



Eccomas Congress 2020



& 14th WCCM

Virtual Congress 11-15 January, 2021

Deformation of spherulitic semi-crystalline polymers: phase field – mechanic coupling

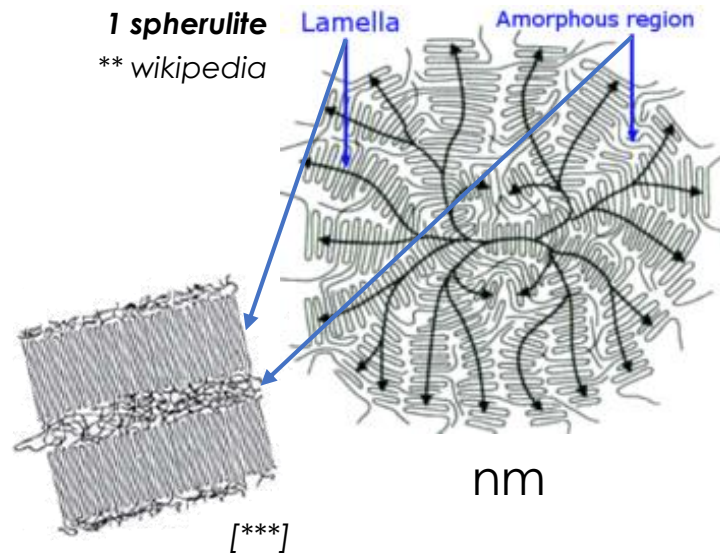
Marc Cornu (*PhD*), Julien Boisse (*associate p.*), Stéphane André (*professor*),
Laboratory of **E**nergetics, **T**heoretical and **A**ppplied **M**echanics

LEMTA

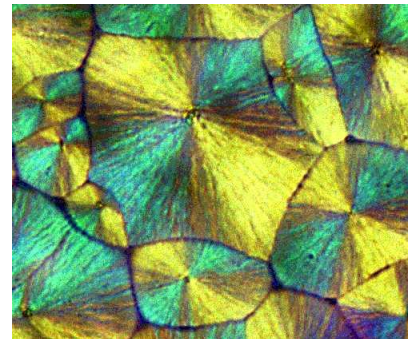


Study materials

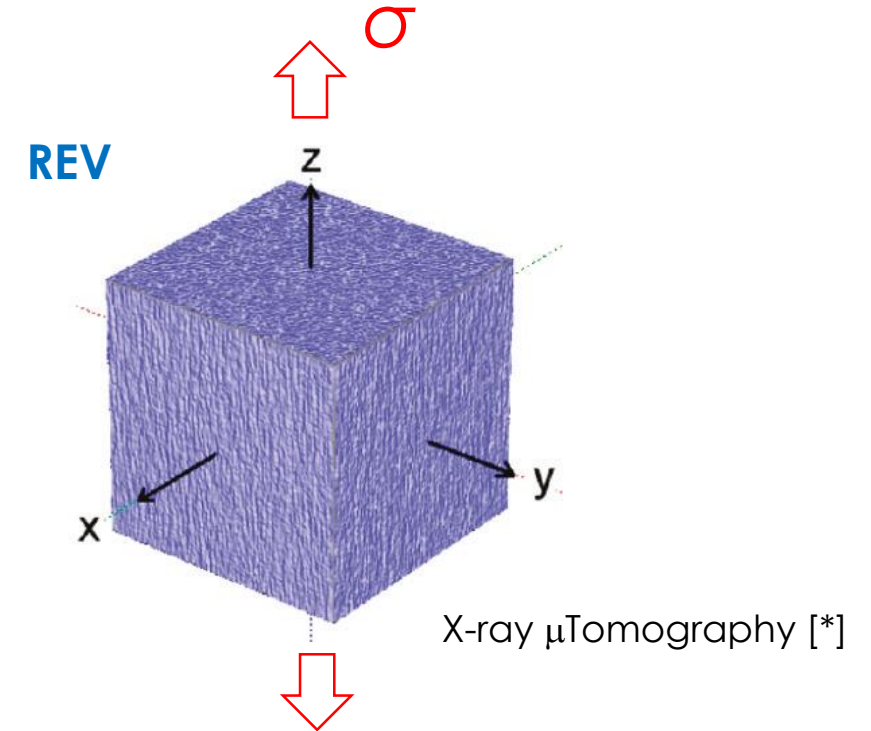
Semi-Crystalline Polymers (SCPs)



spherulitic structure



micron



scale-dependent structure

J.M. Schultz. Review : Deformation mechanisms in crystalline polymers. *Polym.Mat.Sci.*, pages 2034–51, 1974.

