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## Modelling of nanofibrillation process of crystalline disentangled polymers

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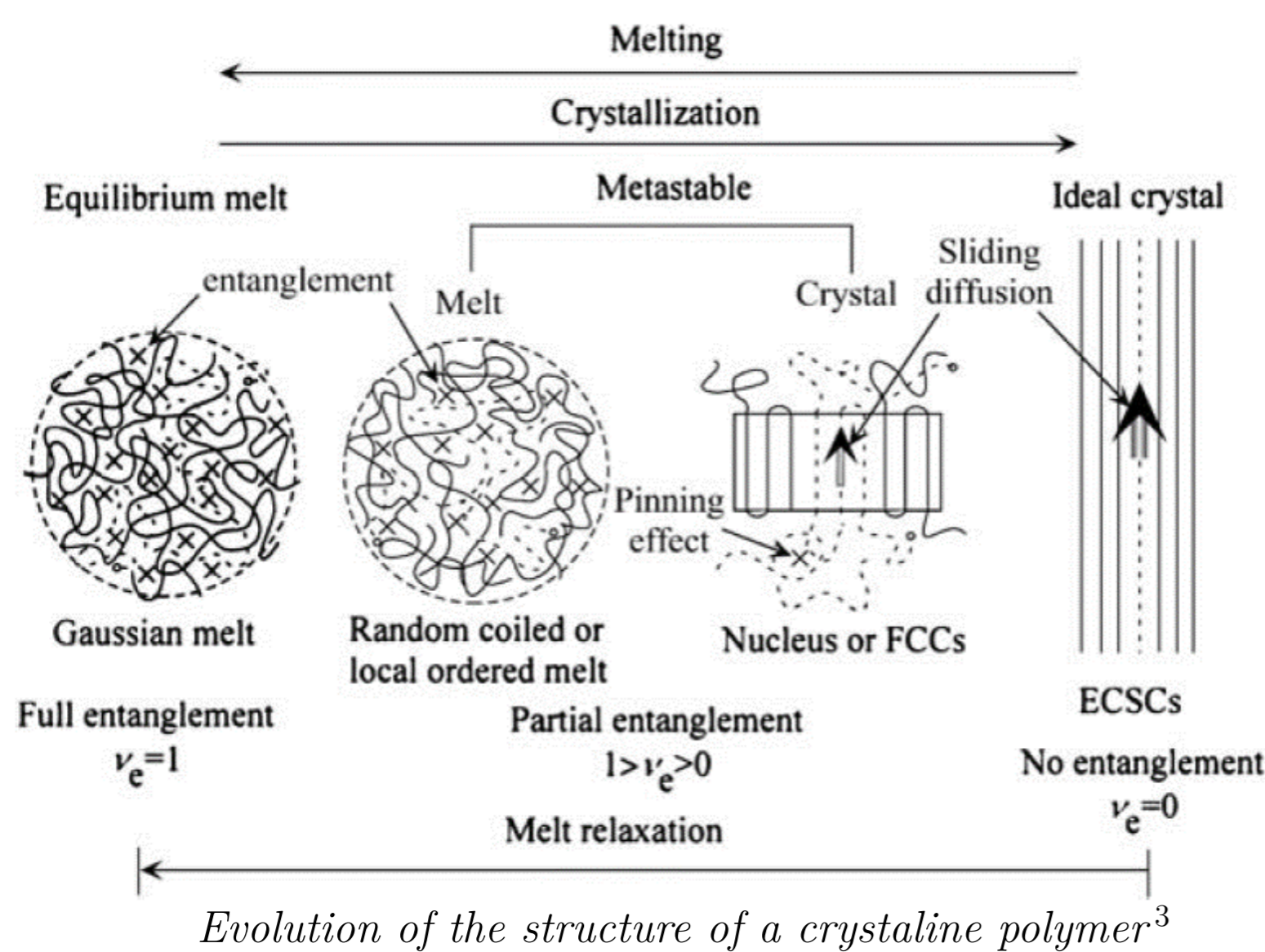
## Contexte

This PhD work is carried out at the Processes and Engineering in Mechanics and Materials laboratory (PIMM) in collaboration with the Centre of Molecular and Macromolecular Studies (CMMS), Łódź, Poland and is dealing with the processing of nanocomposite. CMMS developed a promising **nanofibrillation processing** route based on the **plastic deformation of crystalline disentangled polymers**. In order to further our understanding of the phenomena taking place during the process we resort to **computational modelling**. Due to the **very large deformations** involved, the Constrained Natural Element Method (CNEM) is used to simulate the nanofibrillation process.

