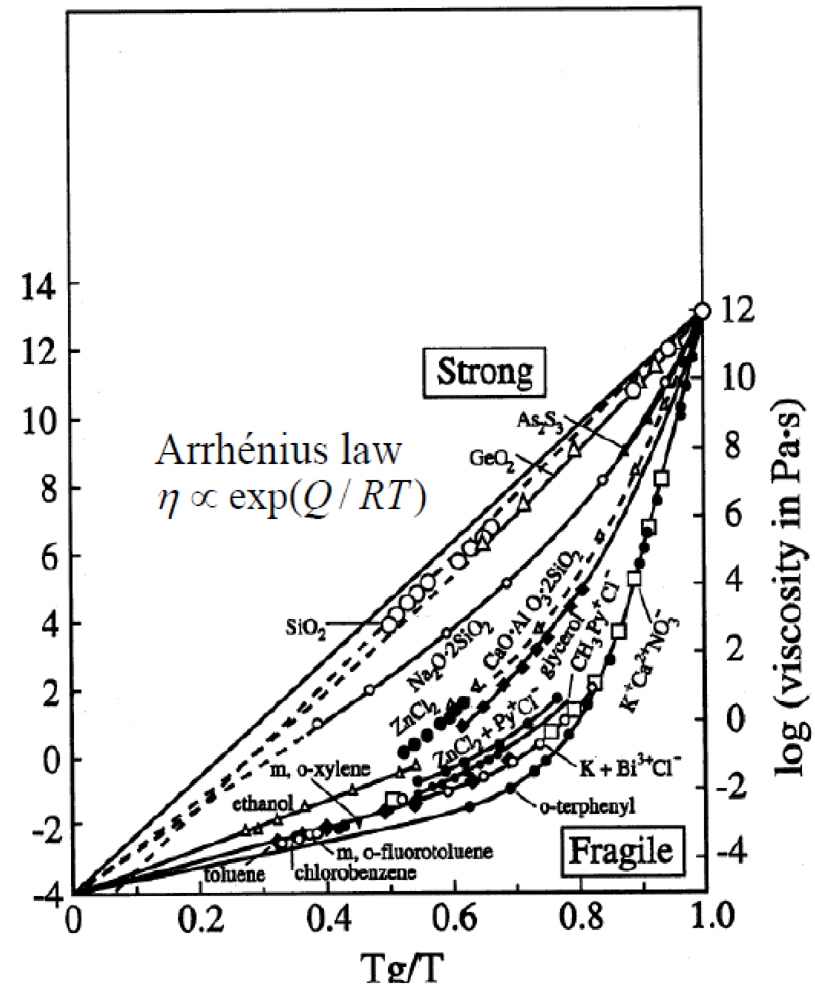
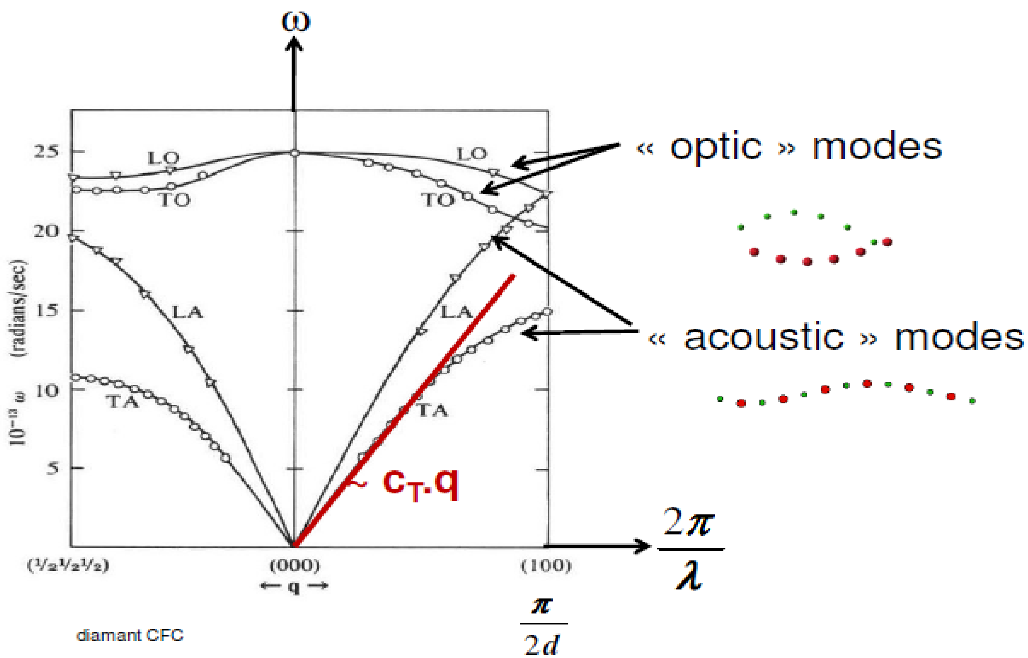


FIGURE 4: Viscosity of amorphous silicates and important technological points in glass manufacture industry (after [49]).



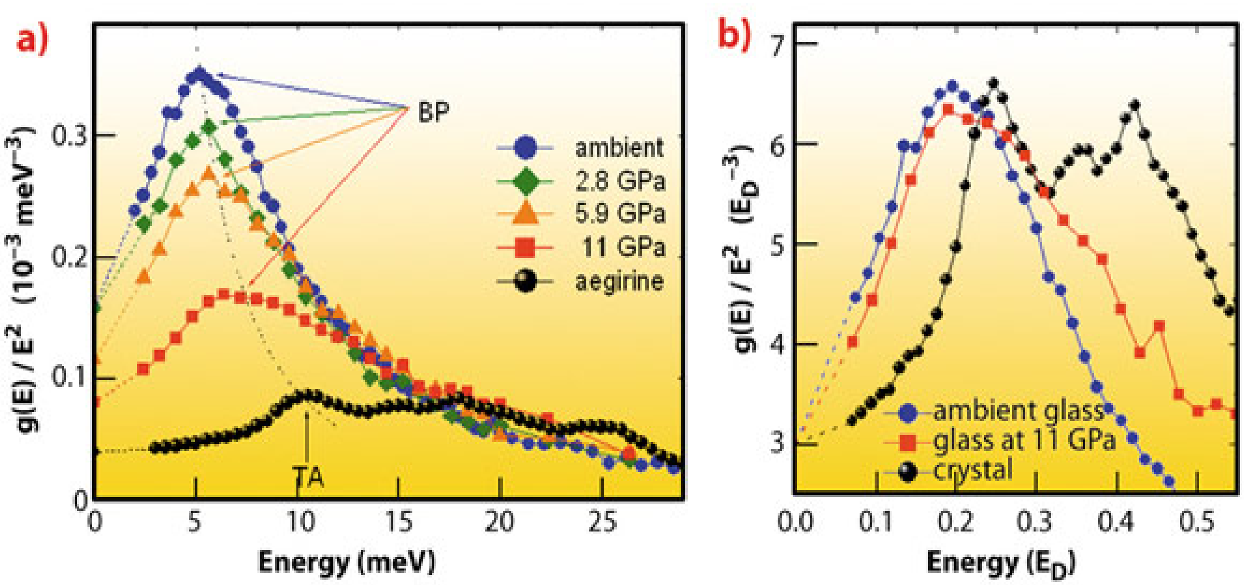


General characteristics : Boson Peak



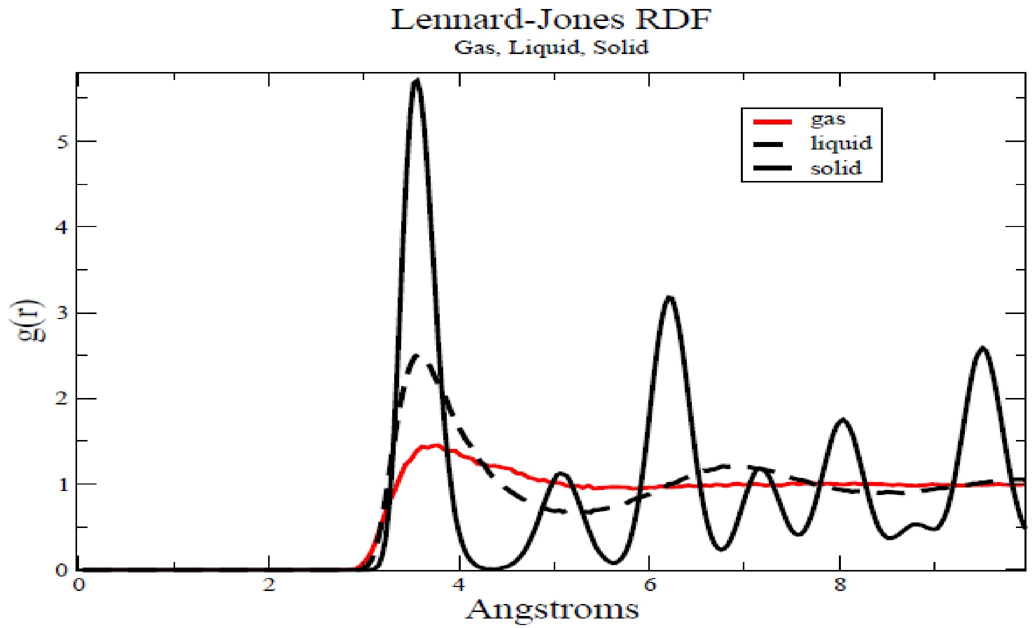
For a cristal
Debye DOS : $g(\omega)=\alpha\omega^2$

Anomalous (excess) density
Of normal modes at low
Frequency in comparison with
Debye prediction



Generation of amorphous systems from a computer

Amorphous system : lack of long range order (like in a liquid)



Order of magnitude for experimental cooling rates of the order of 1 K/s

Need to obtain representative defect ratios

Difficult task especially if electronic degrees of freedom are included

Use classical potentials to obtain the structure … still quench.rates are ~10^{10} K/s !!!

Some examples of classical potentials :

B.K.S. : Potential for silica, long range part is numerically heavy
Improved version for amorphous systems can include cut-off in
the electrostaticinteractions.
(A.Carré et al. J. Chem Phys 127 114512 (2007))

S.W. : Potential for a-Si. Can be modified to tune properties like the
nature of the defects and their numbers, DOS,...

Tersoff : High melting temperature, liquid remains undercoordinated respect to experiments,
some weird mechanical properties

L.J. : Need to use several L..J. Parameters (σ and ε) to prevent crystal formation

EAM/MEAM : Can be used to model metallic glasses.

Some methods to generate amorphous samples

W..W.W. Continuous random network (covalent 4-fold, silicon like) :

Random initial positions and relaxations (for a-Si again):

Vink et al. J.Non-Cryst.Solids 282, 248(2001) uses the ART technique
Guénolé et al. Phys.Rev .B 87 045201 (2013)
France-Lanord et al. J.Phys.Condens. Matter 26 055011 (2014)

Melt and Quench for a-Si systems :

Fusco et al. Phys. Rev.E 82 066116(2010)
France-Lanord et al. J.Phys.Condens. Matter 26 055011 (2014)

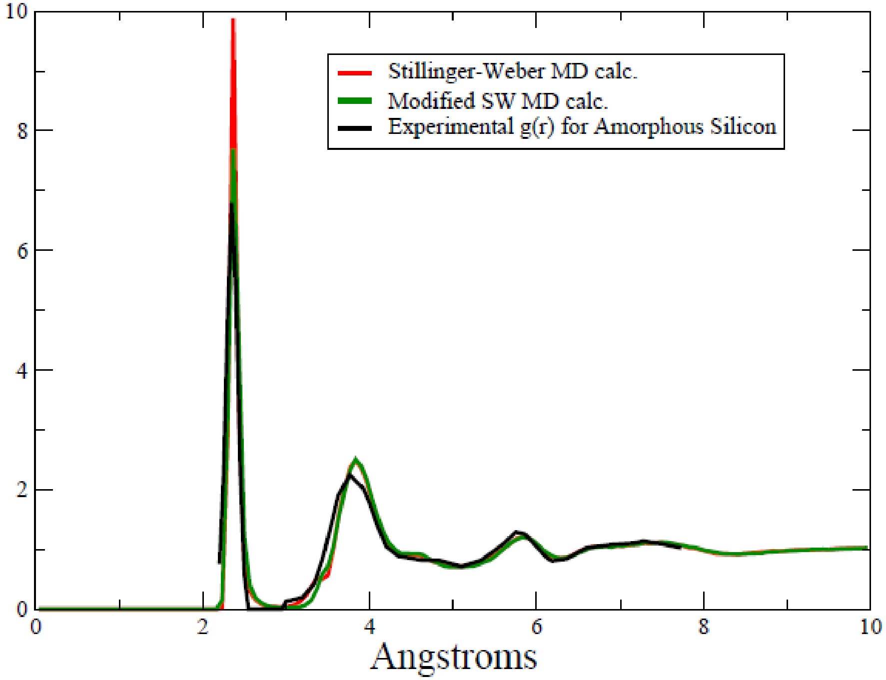
Melt and Quench for SiO2 :