*

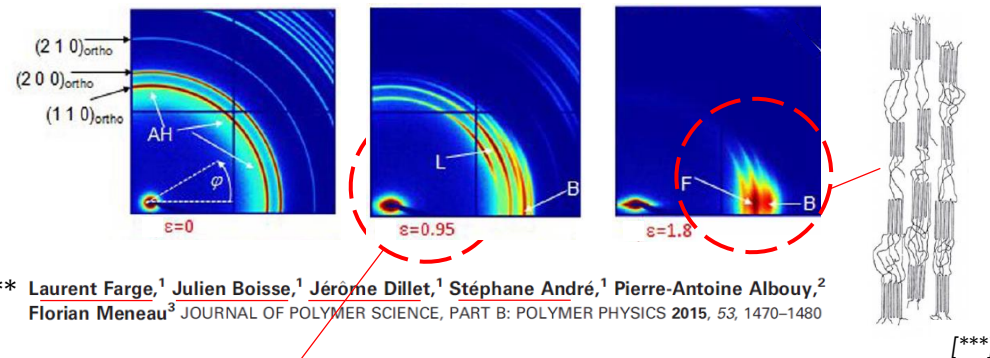
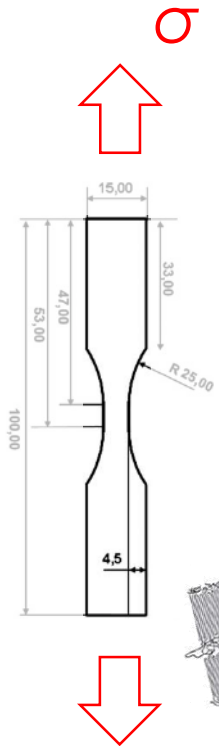
Arnaud Blaise,[†] Christophe Baravian,[†] Stéphane André,^{**†} Jérôme Dillet,[†] Laurent J. Michot,[‡] and Rajmund Mokso[§] *Macromolecules* **2010**, 43, 8143–8152

Experimental facts and motivations

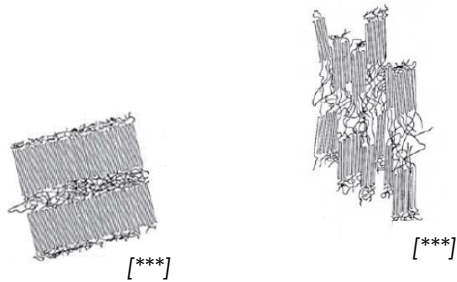
Examples: High Density PolyEthylene (HDPE)

crystal breaking and fibrillation

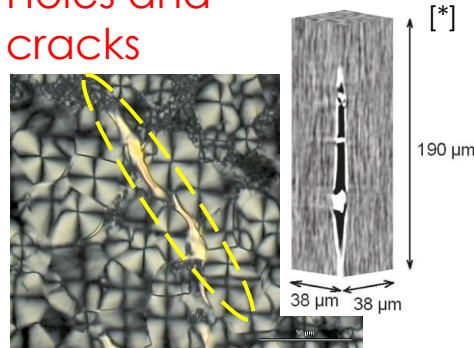
Wide Angle X-ray Scattering (WAXS)



** Laurent Farge,¹ Julien Boisse,¹ Jérôme Dillet,¹ Stéphane André,¹ Pierre-Antoine Albouy,² Florian Meneau³ JOURNAL OF POLYMER SCIENCE, PART B: POLYMER PHYSICS 2015, 53, 1470-1480



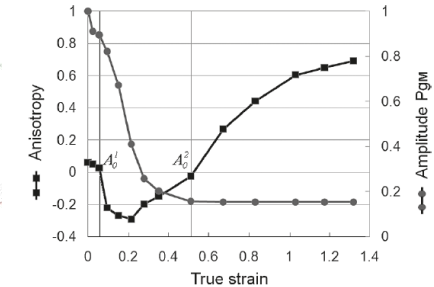
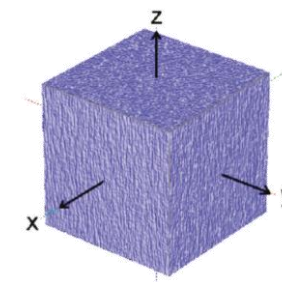
Holes and cracks



**** https://commons.wikimedia.org/wiki/File:Spherulites_with_crack.png

Anisotropy induced by scattering objects

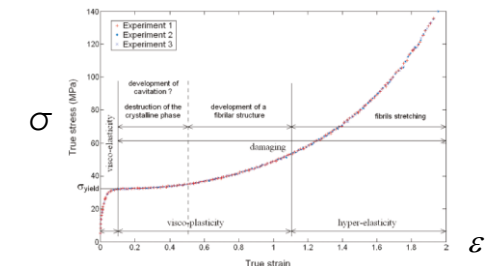
X-ray μ tomography
(AND polarized light scattering)