**Keywords** : crystal plasticity, disentangled polymer, Constrained Natural Element Method, nanofibrillation, nanocomposite, process modelling.

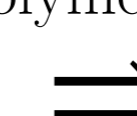
## Disentangled Polytetrafluoroethylene

Crystallisation is the best for preserving disentangement

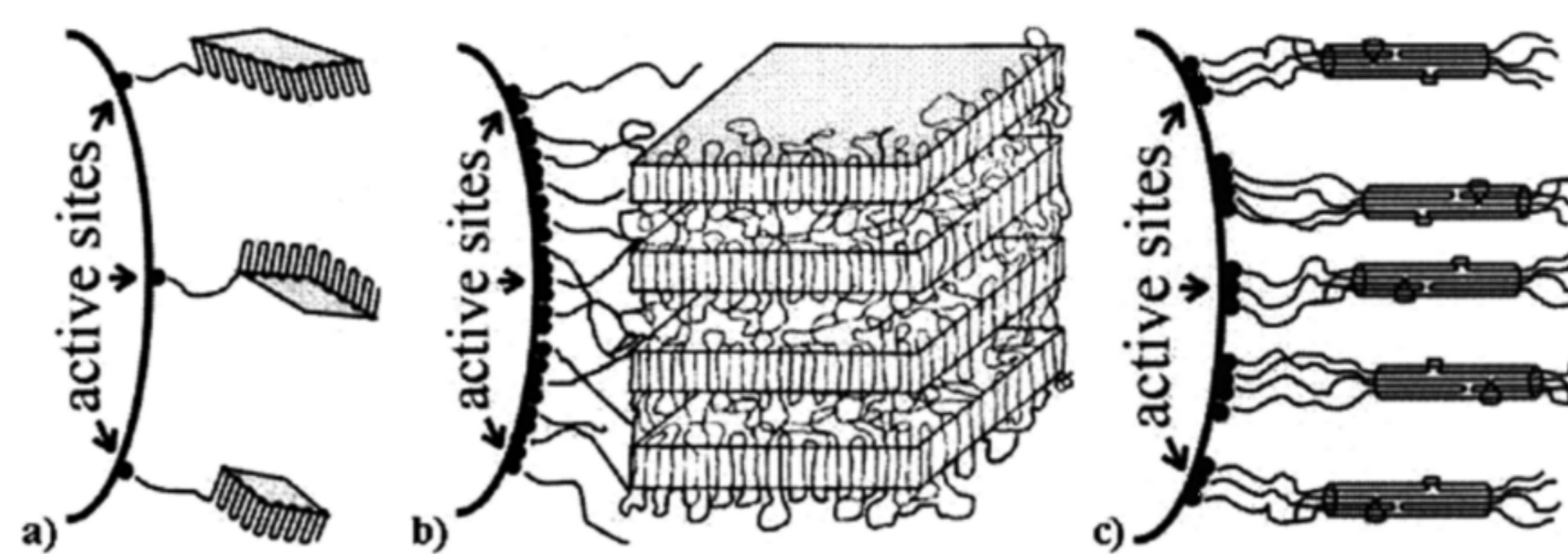


Disentangled PTFE is obtained by crystallisation during polymerisation<sup>4</sup> :

- Number of catalytically active sites very low,
- $T_{polymerisation} \ll T_{melting}$



- Polymerisation rate < Crystallisation rate,
- Independant growth of **monomolecular crystal** called **nascent crystal**,
- High degree of crystallinity ( $\approx 90\%$ ).



Sketch of the local synthesis environment<sup>5</sup> :

- Low density of active catalyst sites → tiny metastable folded crystals,
- High density of active catalyst sites → highly entangled molecules and folded chain crystals,
- Intermediate density of active catalyst sites and equal rate of molecule and crystal formation. → less entangled molecules and extended chain crystals.