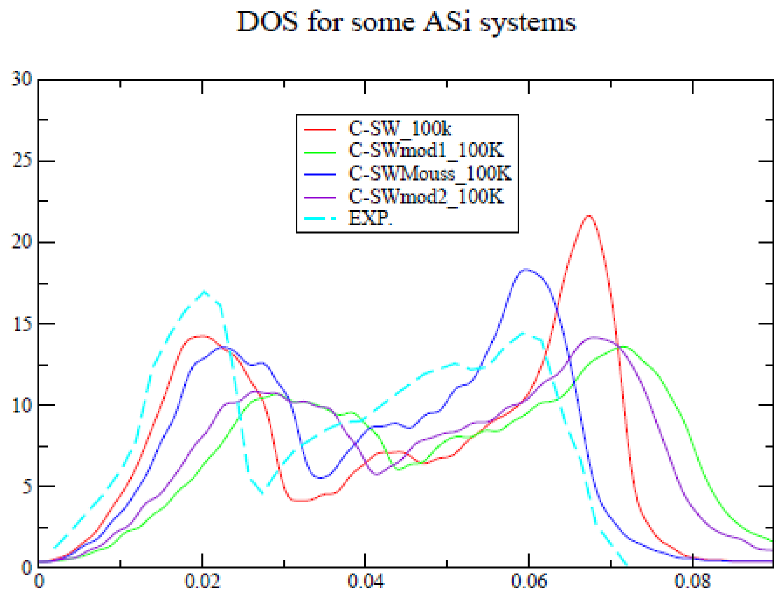
Sarnthein et al. Phys. Rev.B 52 12690 (1995) (all DFT!)
Mantisi et al. Eur. Phys. J. B 85 304 (2012)

Validation, Comparison with Experiments :

a-Si, g(r) from
melt and quench

A-Si density of states :
Various SW models





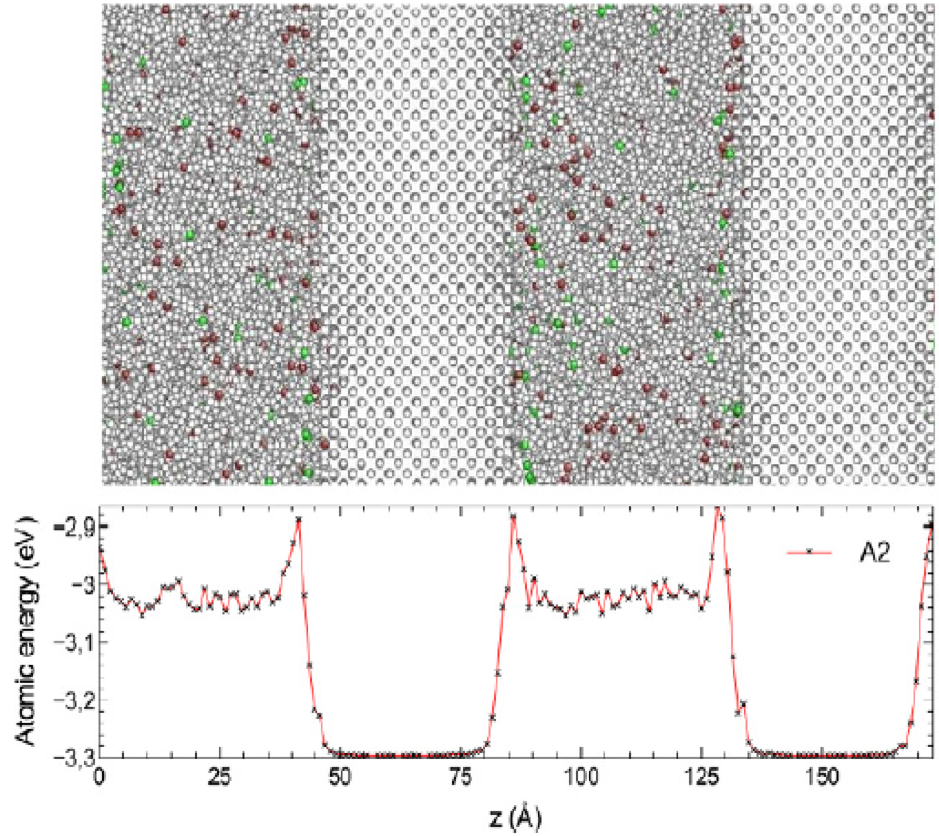
Unit	Tersoff	SW	SWM1	SWM2	Expt.
Density (g/cm^3)	2.31	2.29	2.20	2.24	2.05[a]–2.52[b]
Average coord.	4.07	4.08	3.82	3.88	3.90[c]–3.97[d]
Average angle	108.94	108.87	109.22	109.14	108.6[c]
Angle dev.	11.81	11.68	9.48	10.40	9.4–11[c]
B0 (GPa)	90.54	98.55	99.84	76.18	$\simeq 90$[e]
C44 (GPa)	40.8	34.27	60.74	38.61	$\simeq 50$[e]

[a]Ref. [12]. [b]Ref. [13]. [c]Ref. [14]. [d]Ref. [15]. [e]Ref. [16].

Construction of heterostructures :

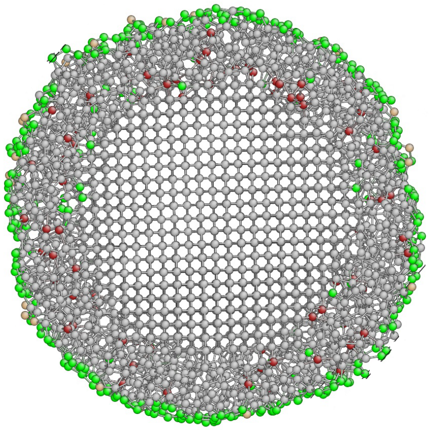
Using a mask :

Study heattransfer at
c-Si / a-Si interface



Combining potentials :

Core shell nanowires



Some properties from MD :

$$D = \int_0^\infty cvv(t)\, dt$$

Self diffusion

$$cvv(t) = \frac{1}{3} < \vec{v}_a(t0)\, \vec{v}_a(t0+t) >_{a,\, t0}$$

Auto correlation of the velocities

$$\lambda_{xy} = \frac{1}{VkT^2} \int_0^\infty < j_x(0)\, j_y(t) > dt$$

Thermal conductivity

$$j_x = d/dt\, \Sigma_a E_a x_a$$

$$\eta = \frac{V}{kT} \int_0^\infty < \sigma_{xy}(t)\, \sigma_{xy}(t) > dt$$

Shear viscosity

$$\sigma_{xy} = \Sigma_a m_a \frac{v_{x,a} v_{y,a}}{V} - \Sigma_a \Sigma_{b>a} \frac{F_{ab,x} r_{ab,y}}{V}$$

Stress Tensor

Elementary Plastic Events in Sheared Amorphous Solid

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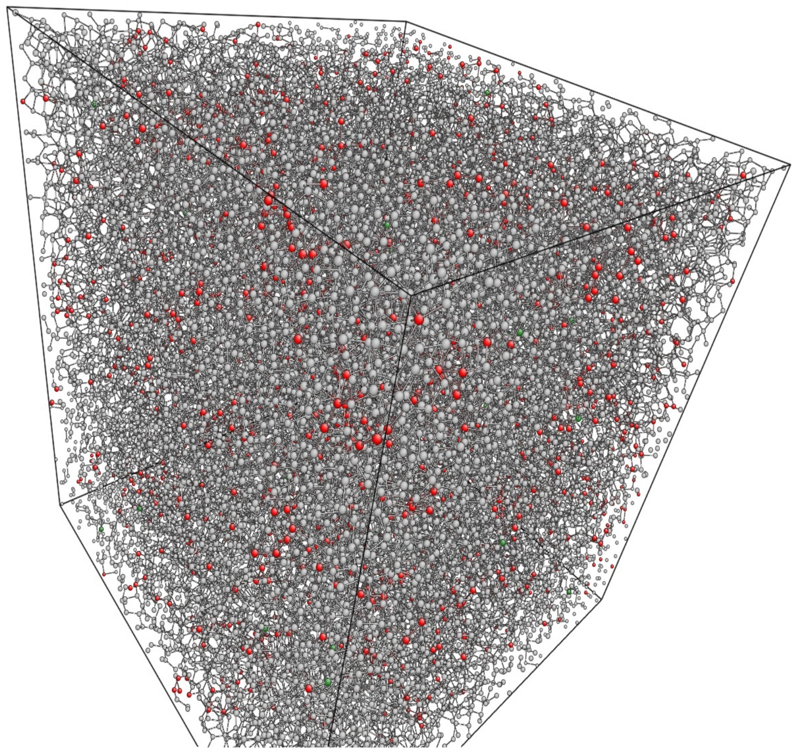
MD SImulations



Annealing at T= 2500 K with the Tersoff potential

$T \simeq 10\,K$ Minimization (damped dynamics)

→ Change potential to SW, SWM1, SWM2

Annealing at 100K (few ps) followed by coordinates and cell minimization (elimination of residual stress)

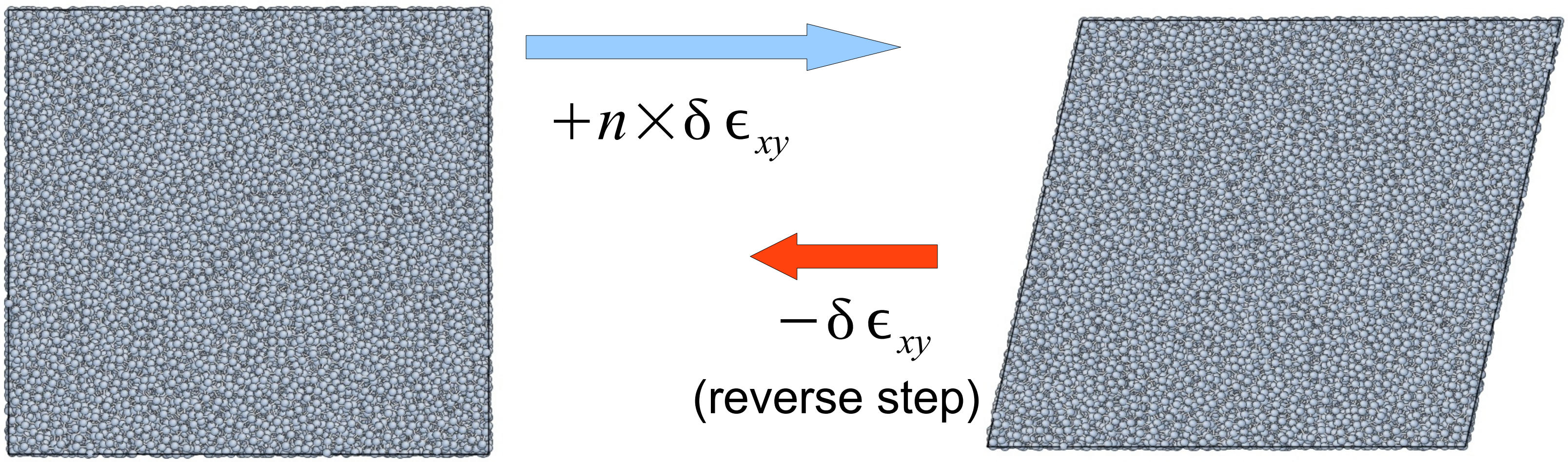
Tersoff : $V_{ij} = f_C(r_{ij})[a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})]$

SW (2body): $V_2(r) = A(\frac{B}{r^4} - 1)\exp(\frac{1}{r - rc})$

SW (3body): $V_3(r_{ij}, r_{ik}) = \lambda \exp[\frac{\gamma}{(r_{ij} - rc)} + \frac{\gamma}{(r_{ik} - rc)}](\cos(\theta_{ijk}) + \frac{1}{3})^2$