* Arnaud Blaise,[†] Christophe Baravian,[†] Stéphane André,^{**†} Jérôme Dillet,[†] Laurent J. Michot,[‡] and Rajmund Mokso[§] *Macromolecules* 2010, 43, 8143-8152

Objectives :

- describe the deformation micro-mechanisms and evolution of the microstructure
- transfer to the engineer's ladder



*** J.M. Schultz. Reviw : Deformation mechanisms in crystalline polymers. *Polym.Mat.Sci.*, pages 2034-51, 1974.



Objective

Phase Field (PF)

applied to the evolution of domains in micromorphic media

Order parameter $\eta =$

- density
- cavitation
- liquid-solid state

$$\frac{\partial \eta}{\partial t} = -L \frac{\delta F}{\delta \eta}$$

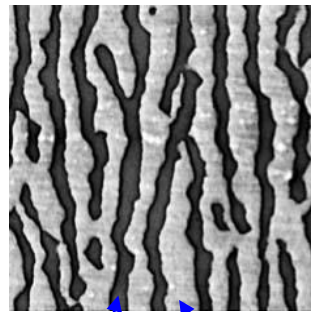
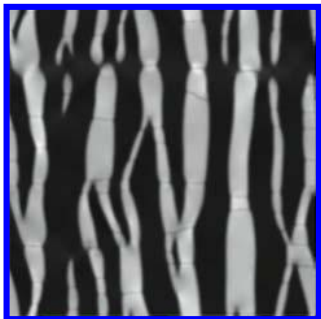
Free Energy $F =$

- Interface
- + elastic
- + plastic
- + Configuration energies

Energy Model :

- Molecular Dynamics
- Experiments (X-ray, light diffusion)

Example : Ni-Al Alloy
Under loading (creep)



phase field
Solid state phase transformation

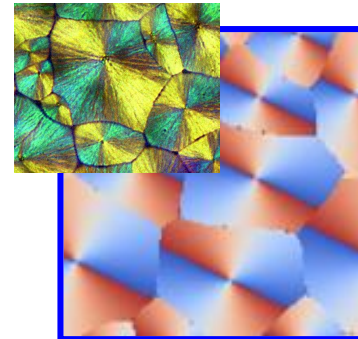
* A. Gaubert et al. Phil. Mag. 90 (2010) 375

deformation
of Polymers



« very few »
PF
applications

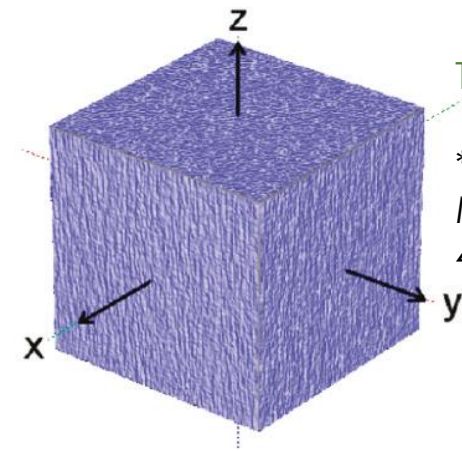
Spherulitic
structure



Phase field
solidification

** marc Cornu 2018

PSC large strain



Tomo. X-ray

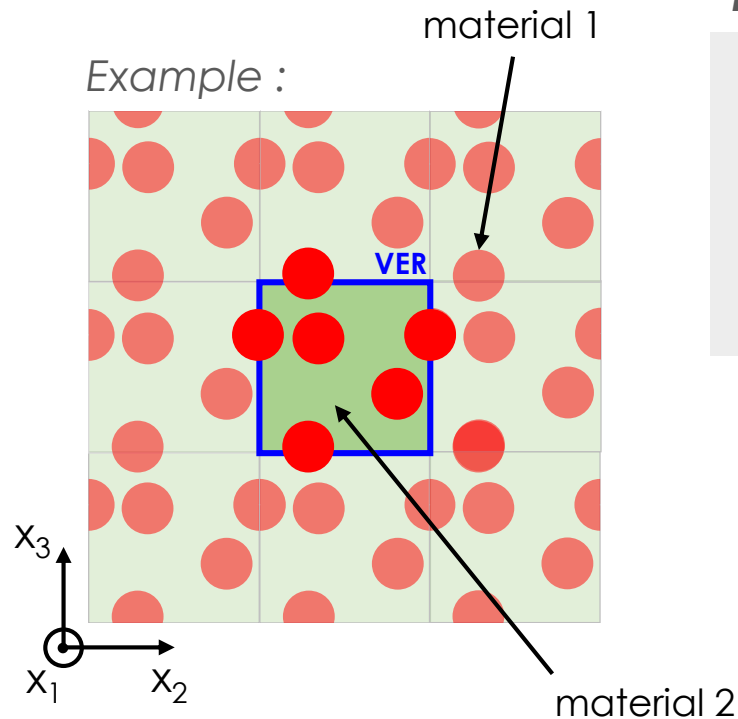
*** A. Blaise,
Macromolecules
43 (2010) 8143

