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# EFFECT OF STRESS RELAXATION ON MECHANICALLY INDUCED CRYSTALLIZATION IN NATURAL RUBBER

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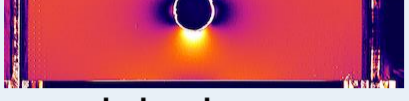
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## Context & Objectives

The usual ways of measuring crystallization in a material are as follows:

- Nuclear magnetic resonance, differential scanning calorimetry, density measures
  - Wide Angle X-ray Diffraction
- no in-situ follow-up  
choice of exposure time, synchrotron proposals, complex post-treatment ...



$$\Delta\theta, \underline{\sigma}, \underline{\epsilon}, \dots \rightarrow \underline{\chi_c}$$

The original approach proposed in this thesis is to be able to measure crystallinity levels using **infrared thermography** and then use a conversion model to obtain a map of crystallinity, and particularly for complex cases: **heterogeneous fields**, **crack bifurcation**, etc. Before setting up such a model, it is necessary to **better understand certain microstructural phenomena** involved in crystallization.

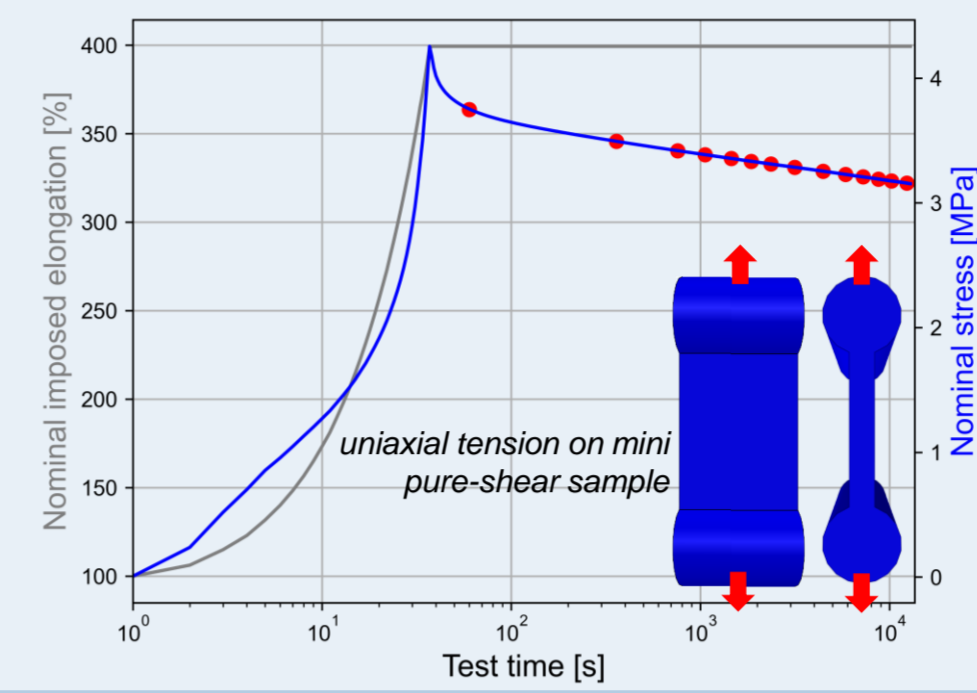
## Material

### Filled & cross-linked rubber :

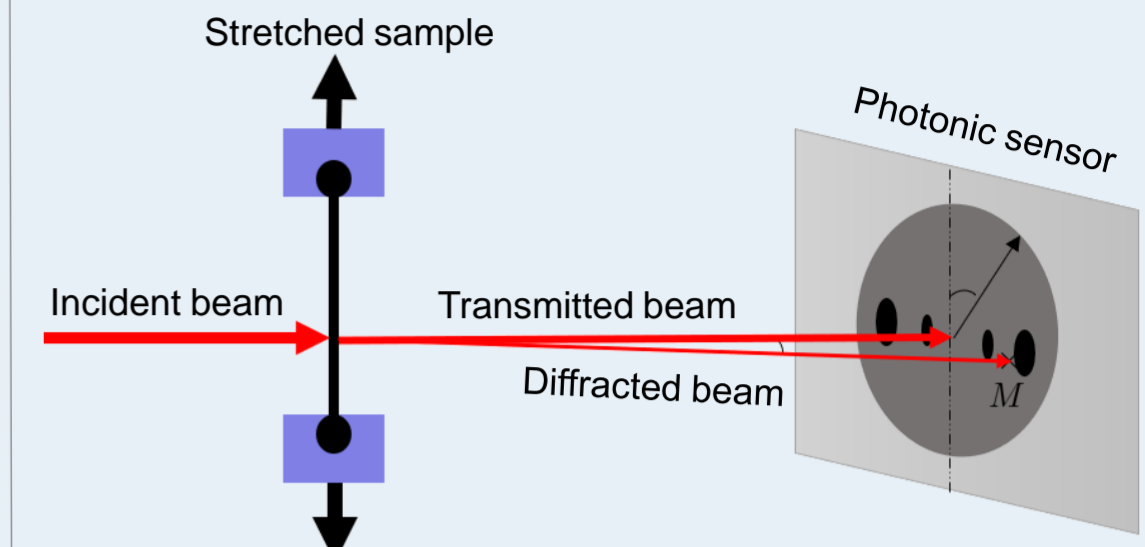
- Matrix : cis-polyisoprene
- Fillers : carbon black
- Vulcanizing agent : sulfur
- Other : processing agents, accelerators, plasticizers, antiozonants, ...

## Performed Tests

- WAXD measures during stress relaxation for different temperatures and elongations



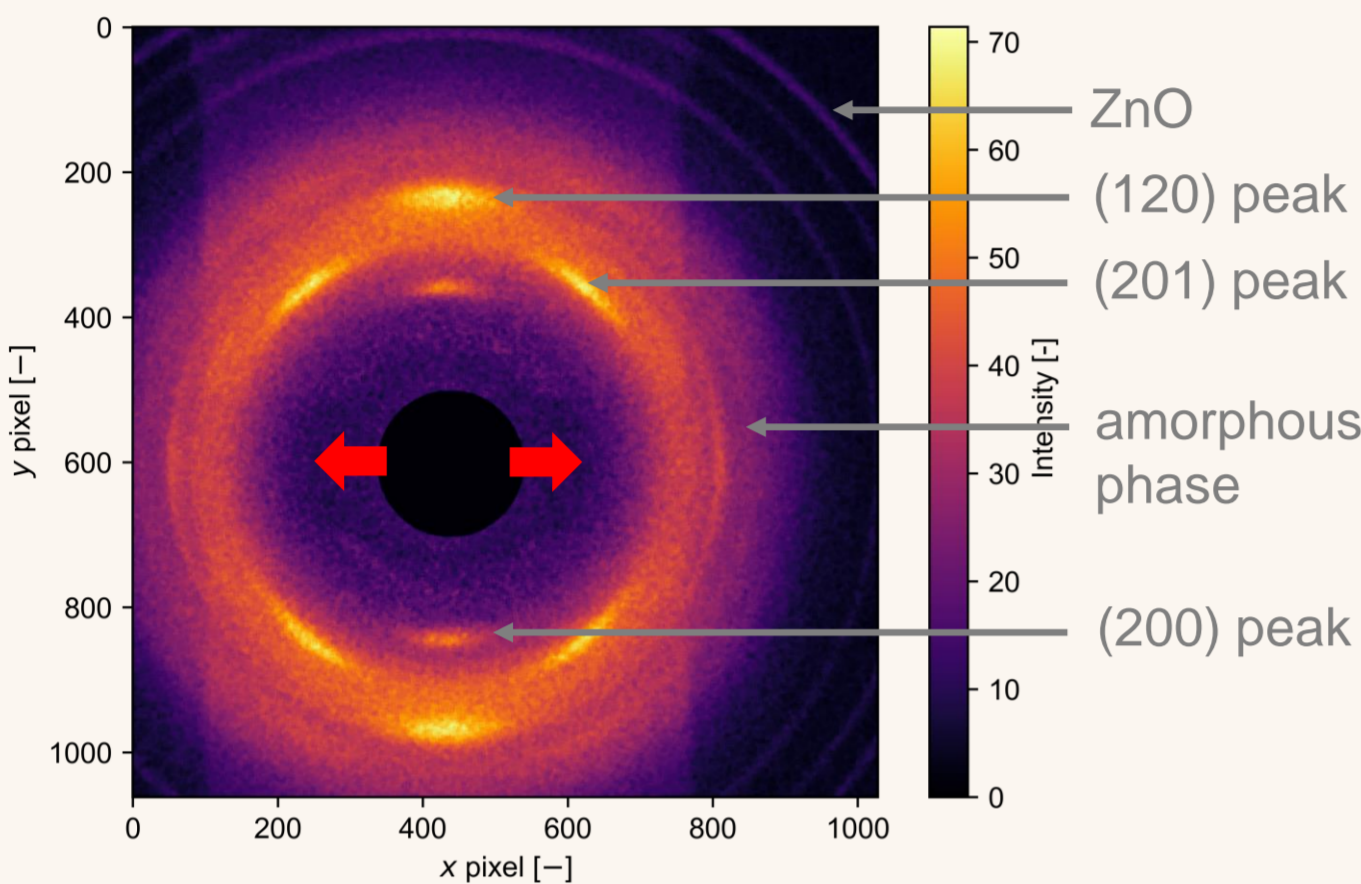
- Experimental setup :