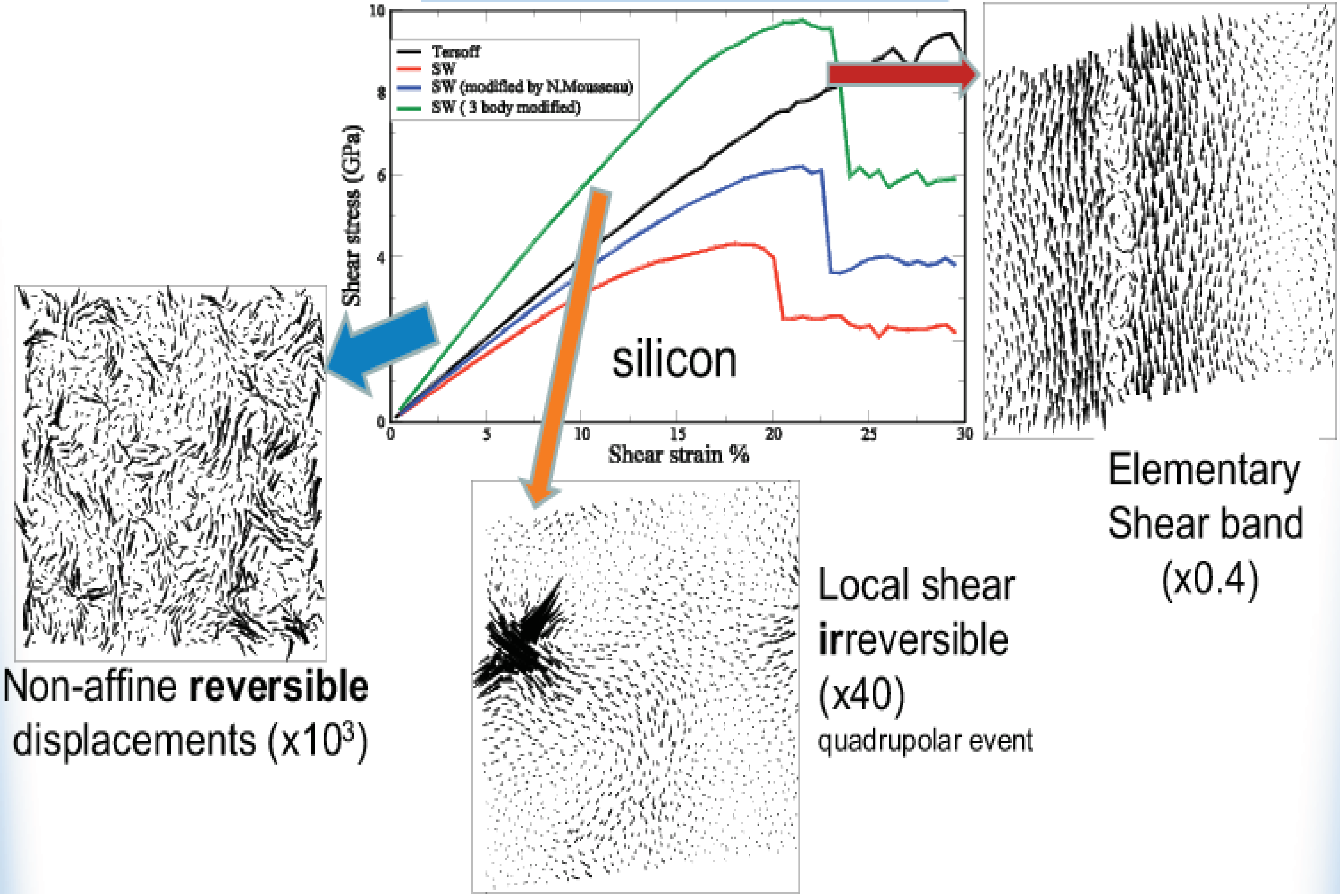
SWM1 : factor 2 on the 3 body term (favours tetrahedral local structure)
SWM2: 0.8 energy scale and factor 1.5 on 3 body term (Mousseau version for A-Si)
+ others "SWM1 like" potentials with different values of λ
+ different quenching rates (10^{11} to 10^{14} K/s)

Mechanical Deformation :

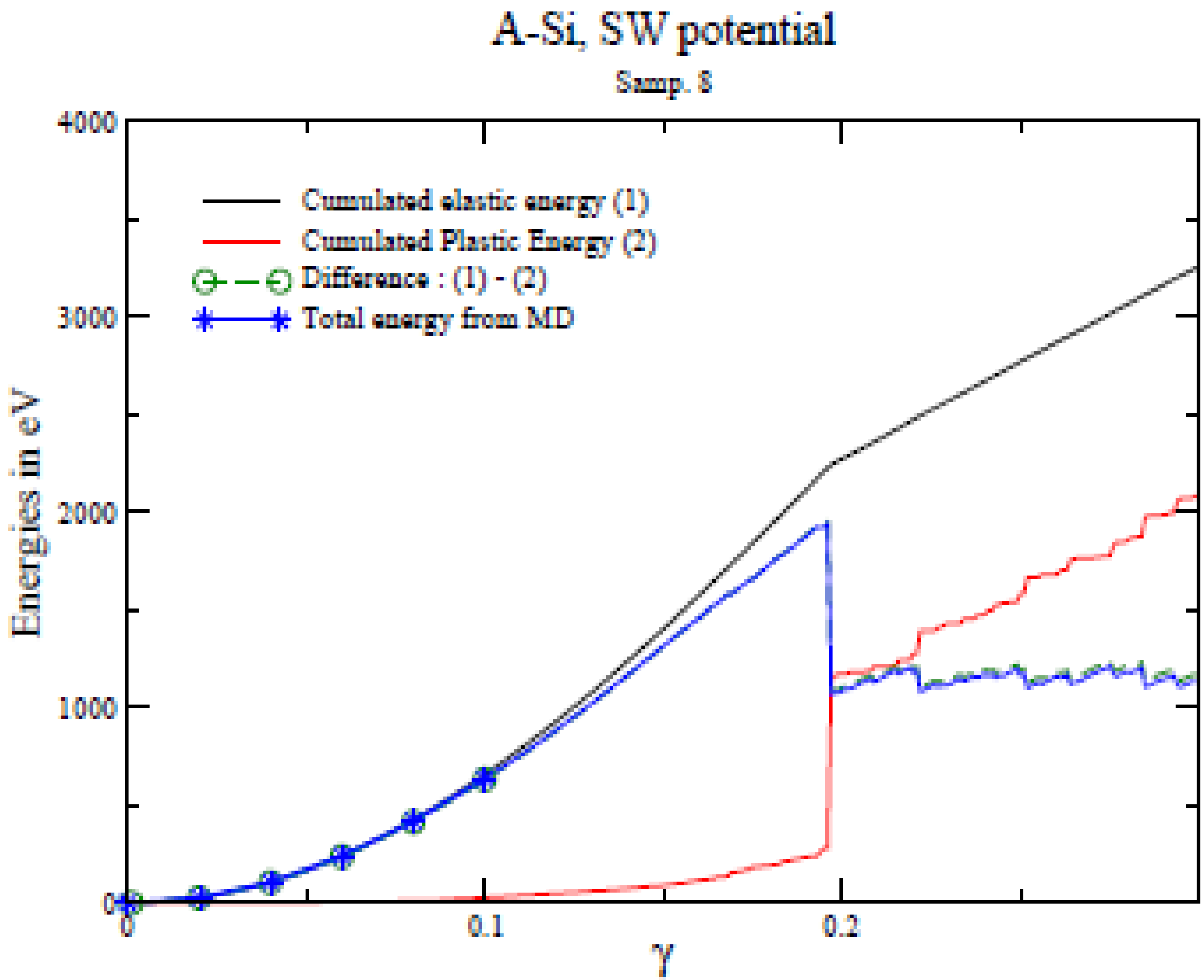


- Successive quasi-static shear strain steps, $\delta\varepsilon_{xy}$ =0.001, until 30-50% deformation
- Strain is imposed via the lattice cell parameters in periodic boundary conditions (no walls)
- Potential energy is minimized through a damped MD at 0K
- Volume is constant
- For each configuration a reverse step is calculated

Atomic displacements



Energy Contributions



→ Contributions : $E_{el} = \int \sigma(\varepsilon) d\varepsilon$ $E_{plas}(\varepsilon) = E_{rev}(\varepsilon) - E_{ini}(\varepsilon)$ $E_{tot}(\varepsilon) = E_{ini}(\varepsilon)$

→ Local contributions ? STATIC !!

Identify Local Plastic Events and define « Plastic Activity »

We have calculate the forward/backward strain steps :

$$c(i)_{ini} = c(i-1)_{ini} + \delta\varepsilon$$

$$c(i)_{rev} = c(i+1)_{ini} - \delta\varepsilon$$

$\longrightarrow$ $\Delta E_{plas} = E_{rev} - E_{ini}$

Evaluate contributions to the plastic energy coming from local atomic terms :

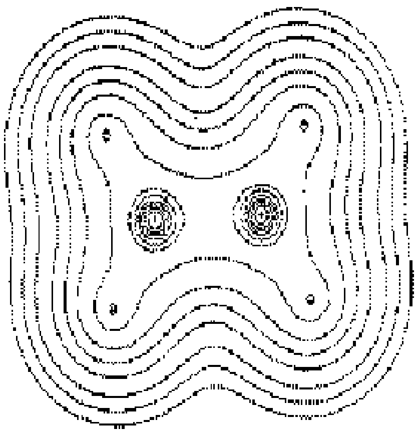
$\longrightarrow$ We construct a local (atomic) positive defined quantity as the norm of the variation of the atomic energy terms :

$$(\Delta E_i)^2 = \sum_j [V_2^{ini}(i,j) - V_2^{rev}(i,j)]^2 + \sum_{j,k} [V_3^{ini}(i,j,k) - V_3^{rev}(i,j,k)]^2$$

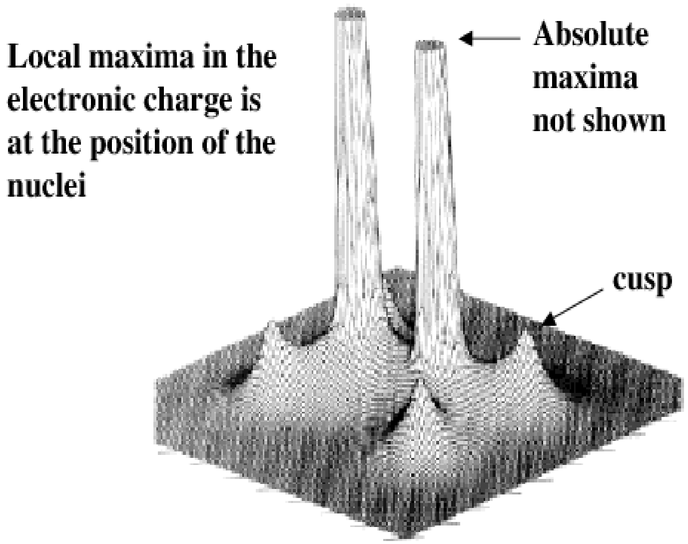
$(\Delta E_i)^2$ Is a local “measure” of plastic activity, invariant respect to translations and rotations

It is coarsed grained and written on a 3D grid to find it's attractors and basins. (Methodolgy similar to Bader charges in Quantum Chemistry)

Basins defined by gradient lines



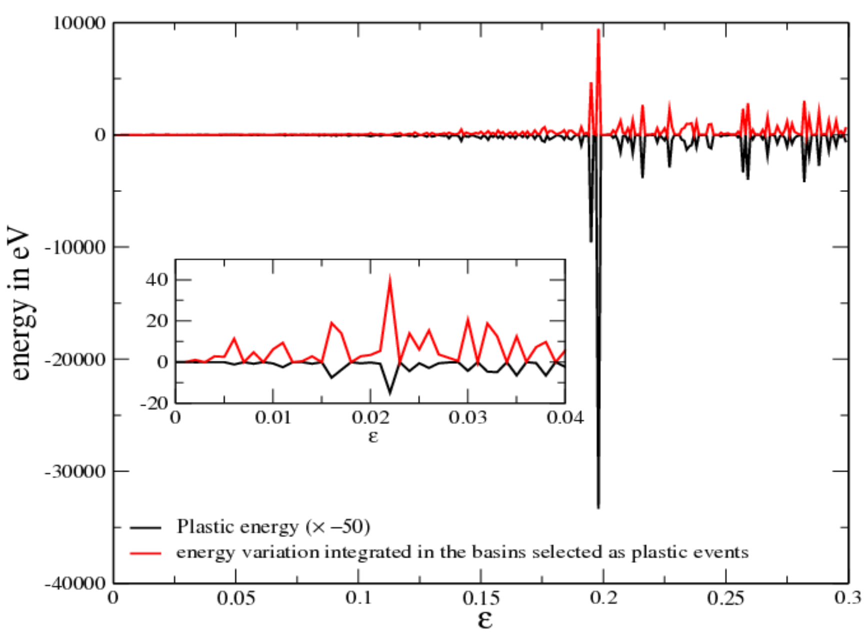
Contour Map

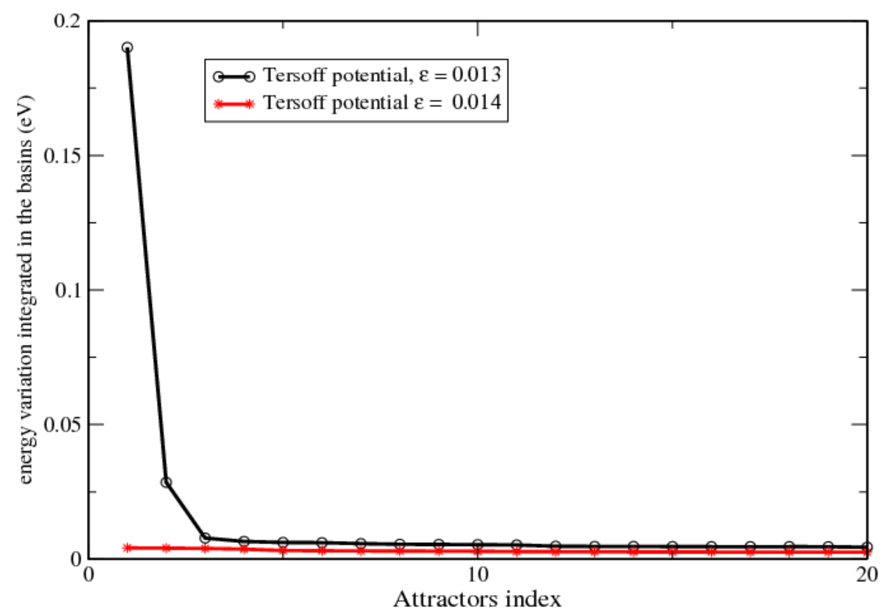


Portrayed as a projection in the third dimension

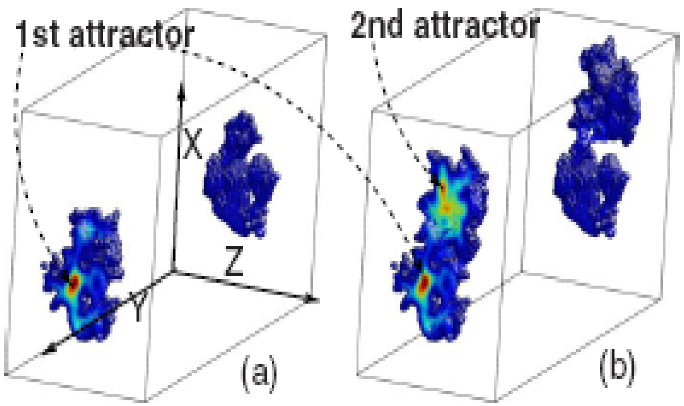
We add some criteria to select Plastic events among the attractors