Disentangled Polymer ⇒ Reduced macromolecular/physical entanglement ⇒ Negligible strain hardening, hence enabling very large plastic deformation ( $\lambda \approx 100.000$ )

## Constitutive equation and plasticity model

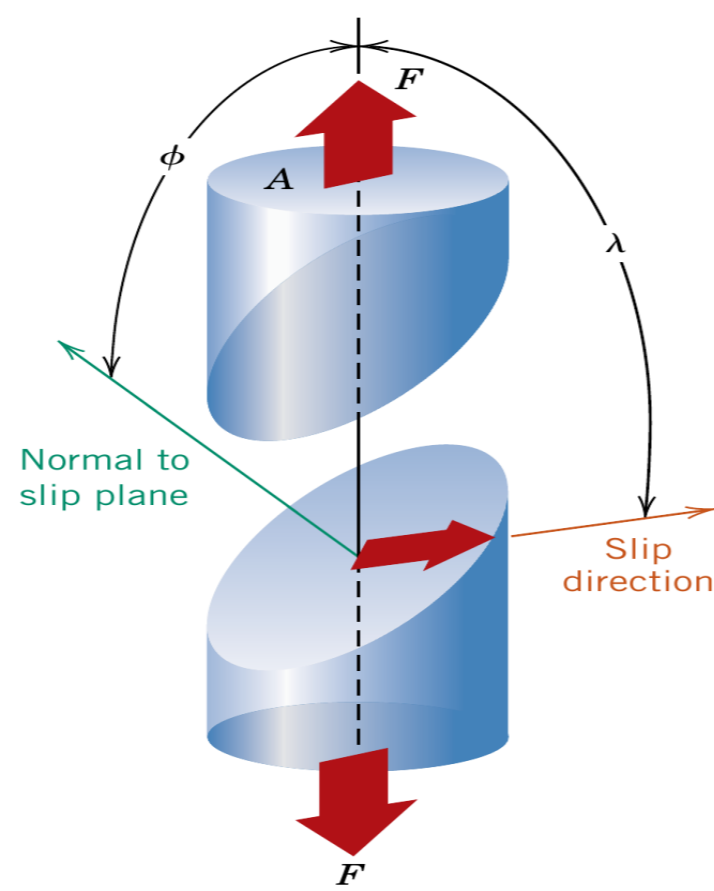
Local equation of the molten matrix polymer dynamics :

$$\begin{cases} \text{div}(\sigma) + \mathbf{f}_d = \rho \gamma & \text{with } : \sigma = -p\mathbf{I} + 2\eta\mathbf{D} \rightarrow \text{Incompressible and Newtonian fluid} \\ \text{div}(\mathbf{v}) = 0 \end{cases}$$

Constitutive equation of the plastic deformation of an inclusion by dislocation slip<sup>6</sup> :

$$\begin{cases} \mathbf{F} = \mathbf{F}_e \mathbf{F}_p \\ \dot{\mathbf{F}} = \mathbf{L}_p \mathbf{F}_p \\ \mathbf{L}_p = \sum_{\alpha=1}^N \dot{\gamma}^{\alpha} \mathbf{m}^{\alpha} \otimes \mathbf{n}^{\alpha} \end{cases}$$

The shear rate is formulated as a function of the resolved shear stress,  $\tau^{\alpha}$  and the critical resolved shear stress (CRSS) of each slip system,  $\tau_c^{\alpha}$   
 $\dot{\gamma}^{\alpha} = f(\tau^{\alpha}, \tau_c^{\alpha})$  with  $\tau_c^{\alpha}$  obtained experimentally.