- Tests performed at INSA Lyon with  $\lambda = 1,54 \text{ \AA}$  and an exposure time of 240s

## 1 Raw data

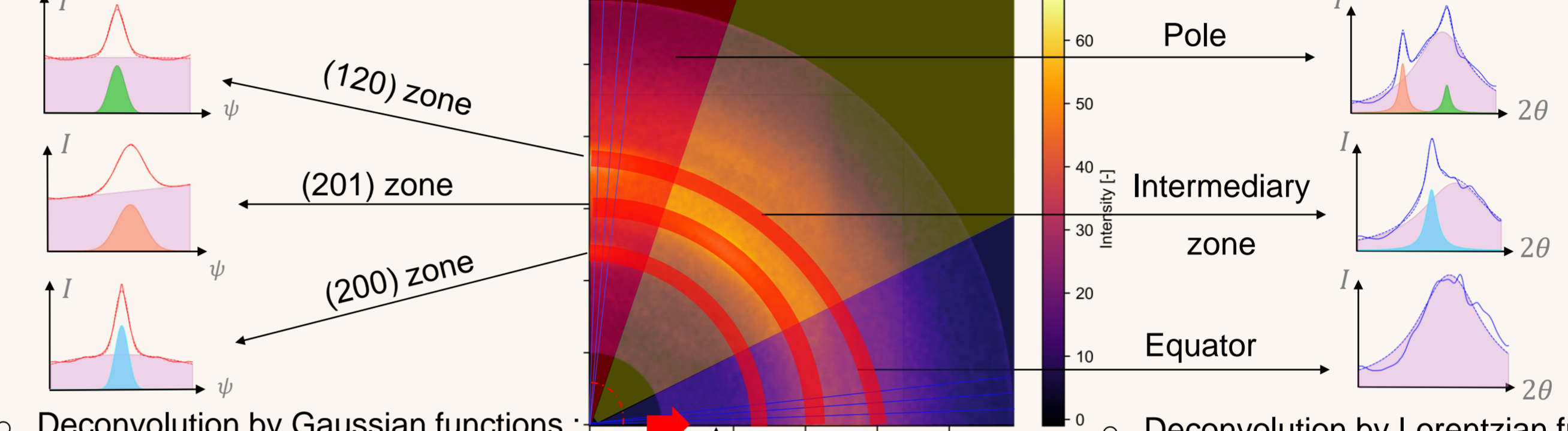
- Identification of  $(d_{hkl})$  peaks and all other classic peaks from literature [1,2]



→ : tension direction

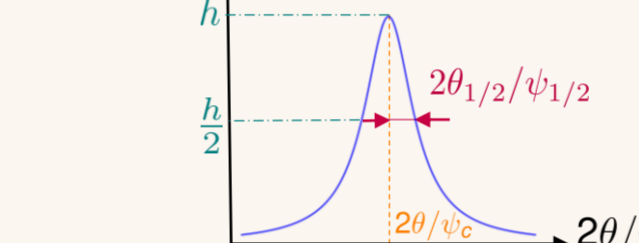
## 2 Profiles & Deconvolutions

- Use of **double symmetry [3]** to average the fourth quarters in one : noise reduction
- Definition of **2 types of profiles and deconvolution** by mathematical functions