Stillinger-Weber potential

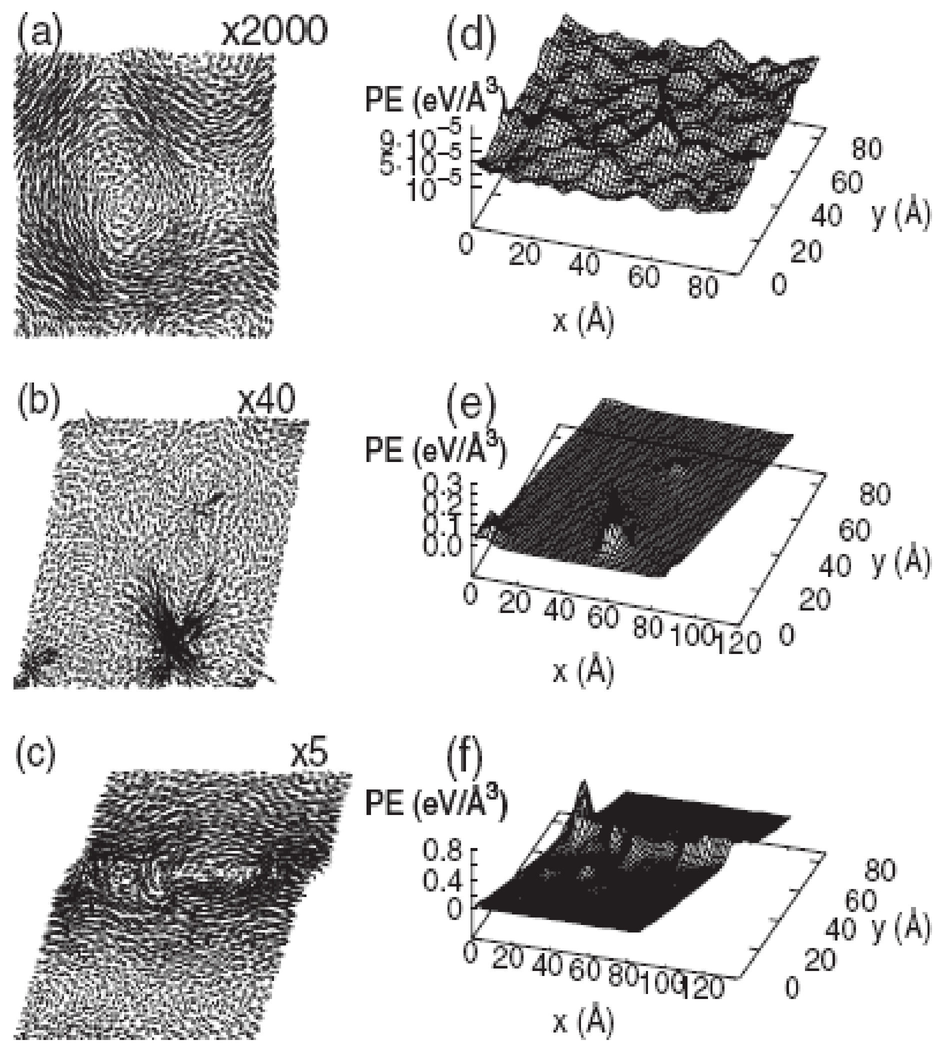




Attractor examples :



Link with displacement field :



Using this technique, we determine plastic events centers.
Compare with :
 Eshelby quadrupoles
 localization of coordination defects in the structure

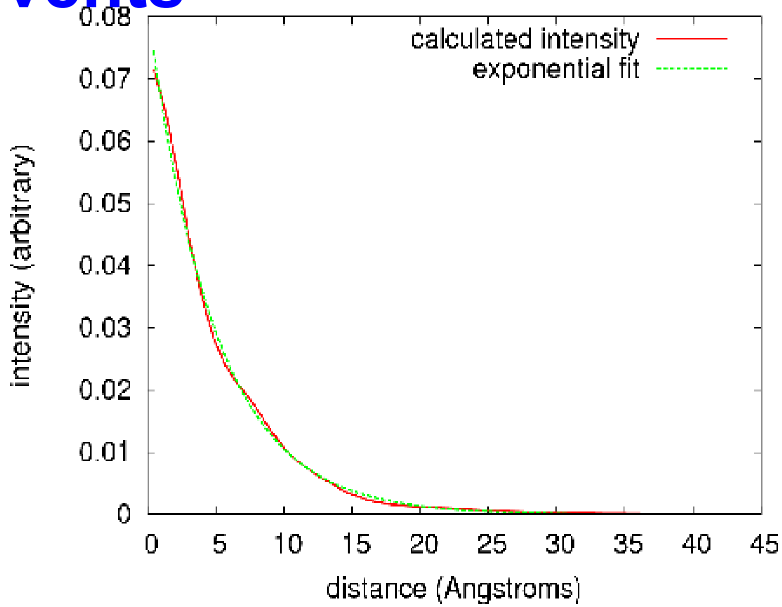
Calculate size of events

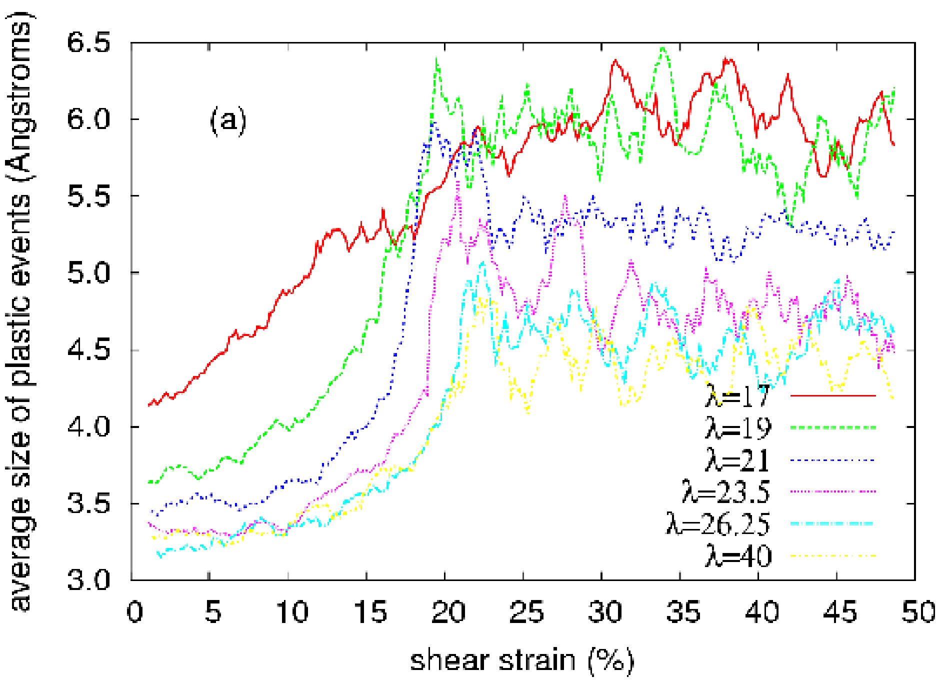
Fusco et al PRE 82 06116 (2010)

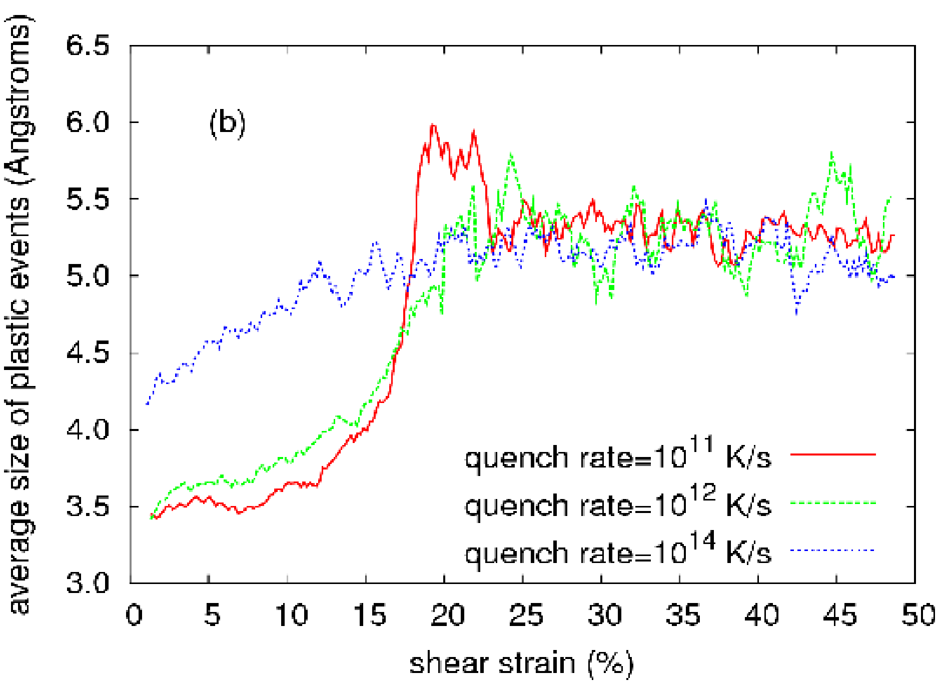
Size of plastic events

The size of the plastic events are evaluated through a fit of the relaxation of the local energy variations at short distances :

$$\Delta E(r) = a \exp(-wr) \text{ (w gives the size)}$$

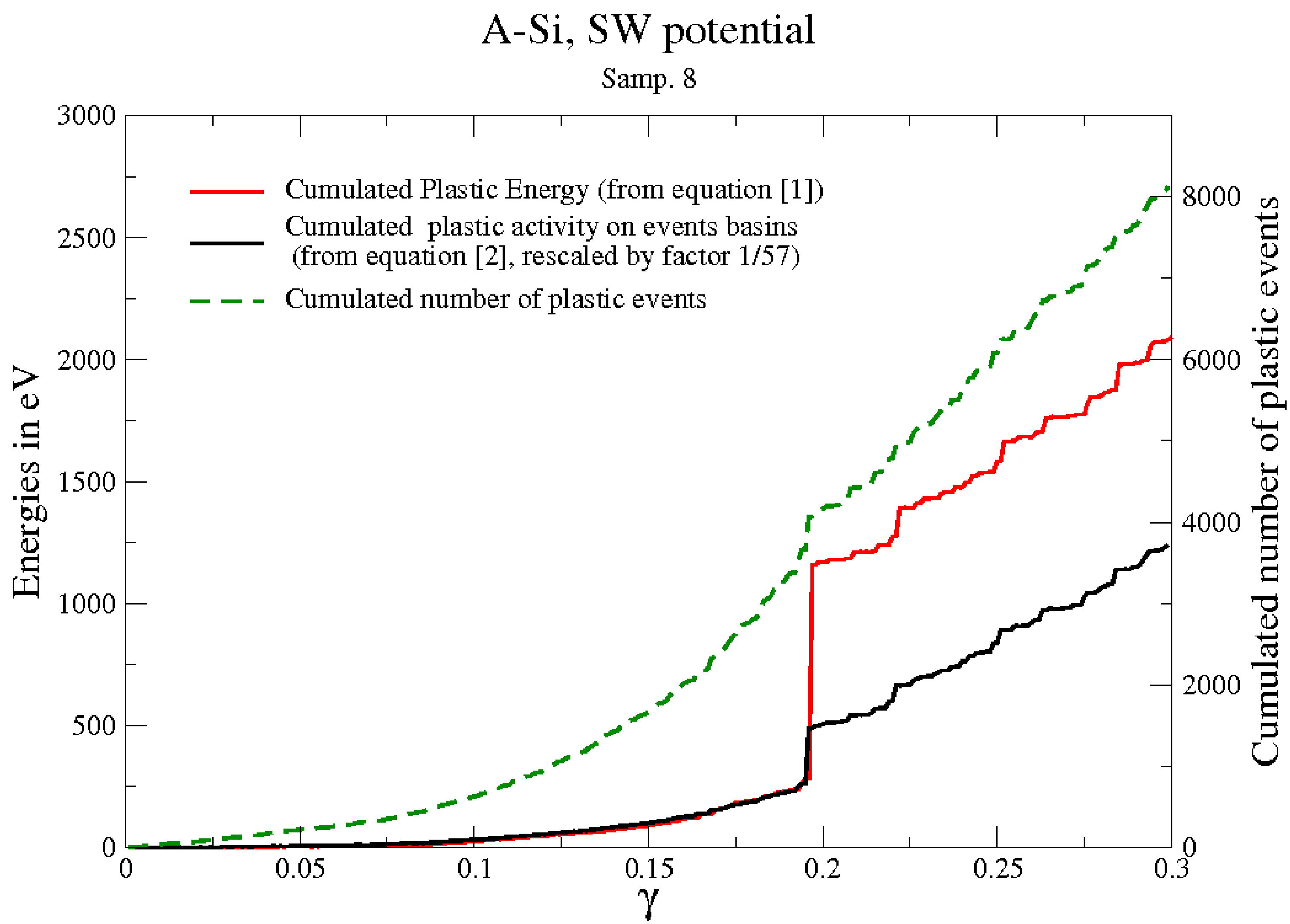






→ Plastic events tend to grow in size until the “Yield point”

Plastic energy .vs. local plastic activity



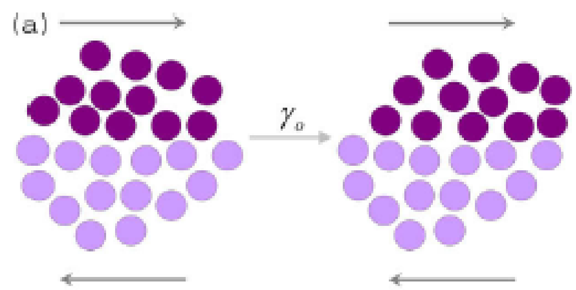
We have identified localized Plastic Events from atomistic calculations

- To which extend can we compare these results with the elasticity of continuum medium ?