Tools

spectral methods / FFT codes for mechanics

* Moulinec et Suquet (1994)

Heterogeneous material with Periodic boundary conditions



$$e(\mathbf{r}) = de(\mathbf{r}) + \bar{e}$$

avec $\langle de(\mathbf{r}) \rangle = 0$

Mechanical equilibrium

$$\begin{cases} \sigma(\mathbf{r}) = c(\mathbf{r}) : \frac{e(\mathbf{r})}{\delta\varepsilon(\mathbf{r}) + \bar{\varepsilon}} \quad \forall \mathbf{r} \in V \\ \mathbf{div} \sigma(\mathbf{r}) = \mathbf{0} \quad \forall \mathbf{r} \in V \\ \bar{\varepsilon} = E + \text{periodicity} + \text{compatibility} \end{cases}$$

Stiffness Tensor of an equivalent homogeneous material $(^0)$

$$c(\mathbf{r}) = c^0 + dc(\mathbf{r})$$

Polarization field (periodic)

Rewriting : $s(\mathbf{r}) = c^0 : e(\mathbf{r}) + [s(\mathbf{r}) - c^0 : e(\mathbf{r})]$

$$\delta\varepsilon(\mathbf{r}) = -\Gamma^0(\mathbf{r}) * \tau(\mathbf{r})$$

$$\bar{\varepsilon} = E$$

Direct space

Lippman-Schwinger equation

$$\hat{e}(\mathbf{k}) = -\hat{G}^0(\mathbf{k}) : \hat{t}(\mathbf{k}) \quad \mathbf{k} \neq \mathbf{0}$$

$$\hat{e}(\mathbf{0}) = \bar{e} = E$$

Fourier space

Tools

spectral methods / FFT codes for mechanics

Simulation of Heterogeneous materials

- A "Representative" Elementary Volume
- A Behaviour Law for each constituent
- An "averaged" loading: uniaxial traction for example.
- ONE type of Boundary Conditions: Periodical, one of the least bad choice (materials science)

Natural trends

- Increasing spatial resolution to better describe local fields
- Increase the size of REVs (representativeness of complex materials)
- Behaviours with more complex "physical bases"
- Towards non-local, multi-physics, code coupling (e.g. phase field)

Finite Elements (FE) Solvers (Standard)

- Limitations quickly reached (size and calculation time)



Fast Fourier Transform « FFT » Solvers

- No meshing
Direct processing of real microstructures ("Tomo" /SEM" images) or models



Best suited for complex microstructures!

Much more efficient than standard EF solvers

- Easy to implement
- Well adapted for Parallelization

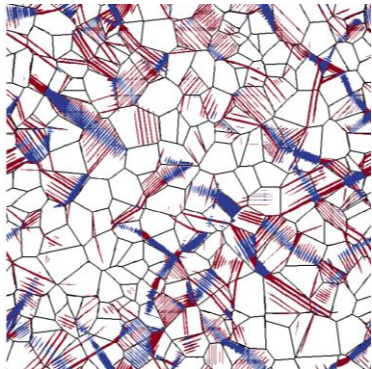
Tools

code : **AMITEX** efficient tool (massively //)
simulation behavior
of Heterogeneous Materials
 *Lionel Gélébard*



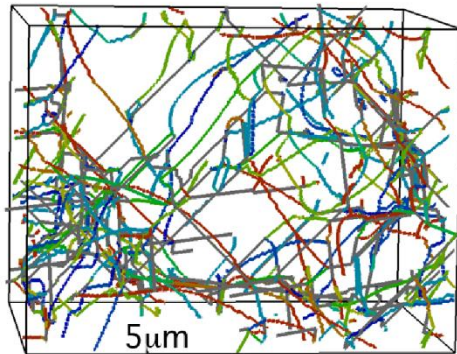
- Behavior law \Leftrightarrow **UMAT** (Abaqus, Cas3M, AMITEX ...)
- Large strain (Total Lagrangian)
- Numerous couplings under development:

Crystalline plasticity non-local



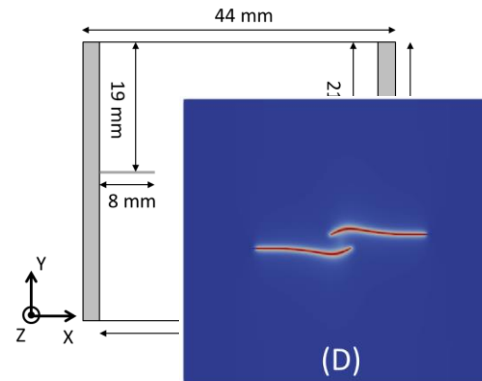
PhD Aldo Marano
(2019 - **CEA/SRMA**)