- Deconvolution by Gaussian functions :

$$g(\psi, [h, \psi_c, \psi_{1/2}]) = h \exp\left(-\left(\frac{\psi - \psi_c}{\frac{\psi_{1/2}}{2\sqrt{\ln(2)}}}\right)^2\right)$$



$$L(2\theta, [h, 2\theta_c, 2\theta_{1/2}]) = \frac{h}{1 + \left(\frac{2\theta - 2\theta_c}{\frac{2\theta_{1/2}}{2}}\right)^2}$$

## 3 Lattice parameters

- Hypothesis of **orthorhombic lattice** for natural rubber
- Calculation of lattice parameters :

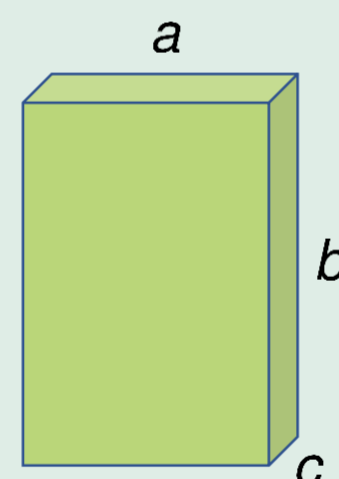
- $\lambda = 1,54 \text{ \AA}$
- $2\theta_{hkl}$  : Bragg's angle at center of the  $(hkl)$  peak

- Bragg's formula :

$$2d_{hkl} \sin(\theta_{hkl}) = n\lambda, \quad n \in \mathbb{N}^*$$

- Interreticular distance  $d_{hkl}$  for orthorhombic lattice :

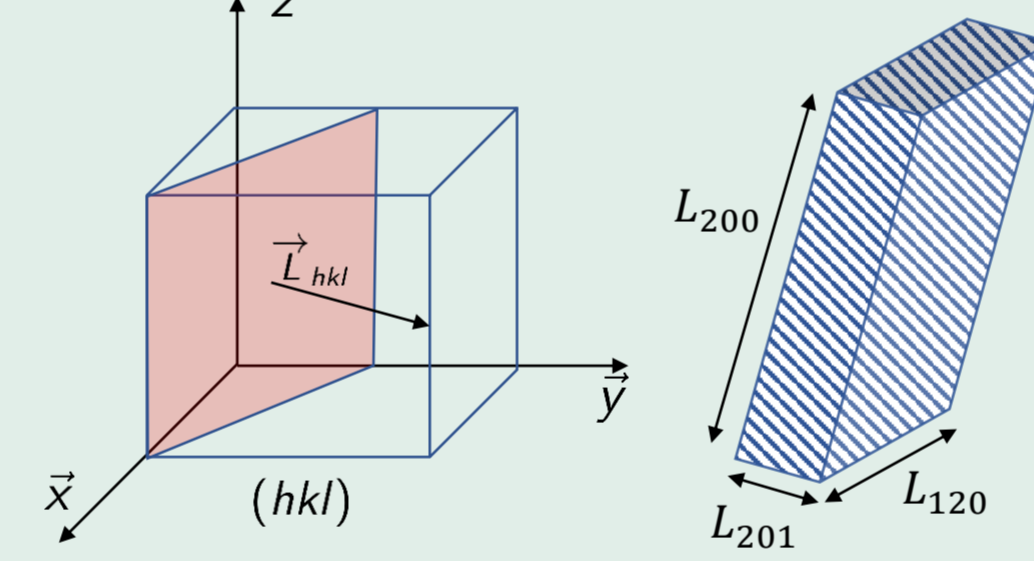
$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}}$$



	Beurrot, 2012 [3]	Poompradub, 2005 [4]	Here study
$a$ [Å]	12,9	12,7	13,0
$b$ [Å]	9,3	9,1	9,4
$c$ [Å]	8,6	8,3	8,5