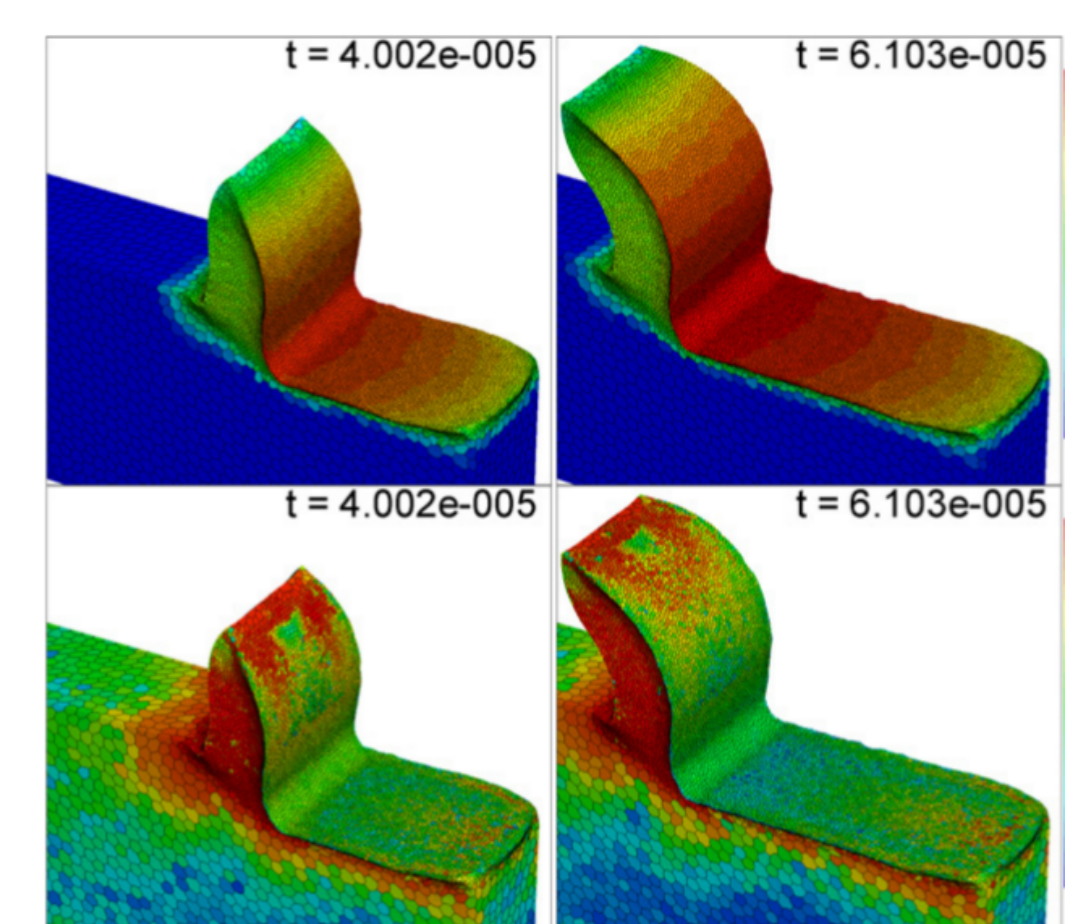
Resolved shear stress  $\tau$  produced on slip system  $\alpha$  by an applied force  $F$

## Computational approach

The Constrained Natural Element Method (CNEM) is an extension of the Natural Element Method (NEM)<sup>7</sup>

- Based on a field interpolation like the Finite Element method (FEM),
- Used interpolation function : function of *natural neighbour* type (ex : Sibson or Laplace function),

- ⇒ Quality of the solution independant of the quality of the mesh,
- ⇒ The mesh is modify at each iteration,
- ⇒ Meshless method for finite deformation framework.