Dislocations Dynamics (DD)



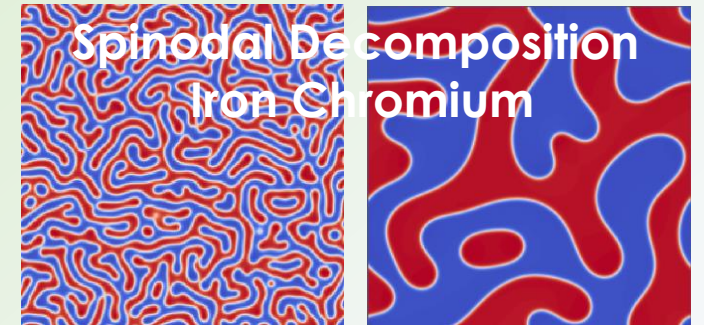
Post-doc Francesca Boioli
(**M4F/ONERA-CEA project**)

Phase Field for damage



Yang Chen
(**CEA/Oxford University**)

Phase Field for solid state Phase Transformation and diffusion



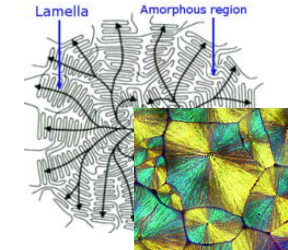
Julien Boisse ( / )

+ **PostDoc ANCRE**
Andrée DeBacker / january 1st 2021

 Phase Field for SCPs ???

Steps

Objective : describe the deformation micro-mechanisms and evolution of the spherulitic microstructure



AMITEX

<http://www.maison-delasimulation.fr/projects/amtex/html/index.html>

1 **Design**
of a Typical Spherulitic
microstructure

Tool : Neper
<https://neper.info/>

2
Mécanique
pure

development of a
viscoelastic behavior law

Tool : AMITEX
Format : UMAT (fortran95)

PhD Marc Cornu (2018-2021)

3
couplage **Modeling**
of microstructure evolution
mechanisms

model:
Phase field/mechanical
coupling

development : AMITEX
+ Postdoc 1y January 2021

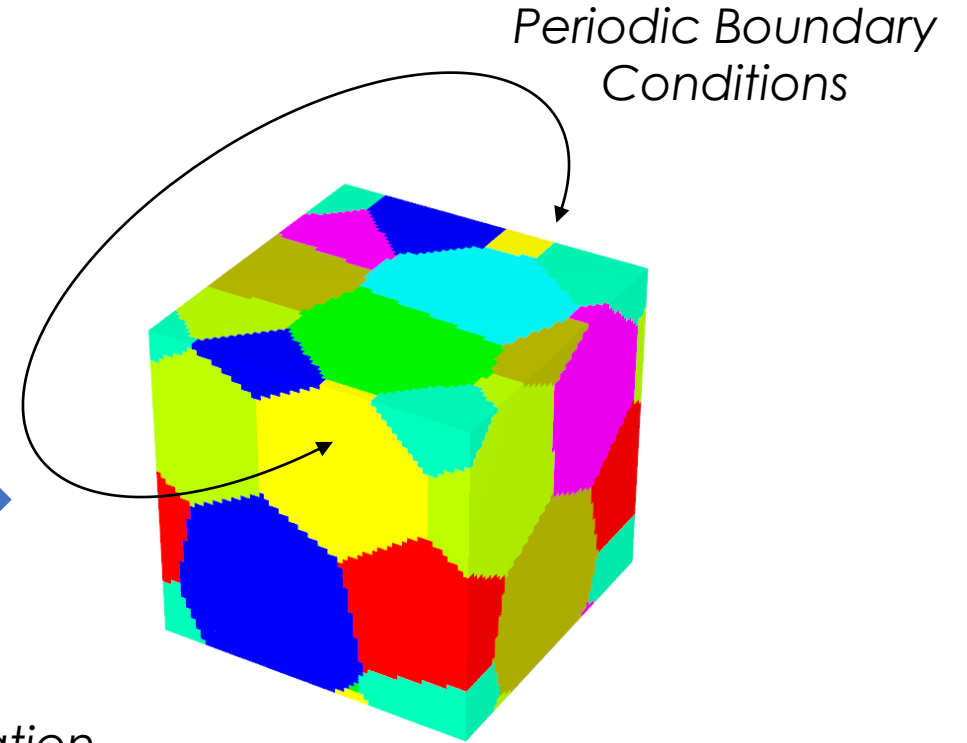
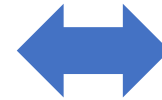
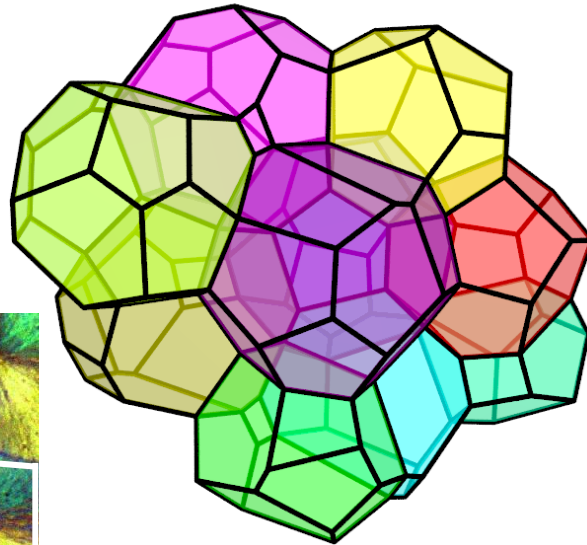
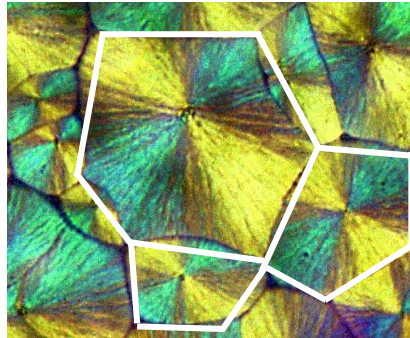