## 4 Crystallites size

- Three characteristic lengths :  $L_{200}, L_{201}$  &  $L_{120}$

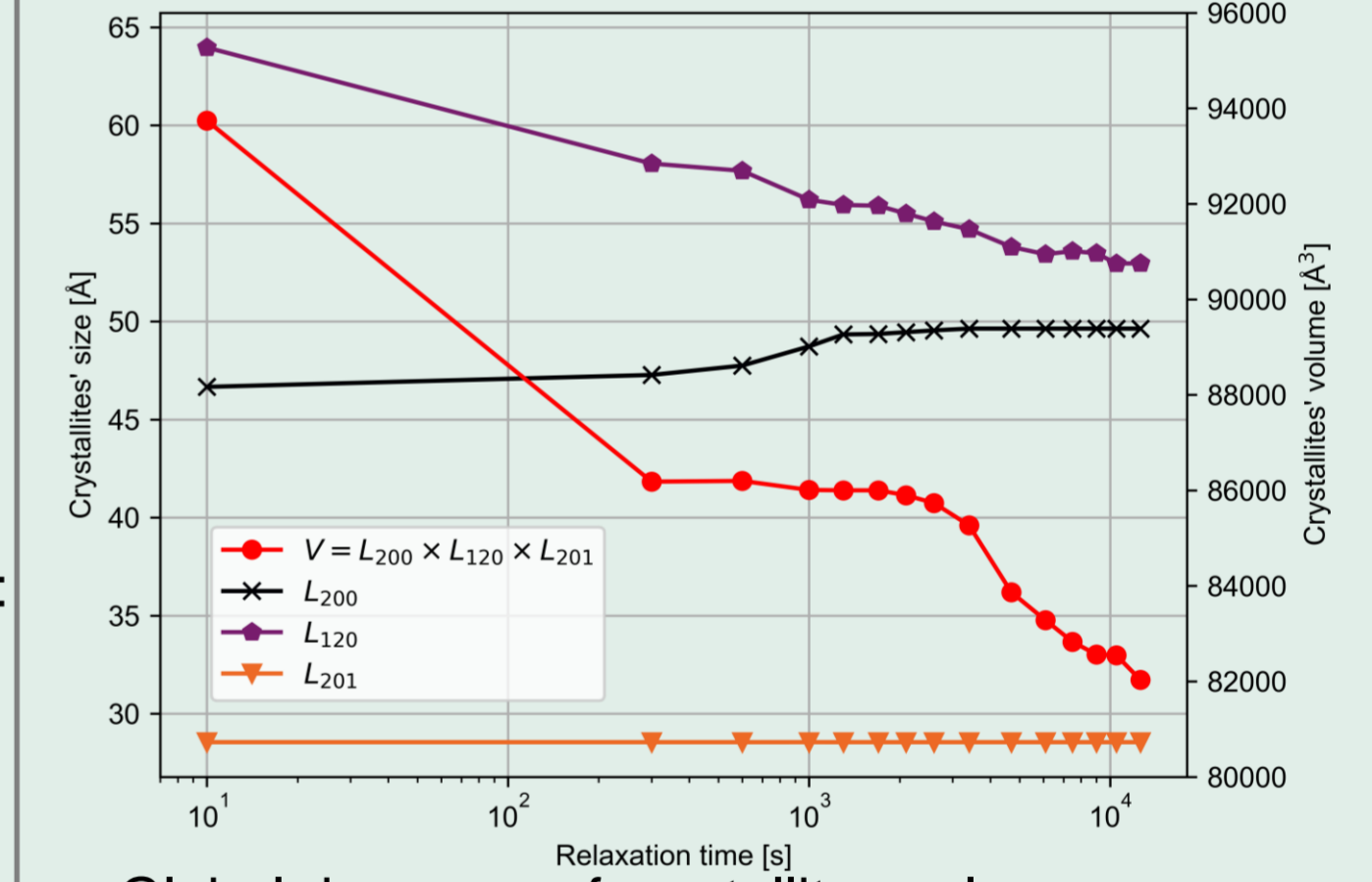


- Size calculated by **Debye-Scherrer formula** :

$$L_{hkl} = \frac{\lambda}{2\theta_{1/2, hkl} \cos(\theta_{hkl})}$$

- $\lambda = 1,54 \text{ \AA}$
- $\theta_{hkl}$  : half Bragg's angle at center of the  $(hkl)$  peak
- $2\theta_{1/2, hkl}$  : FWHM of the Lorentzian function

- $L_{hkl}$  represents the size of crystallites in the direction orthogonal to the  $(hkl)$  plane