- Bridge with mesoscopic models

- Validation, identification of important parameters to describe plastic behaviour

Elements to describe plasticity in an amorphous system :



"Shear Transformation Zone"

Argon Acta.Metall. 27 47 1979

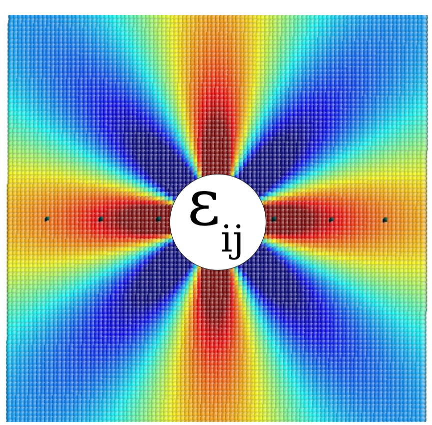
Irreversible shear transformation
(dozen of particles)

Continuum mechanics :
Elastic field due to a shear inclusion

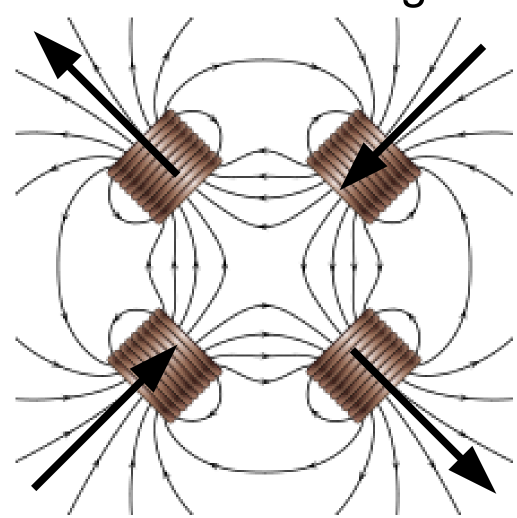
$$\sigma_{ij}=\frac{a^3}{2(1-\nu)R^3}\Big\{\frac{p_{ij}}{15}\Big(10(1-2\nu)+6\frac{a^2}{R^2}\Big)$$
$$+\frac{p_{ik}x_k x_j+p_{jk}x_k x_j}{R^2}\Big(2\nu-\frac{a^2}{R^2}\Big)+\frac{\delta_{ij}p_{kk}}{15}\Big(3\frac{a^2}{R^2}-5(1-2\nu)\Big)$$
$$+\frac{\delta_{ij}p_{kl}x_k x_l}{R^2}\Big((1-2\nu)-\frac{a^2}{R^2}\Big)-\frac{x_i x_j p_{kl}x_k x_l}{R^4}\Big(5-7\frac{a^2}{R^2}\Big)$$
$$+\frac{x_i x_j p_{kk}}{R^2}\Big(1-\frac{a^2}{R^2}\Big)\Big\}$$

$$u_i=\frac{(1+\nu)a^3}{2(1-\nu)E}\Big\{\frac{(2p_{ik}x_k+p_{kk}x_i)}{15R^5}(3a^2-5R^2)$$
$$+\frac{p_{jk}x_j x_k x_i}{R^7}(R^2-a^2)+\frac{4(1-\nu)p_{ik}x_k}{3R^3}\Big\}$$

$$p_{ij}=\frac{E}{(1+\nu)}\Big\{\epsilon_{ij}+\nu\delta_{ij}\frac{\epsilon_{kk}}{1-2\nu}\Big\}$$



Displacement field has the symmetry
Of a field from a magnetic quadrupole



Many mesoscopic models ...

Free volume theory (Spaepen et al)

Mean Field STZ theory (Falk, et al)

Pinning/Depinning (Vandembroucq et al)

Fluidity models (Picard et al)

KFC-FE models (Schuh et al)

QPD model (Perez et al)

...

These models can give : Yield, plastic flow, plastic hardening, shear bands, complex rate dependent behaviour ..

Validation at the microscopic (atomic) scale?

Pinning /Depinning models : stress(σ) = elastic contrib. (μγ) + stress from Local event G(x,y,x',y')

J.C. Baret et al.
PRL 89 195506 (2002)

Eshelby-like stress redistribution upon event
Local (random) stress threshold

Fluidity models : $$\dot{\sigma}(x,y,t)=\mu\dot{\gamma}+2\mu\int G(x',y',x,y)\dot{\varepsilon}^{pl}(x',y')$$

G.Picard et al
PRE 71 010501 (2005)

Eshelby-like stress redistribution upon event
Fixed stress threshold
Visco-elastic plastic rate : $$\dot{\varepsilon}^{pl}(x,y,t)=\frac{n(x,y,t)}{2\mu\tau}\sigma(x,y,t)$$

n(x,y,t) depends on characteristic times when it switches from elastic (n=0) to plastic (n=1) or vice-versa.

KMC-FE models : Define STZs on a FE grid

Homer et al
Acta Mater. 57 2823 (2009)

Use an activation rates that depends on
Typical STZ barrier and local stress : $$\dot{s}=\nu_0\exp\left(\frac{-\Delta F+\tau\gamma_0\Omega_0}{kT}\right)$$

Eshelby-like stress redistribution upon event

Fitting displacements with Eshelby inclusions

Least square fit from the difference of MD displacements and a sum of Eshelby inclusions centered on detected plastic events

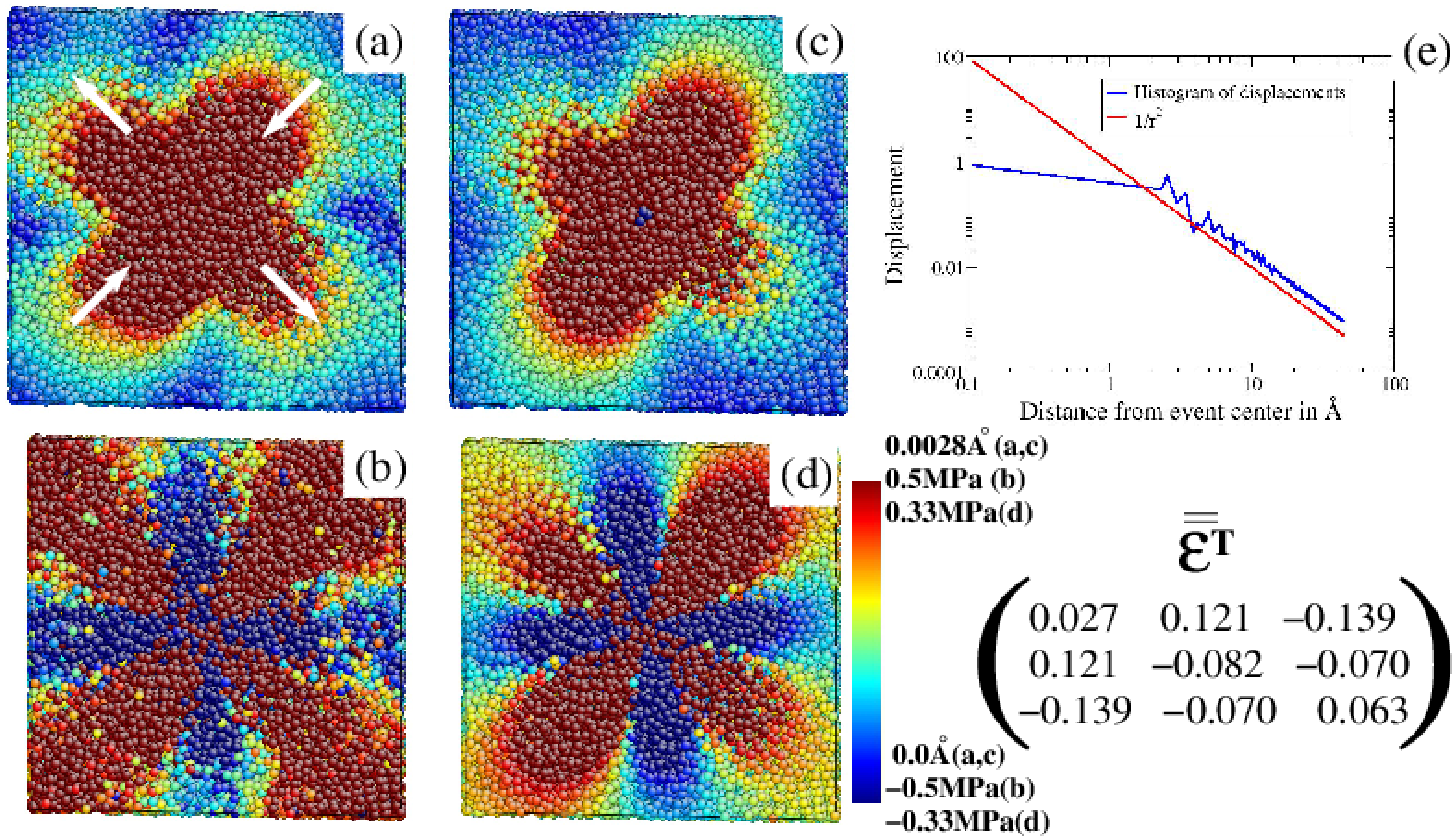
Variational parameters : Transformation strain tensor (6 components)

Other parameters : inclusion radius, average elastic constants

Rules : use homogeneous infinite body solutions,
Spherical inclusions
do not fit regions inside inclusions
Use events that represent more than 90% of plastic activity

Technique : Damped dynamics algorithm

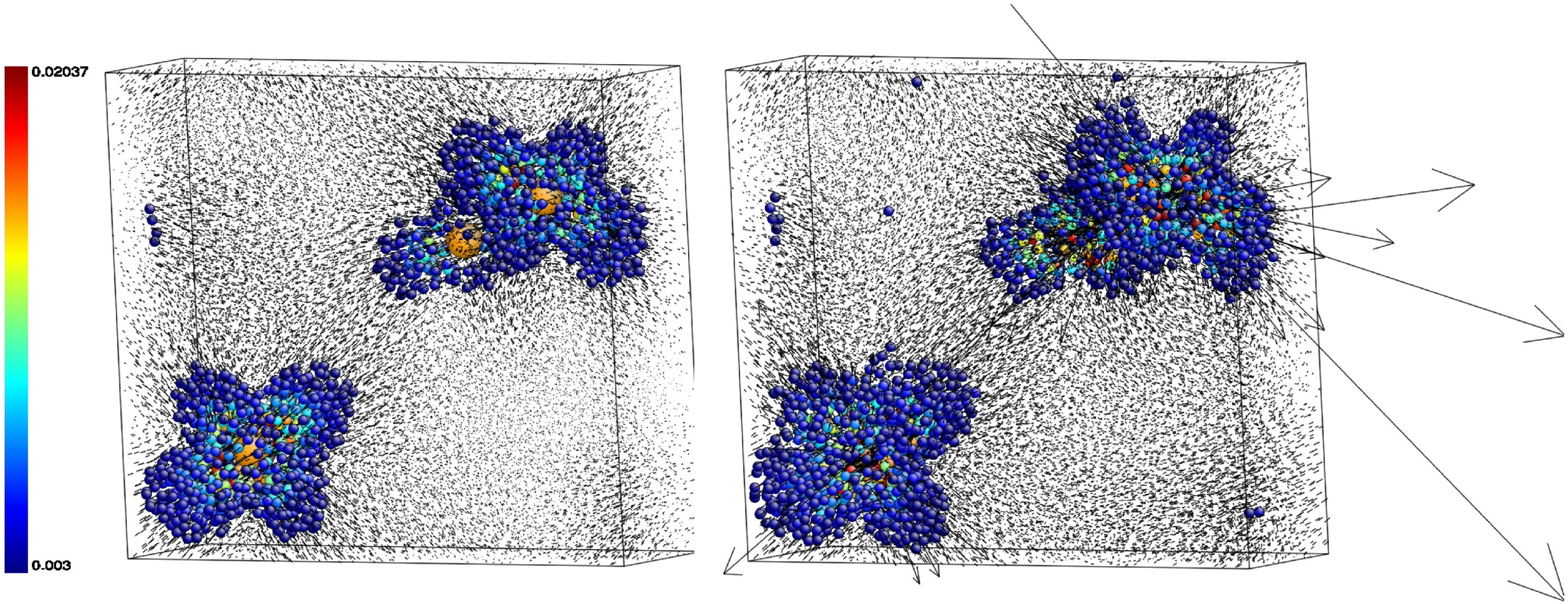
Results on events extracted from the simulation and studied alone using a small rescaling factor : ::



$$\overline{\overline{\varepsilon}}^{T} \quad \begin{pmatrix} 0.027 & 0.121 & -0.139 \\ 0.121 & -0.082 & -0.070 \\ -0.139 & -0.070 & 0.063 \end{pmatrix}$$