Simulation of cutting<sup>8</sup>

Appropriate numerical method modelling the nanofibrillation process



## Modelling of nanofibrillation sheared by a viscous polymer matrix

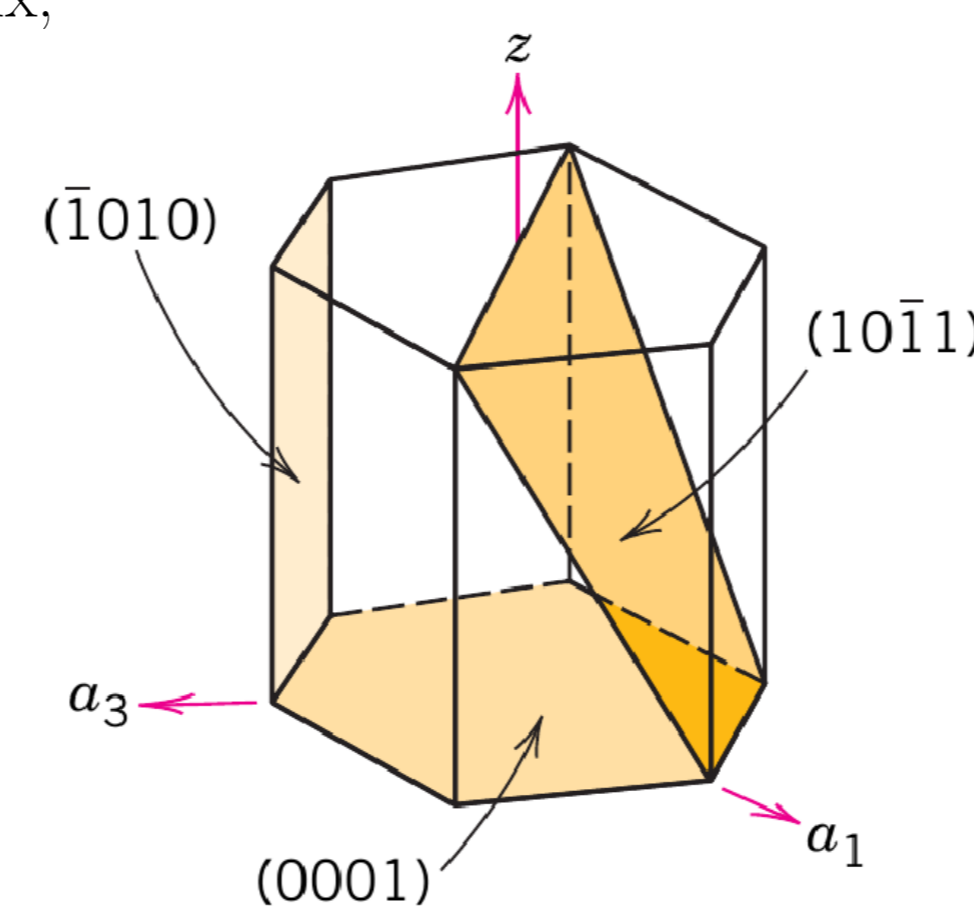
We are going to model the nanofibrillation process of **disentangle PTFE** sheared by **viscous molten polymer matrix of PS** for three experimental setups :

- Single monomolecular crystal plastically sheared by viscous molten polymer matrix,
- Polycrystalline inclusions plastically sheared by viscous molten polymer matrix,
- Multiple inclusions plastically sheared by viscous molten polymer matrix.

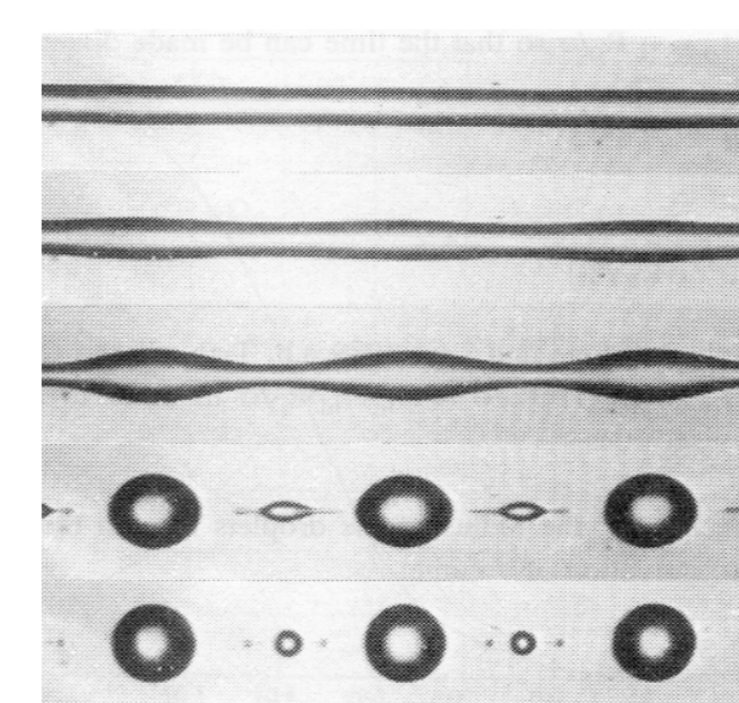
These models depend on multiple parameters.