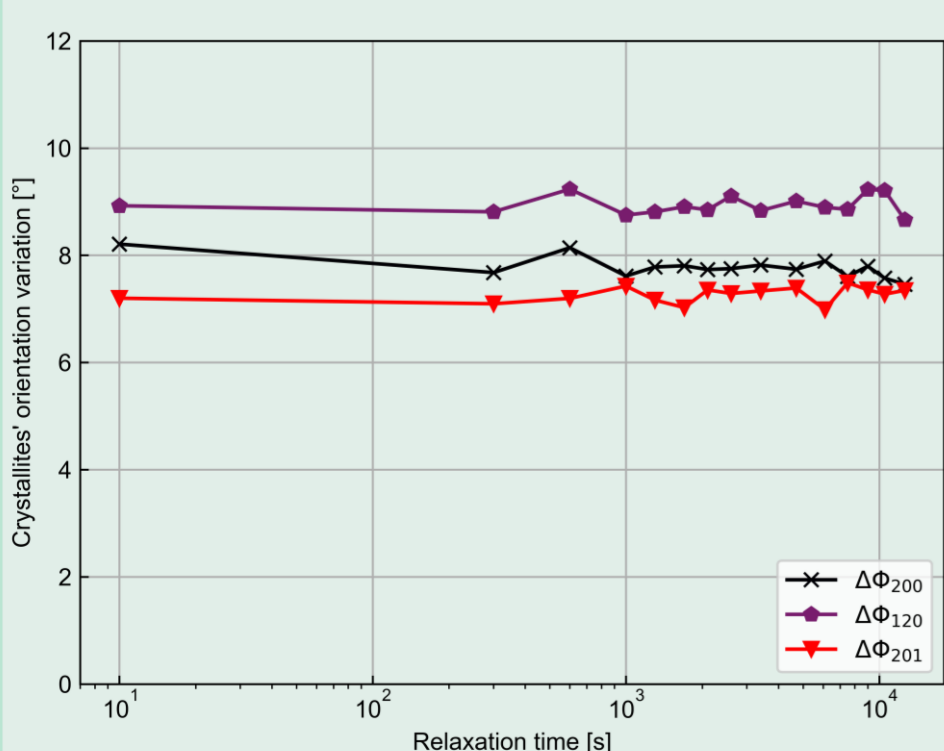
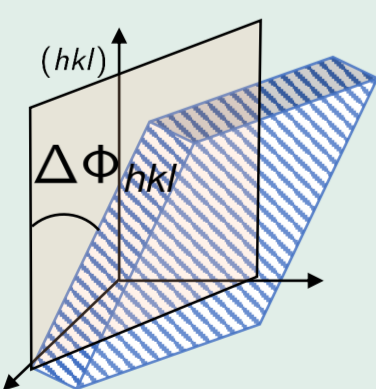


- Global decrease of crystallites volumes

## 5 Crystallites orientation

- Crystallites orientation variations  $\Delta\Phi_{hkl}$  are given by full width at half maximum (FWHM) of the Gaussian function :