- Symmetry and power law correspond to shear Eshelby event

Nature of the plastic events

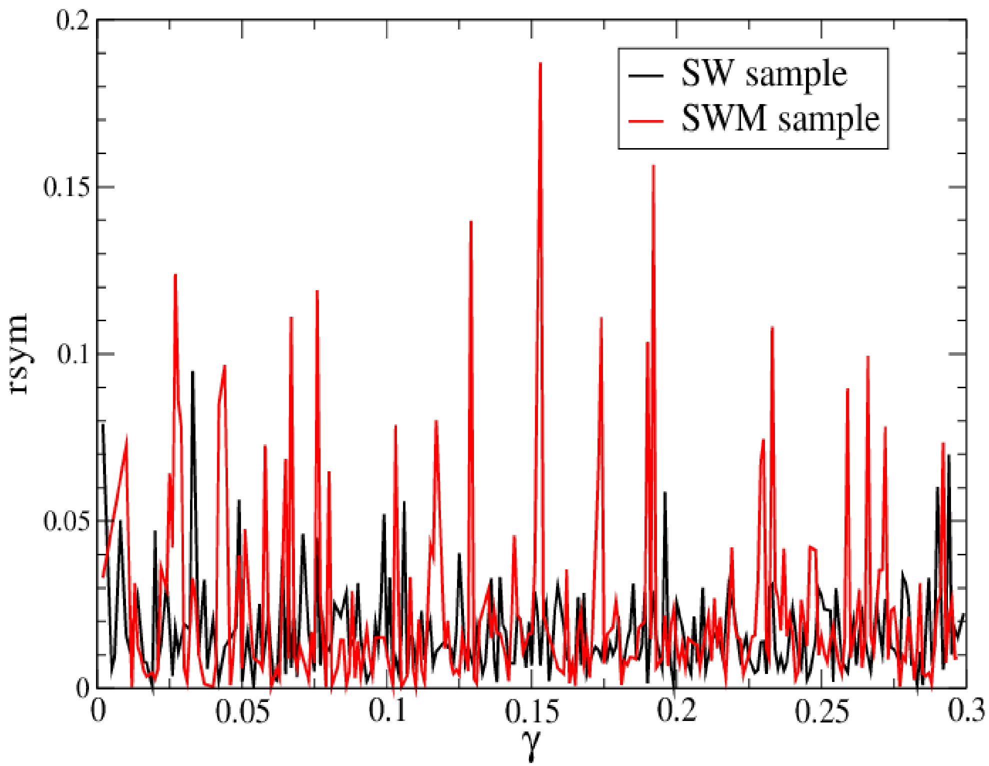


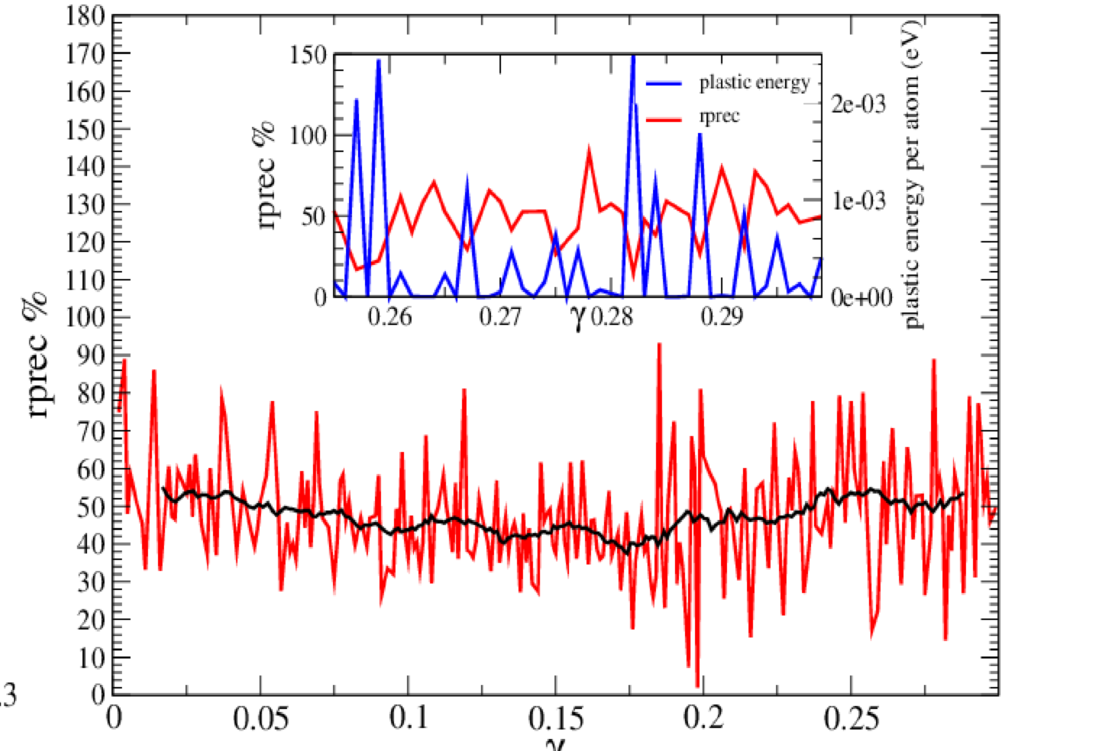
- Events centers do correspond to detected plastic events
- Shear inclusions describe well the overall structure of the displacement field with characteristic cross shaped structures.
- Max. errors are found close to the centers

Typical errors & symmetry

Rsym : ratio between (sum of displacements square due to diagonal components of ε^T)
and (sum of displacements square due to shear components of ε^T)

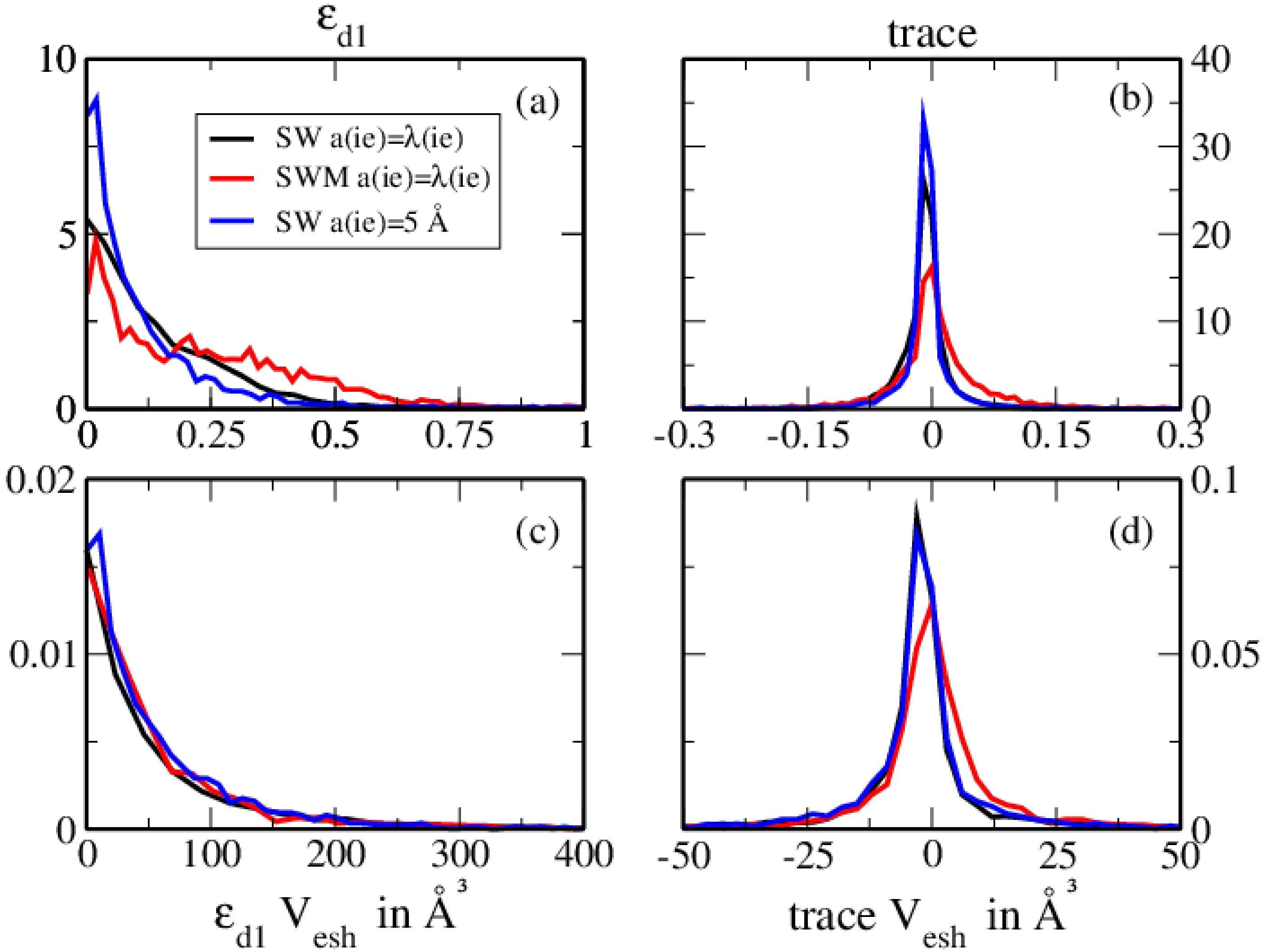
Rprec : ratio between (final objective function) and (initial objective function)





- Shear components dominate, more for SW than SWM
- Qualitative agreement between MD and Eshelby fit is obtained
- Can we achieve a more quantitative agreement ?

Distributions of Eshelby Transformation Tensors



ε V represents the robust output of the fit

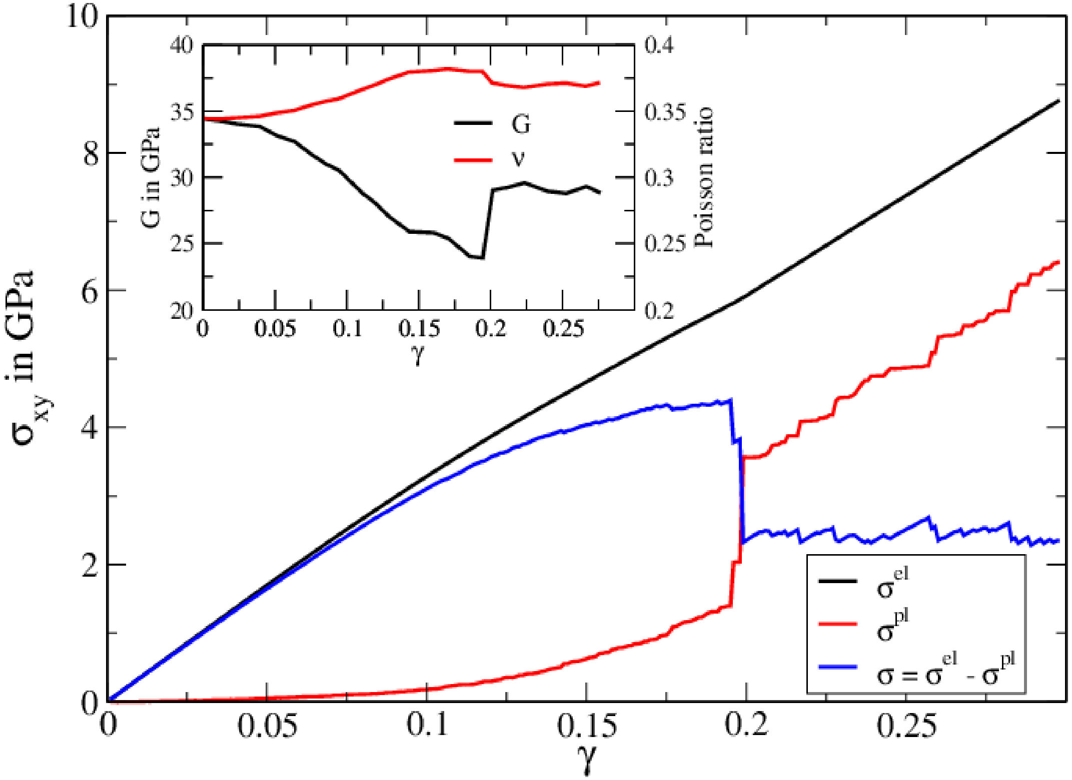
Stress-Strain relations evaluated from the Eshelby shear inclusions