**Experimental parameters :**

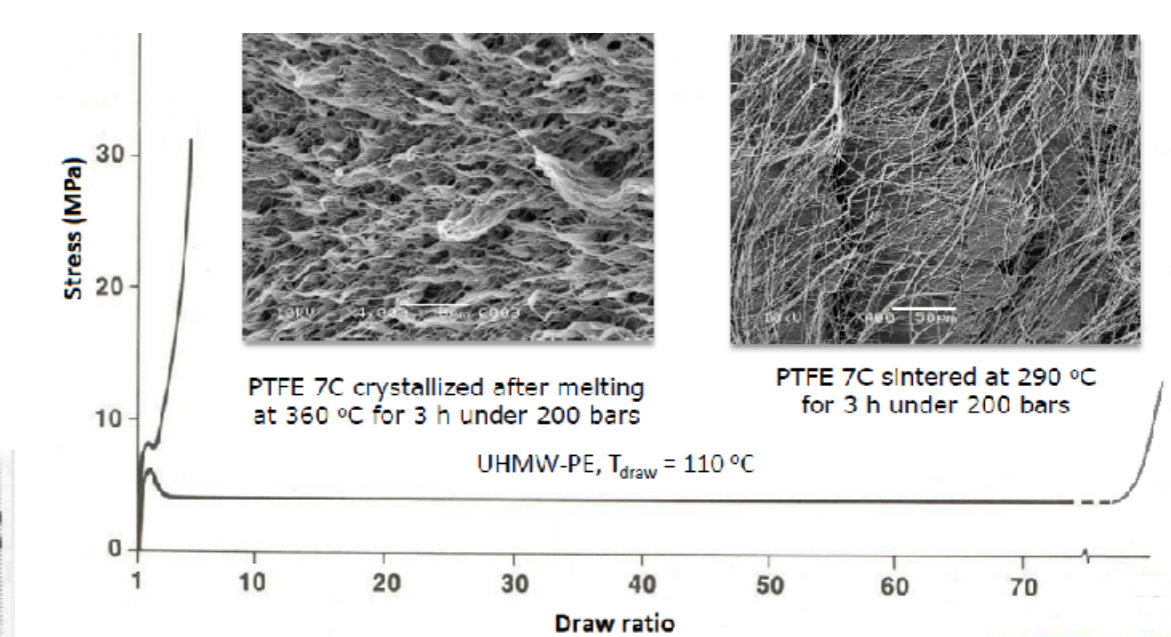
- CRSS of each PTFE slip system,
- Elastic moduli of PTFE,
- Temperature,  
 $T_{softening}(PS) = 170^{\circ}C < T < T_{melting}(PTFE) = 327^{\circ}C$
- Shear rate,
- Time,
- Capillary number :  
 $Ca = \frac{\tau R}{\sigma} = \frac{\dot{\gamma} R}{\sigma}$  with  $\sigma$  surface tension, R diameter of the inclusion and  $\tau$  shear force.