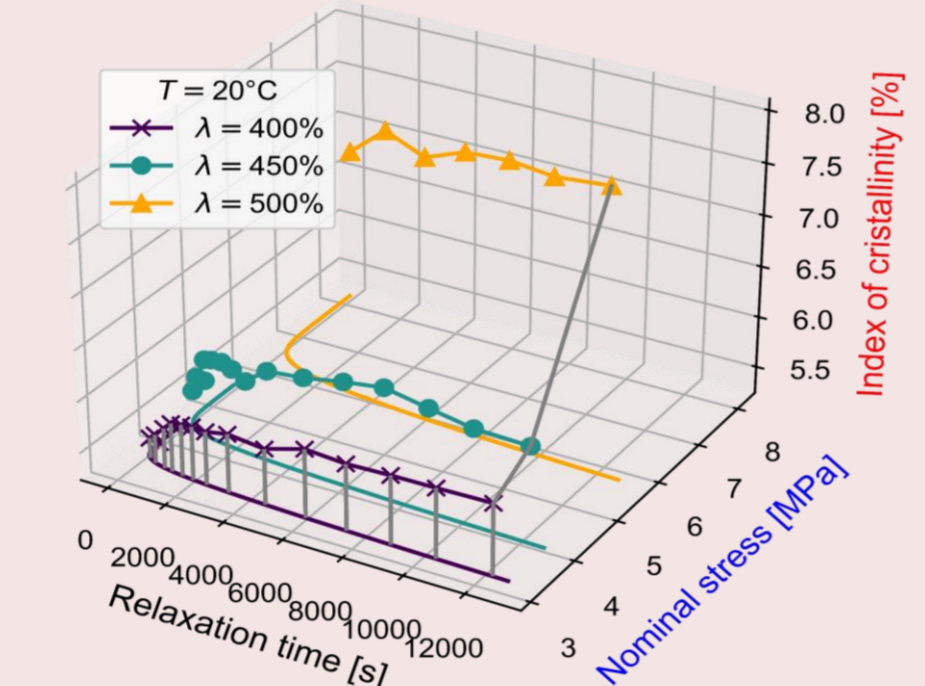
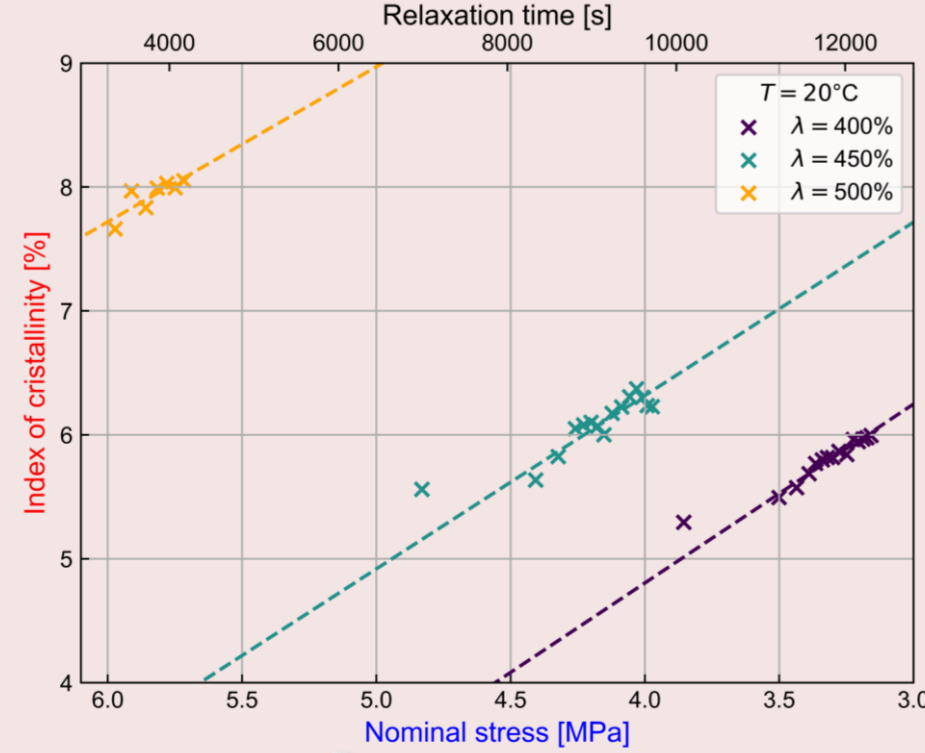
$$\Delta\Phi_{hkl} = \psi_{1/2, hkl}$$