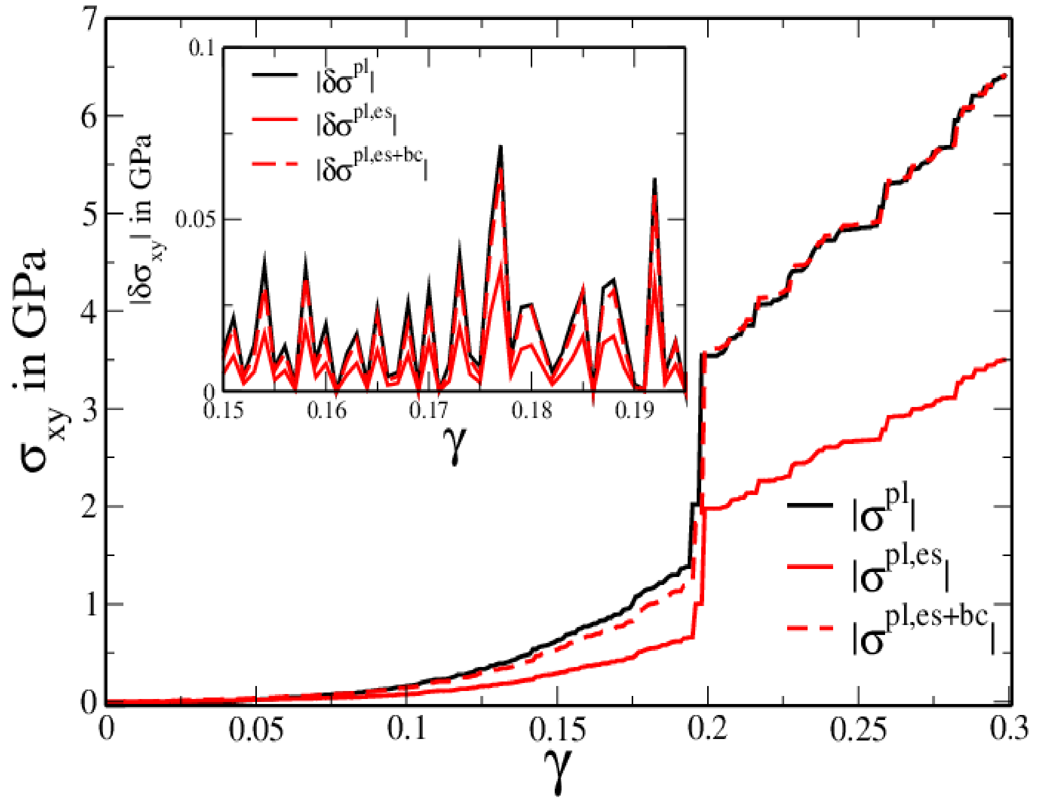
$$\delta\sigma_{xy} = \delta\sigma_{xy}^{el} + \delta\sigma_{xy}^{plas}$$

$$\delta\sigma_{xy}^{plas} = \sum_e \sigma_{xy}^{Es}(e)$$

$$\delta\sigma_{xy}^{el} = G(\epsilon)\,\delta\epsilon_{xy}$$

$$\delta\sigma_{xy} = \delta\sigma_{xy}^{el} + \alpha\,\delta\sigma_{xy}^{plas}$$





- Homogeneous strain correction to match BC
- 1 adjustable parameter α

Stress-Strain relations evaluated from the Eshelby shear inclusions

$$\delta\sigma_{xy} = \delta\sigma_{xy}^{el} + \delta\sigma_{xy}^{plas}$$

$$\delta\sigma_{xy}^{el} = G(\epsilon)\,\delta\epsilon_{xy}$$

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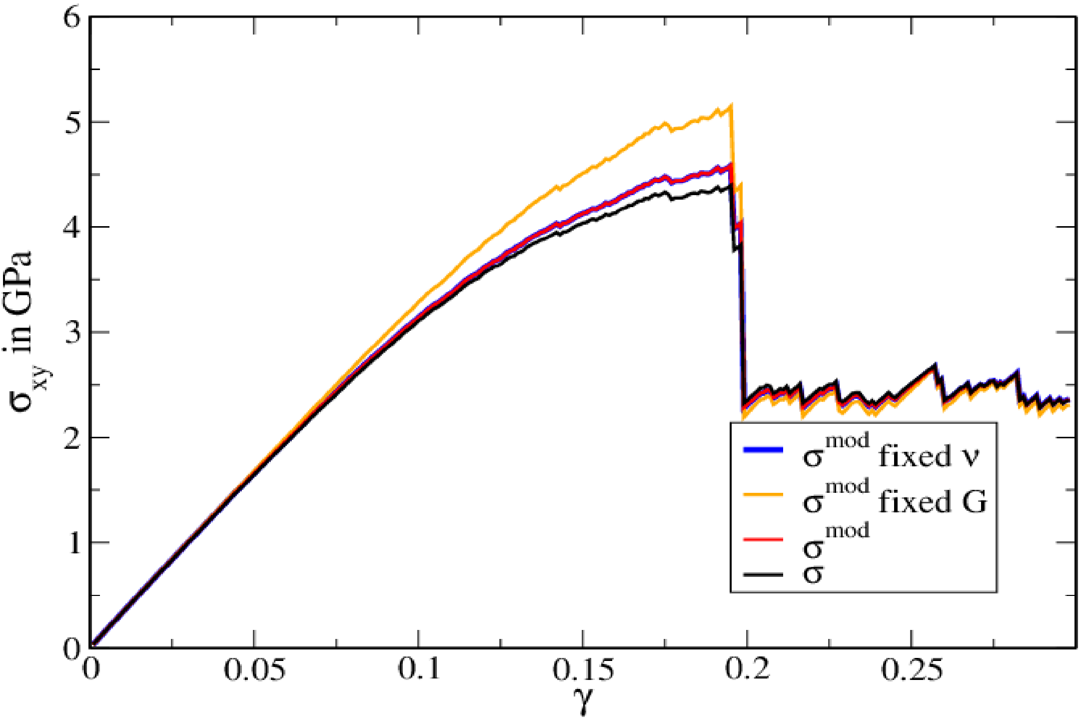
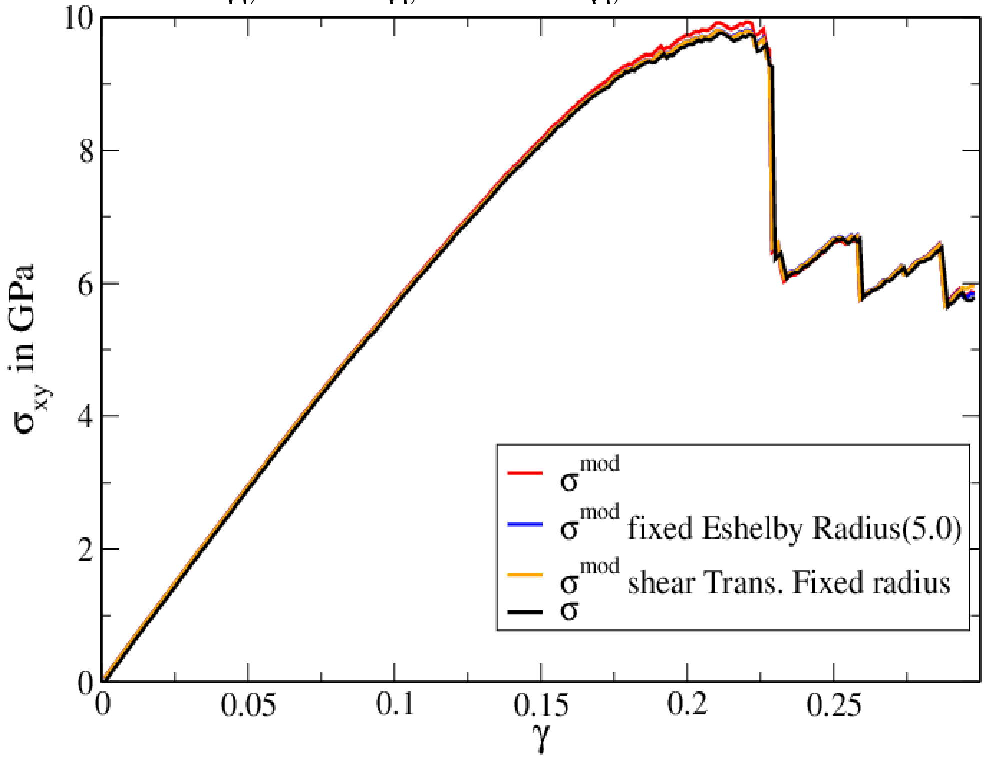
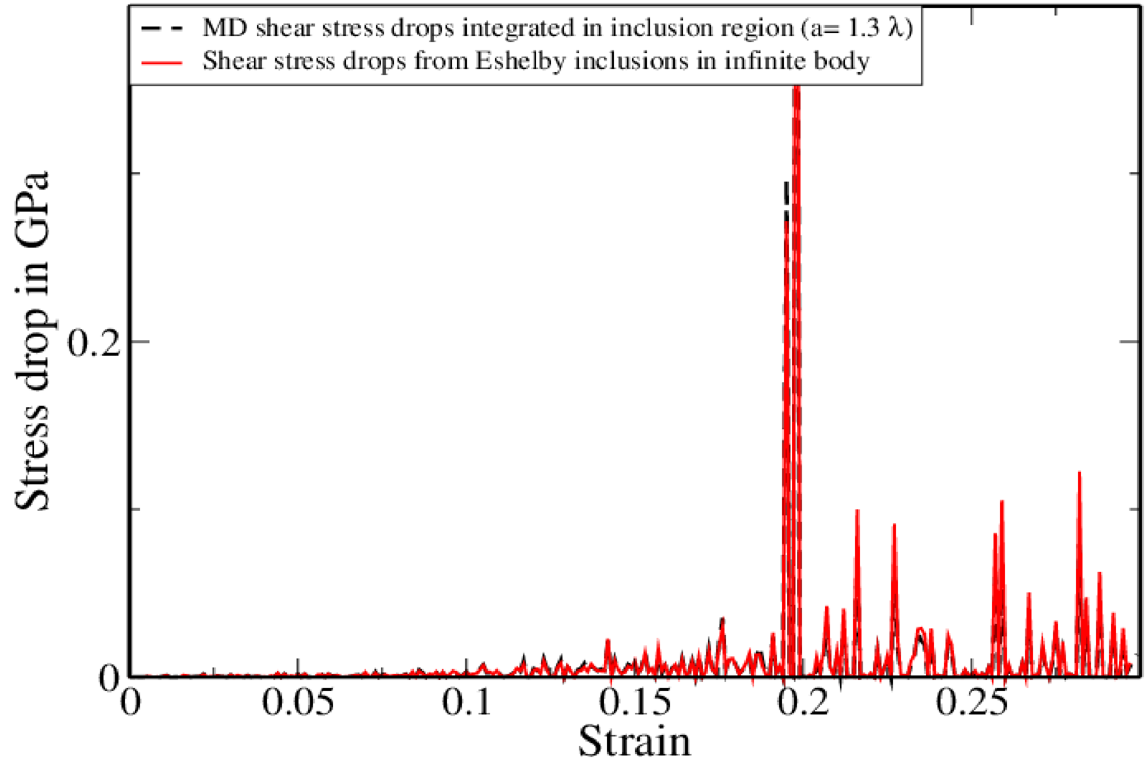
$$\delta\sigma_{xy} = \delta\sigma_{xy}^{el} + \alpha\,\delta\sigma_{xy}^{plas}$$



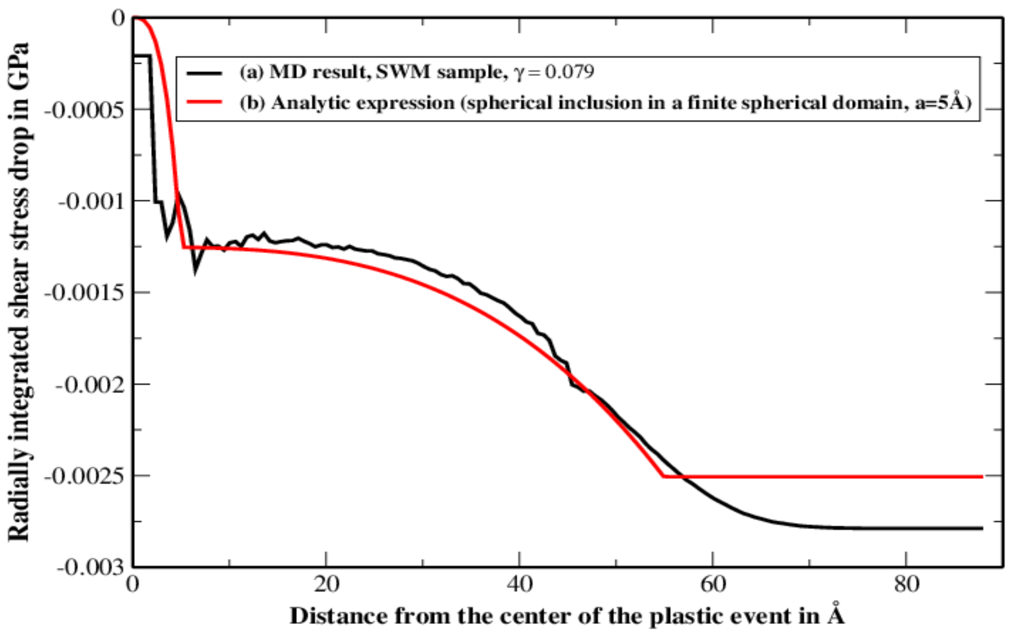


- Continuum elastic solutions of shear inclusions describe well the development of plasticity
- … providing we evaluate their intensity and number, and the use of a variableG
- Variable poisson parameter and precise Eshelby radius are not crucial
- No need of diagonal components to represent shear stress
- What is the origin of the parameter α close to 2 ?