Design of a typical microstructure

... on the scale of **several spherulites**

“Multigranular”
structure
several spherulites



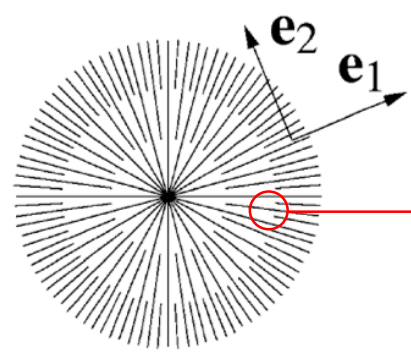
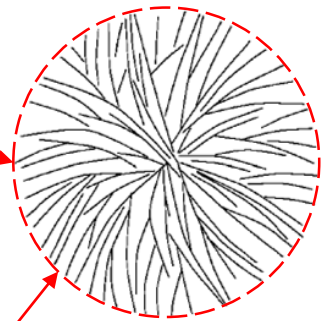
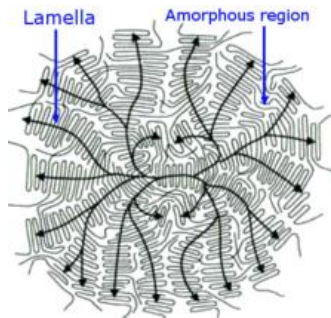
Neper : Polycrystal Generation
and Meshing
* <https://neper.info/>

**Example : 10 Spherulites with Periodic Boundary Conditions
for use in an FFT Code**

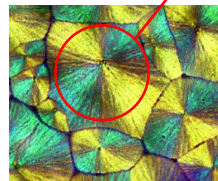
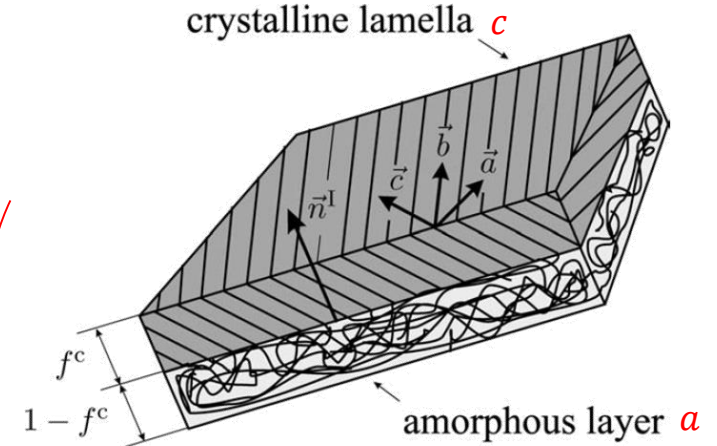


Design of a typical microstructure

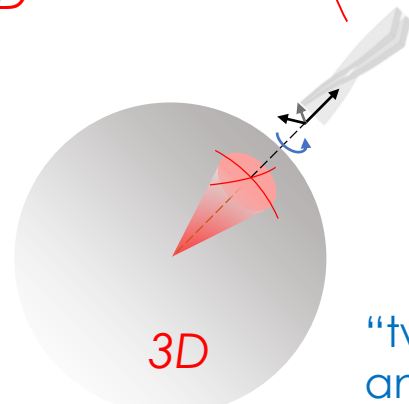
... on the scale of a **single spherulite**



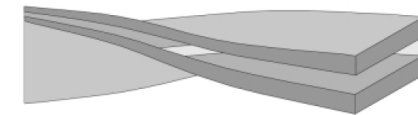
2D



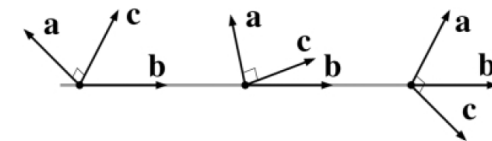
amorphous
"between 2" spherulites



3D



(a)



"twisting" of a lamella
and crystal orientation

* Allan P, Bevis M. Phil Mag 1977;35:405–30.