- No variation of crystallites orientation during stress relaxation

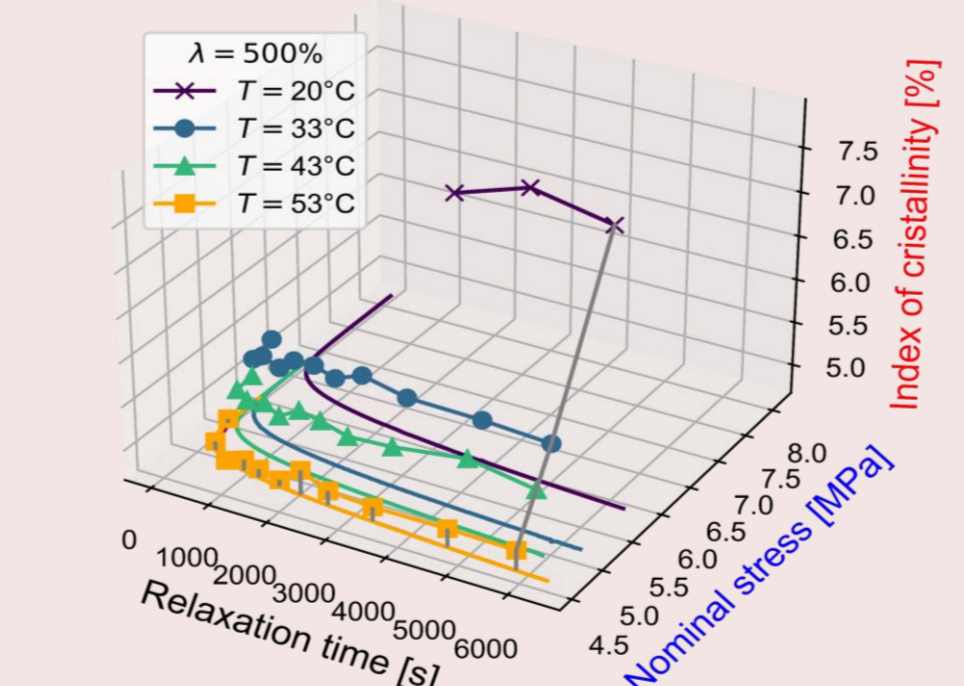
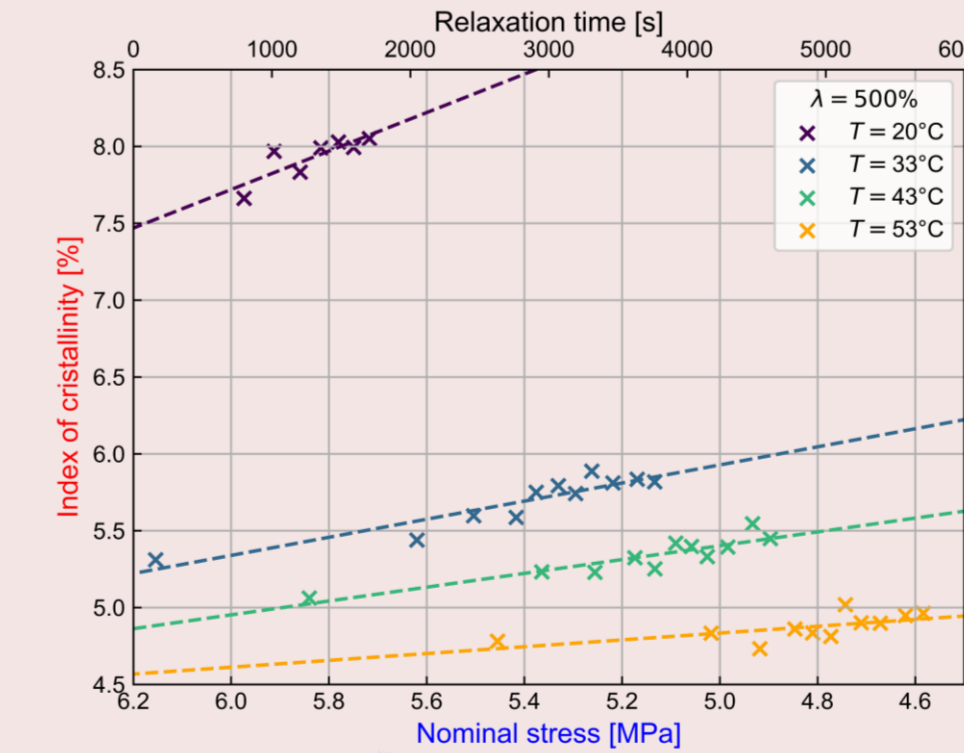
## 6 Crystallinity

- Effect of imposed elongation :



- During **stress relaxation**, the **index of crystallinity  $\chi$**  varies linearly with **nominal stress  $\sigma$** . The  $\frac{\partial\chi}{\partial\sigma}$  coefficient remains the same whatever the value of the imposed elongation.

- Effect of temperature :



- During **stress relaxation**, temperature has two effects : it leads to lower **indexes of crystallinity  $\chi$**  and it reduces the  $\frac{\partial\chi}{\partial\sigma}$  coefficient (i.e. mechanically induced crystallization kinetics).

## Conclusion & Perspectives

There are first results for this study. During stress relaxation :

- The crystallinity index increases while the volume of crystallites decreases. It is probably due to a **fragmentation** of crystallites.
- The coefficient  $\frac{\partial\chi}{\partial\sigma}$  remains constant i.e. the **crystallinity index evolves linearly with stress**. This coefficient also decreases with temperature. Next steps of this study are *in-situ* WAXD measures on more complex sollicitations : **relaxing and non-relaxing cyclic tests**.

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