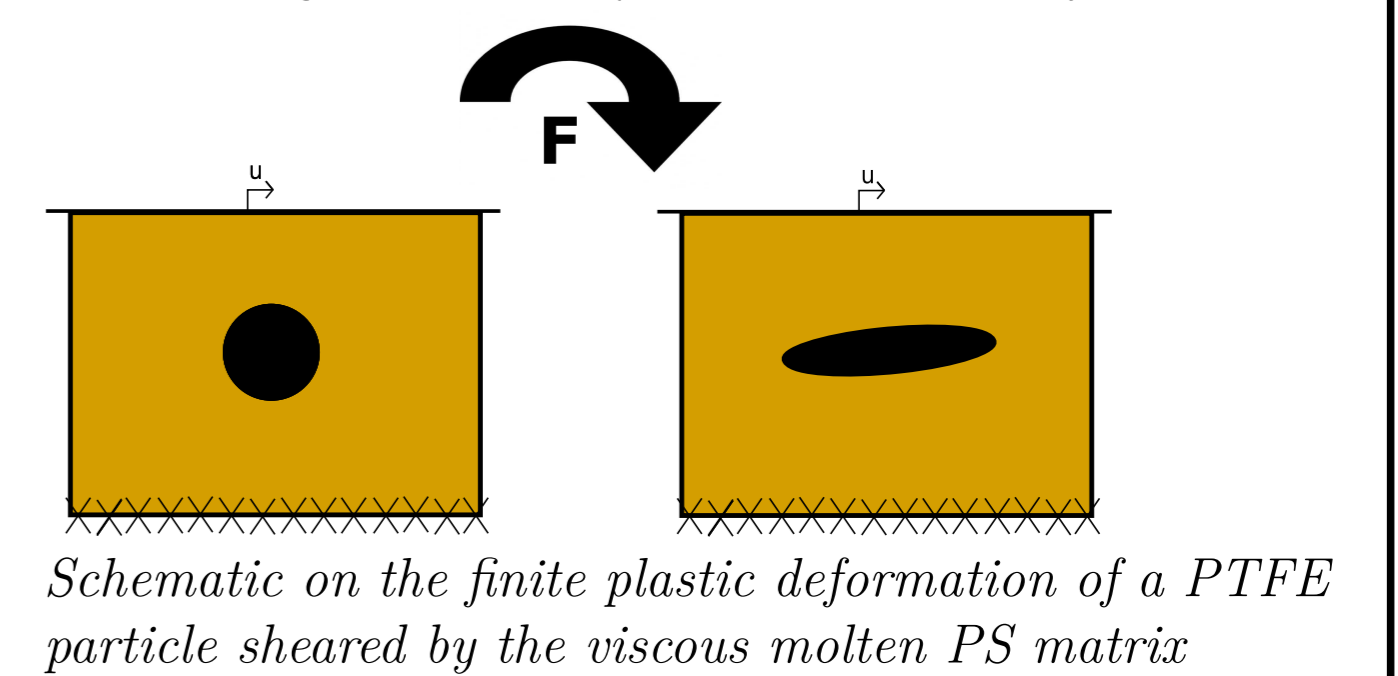
Hexagonal structure of crystalline phase IV of PTFE



Effect of the capillary number<sup>10</sup>



No hardening properties of nascent PTFE crystals<sup>4</sup>



Schematic on the finite plastic deformation of a PTFE particle sheared by the viscous molten PS matrix

## Conclusions and outlook

- Numerical implementation of crystal viscoplasticity framework within CNEM,
- Modelling the nanofibrillation process via viscous shearing for disentangled polymer,
- Development of a numerical predictive tool for the nanofibrillation process.

<sup>3</sup>[Loos al., 2002] J. Loos, M. Arndt-Rosenau, U. Weingarten (2002), P.J. Lemstra, Volume 48, issue 2, pp 191-198.

<sup>4</sup>[Jurczuk al., 2013] K. Jurczuk, A. Galeski, E. Pjorkowska, (2013), Polymer, Volume 54, Issue 17 pp 4617-4628.

<sup>5</sup>[Hikosaka al., 2005] Hikosaka. et al. (2005), Adv.Polym.Sci. 191, pp 137-186.

<sup>6</sup>[Rice al., 1971] Rice J.R., (1971), J. Mech. Phys. Solids, Volume 19, pp 433-455.

<sup>7</sup>[Yvonnet al., 2003]Yvonnet et al. (2003), International journal for numerical methods in engineering, Volume 60, Issue 8, pp 1451-1474.

<sup>8</sup>[lloul al., 2011]L. lloul, P. Lorong, (2011), Computer & Structures, Volumer 89, Issue11-12, pp 940-958.

<sup>9</sup>[Manas-Zloczower, Ica, 2009] Manas-Zloczower, Ica, (2009), 2nd edition, Carl Hanser Verlag GmbH & Co. KG .