Local Contributions ::

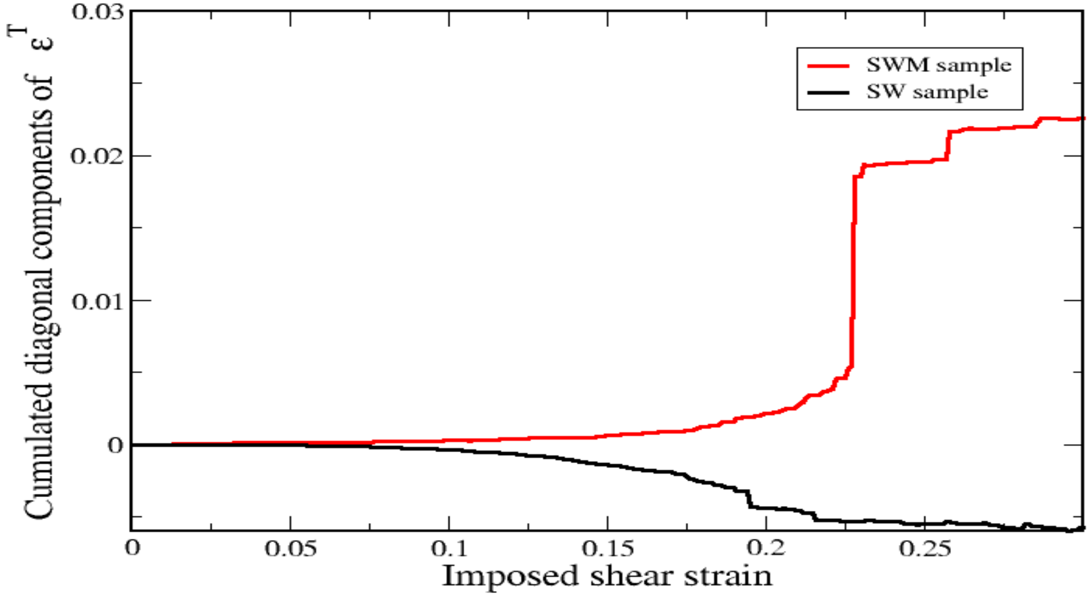


Spatial shear stress redistribution



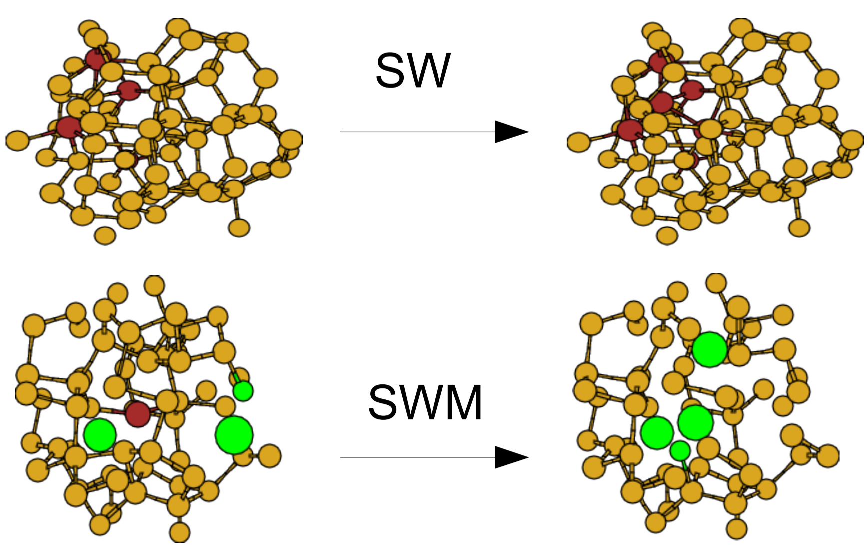
Volume and pressure Variations

Diagonal elementsof Eshelby transformation strain tensors :



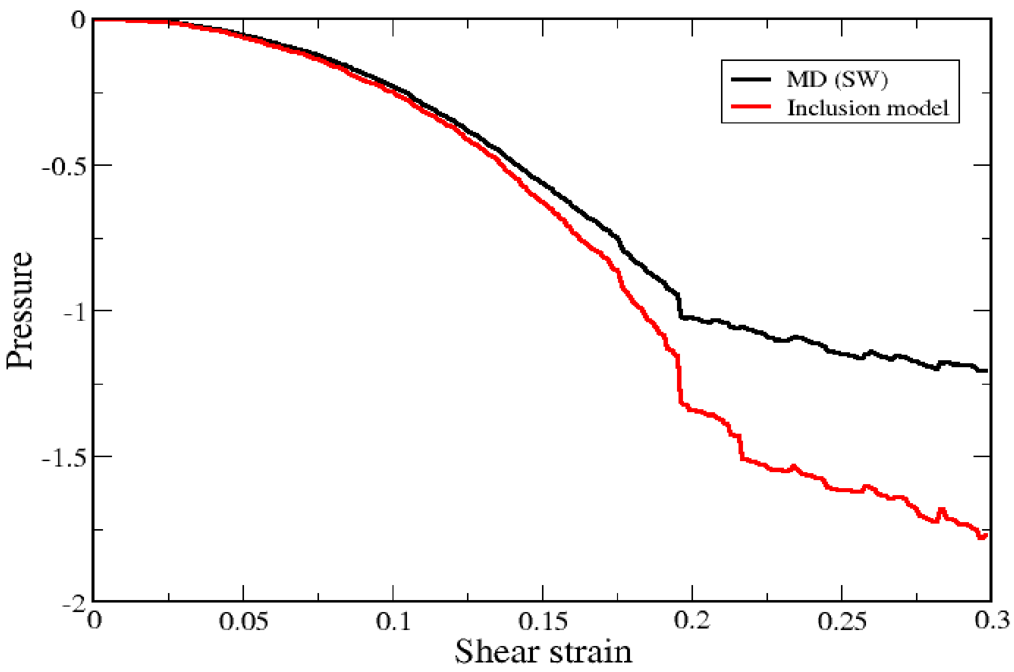
•Volume decrease around SW plastic event
•Volume increase around SWM plastic event
Large variations at band formation ???

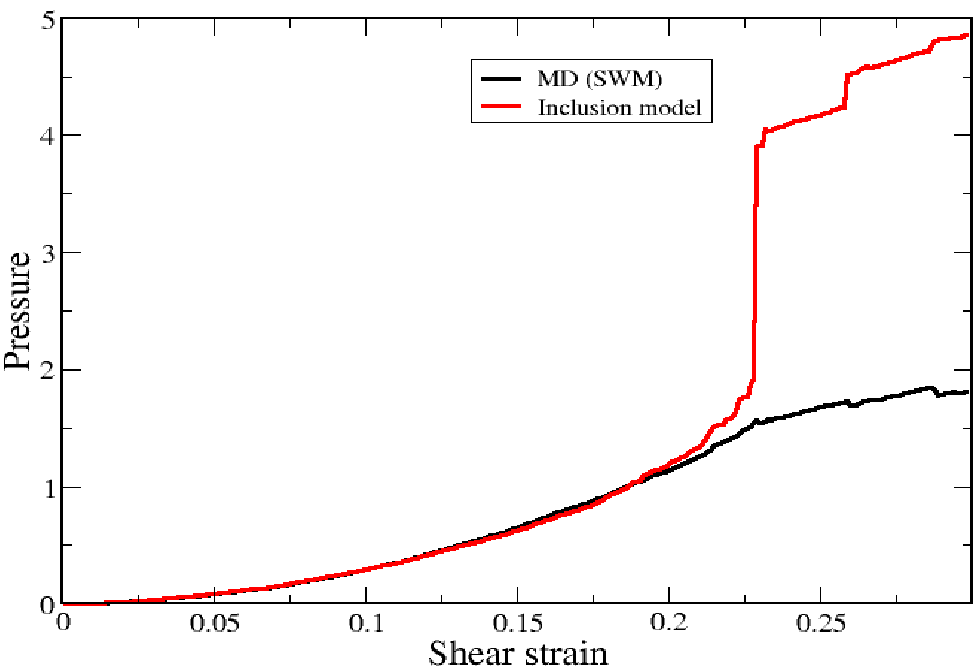
Consistent with atomistic structure around plastic event :



• Explained by 3 body param
•Linked to relative brittle/ductile behaviour of SW and SWM
•Hard sphere plasticity fails at atomic scale
•Inclusion model quantitative respect to pressure ?

Volume and pressure Variations

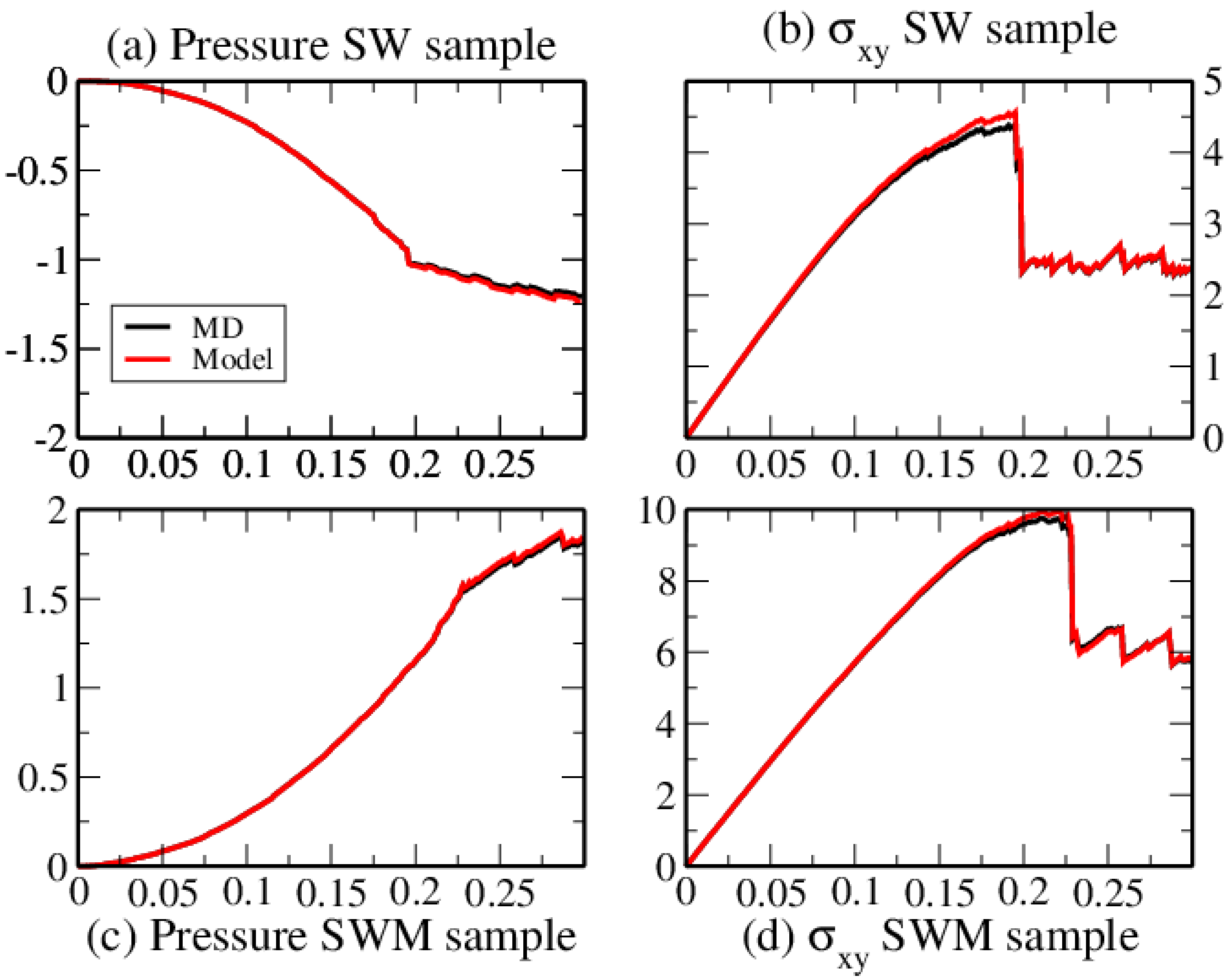




Inclusion mode lis no more accurate $\delta P = \delta P^{el} + \alpha \delta P^{plas}$

Reasons : elastic term more difficult to evaluate
Many sets of inclusions give similar accuracy, especially with lot of inclusions
Large jumps are due to numerical artefact

Adding pressure in the fit :



Conclusions and Perspectives

•Main features of plasticity can be described through Eshelby inclusion representation

•Allow better comparison between exp./theory.

•Important parameter here is mainly the average shear modulus,
for a sheared bulk the size of events and their shapes are not crucial

•Small scale details determine the occurrence of events but once they are
generated these events are well described by continuum medium elasticity.

•Boundary conditions matter but can be discussed even using a simple infinite elastic body solutions. For any quantitative model they largely affect the results and should be considered.