Spherulite structure and simplified model

* Allan P, Bevis M. Phil Mag 1977;35:405–30.

** Gautam S, Balijepalli S, Rutledge GC. Macromolecules 2000;33:9136–45.

2

development of a viscoelastic behavior law

... on the scale of **several lamellae**

mechanical properties ?

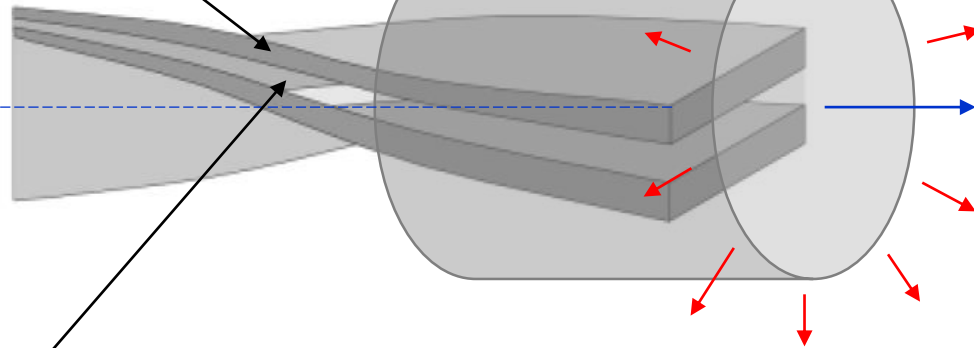
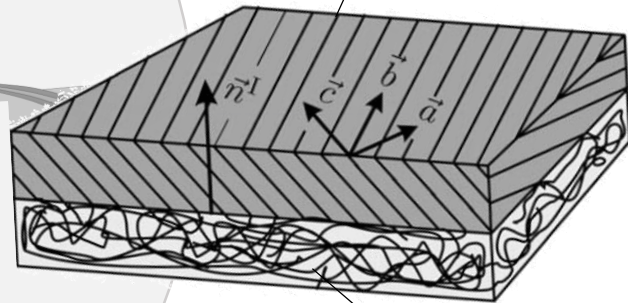
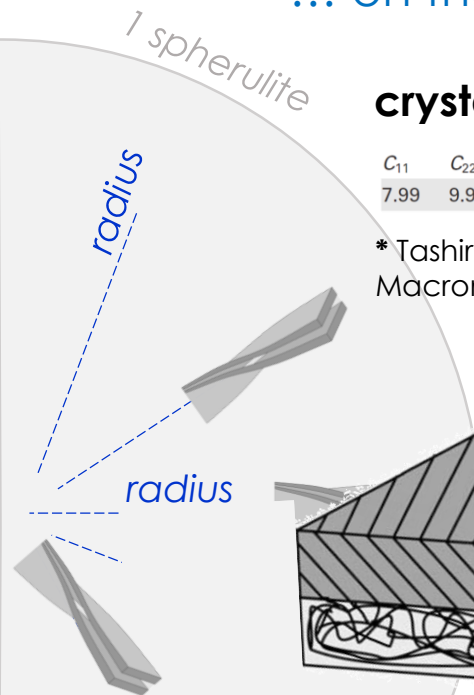
crystal orthotropic elastic

C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}
7.99	9.92	315.92	3.28	1.13	2.14	3.62	1.62	3.19

* Tashiro, K.; Kobayashi, M.; Tadokoro, H. *Macromolecules* 1978, 11, 914–918.



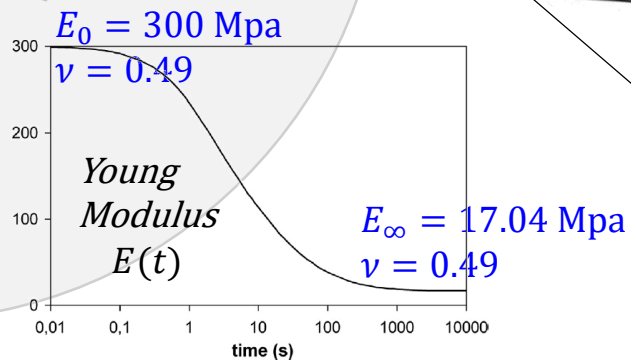
... approximation / homogenization
viscoelastic transversal isotropic



Voigt notation

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & & & & & & & \\ & C_{22} & C_{23} & & & & & & & 0 \\ & & C_{33} & & & & & & & \\ & & & C_{44} & & & & & & \\ \text{sym} & & & & C_{55} & & & & & \\ & & & & & C_{66} & & & & \end{bmatrix}$$

$$\frac{C_{33} - C_{23}}{2} = C_{66}$$



Amorphous viscoelastic isotropic

** J.M. Teixeira Pinto et al., *International Journal of Fatigue* 54 (2013) 133–142

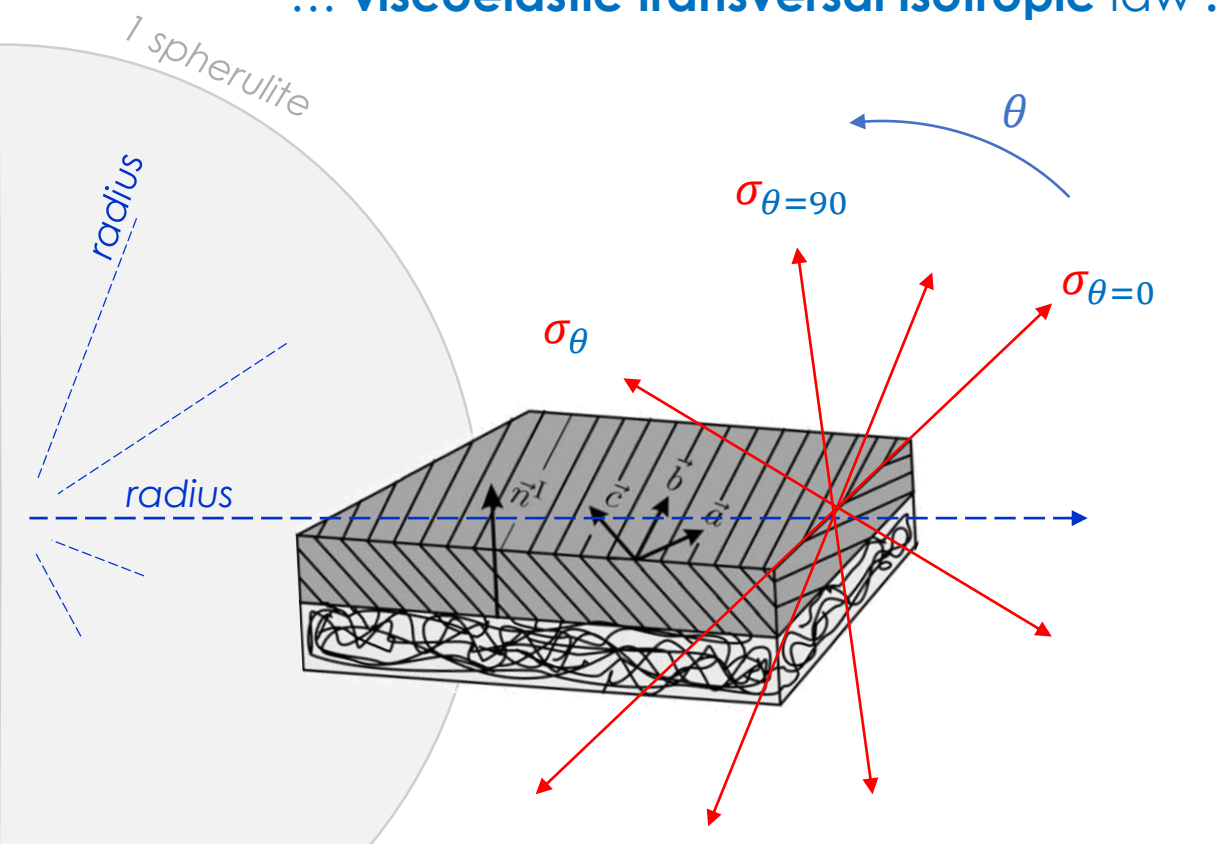


- 5 long time elastic parameters
- 5 short time elastic parameters
- 5 corresponding relaxation times

2

development of a viscoelastic behavior law

... viscoelastic transversal isotropic law : **parameters ?**



Multiples tensile mechanical tests
on 1 lamella (crystal/amorphous)

With FFT **code** AMITEX

FFT computations

$$\bar{\sigma}_{\theta} \Rightarrow \bar{\epsilon}_{\theta}$$

$\bar{\mathbf{C}}_{\theta}$ **1 Stiffness matrix (monoclinic) for each angle**

average over all angles θ

Result : transversal isotropic

5 short time elastic parameters

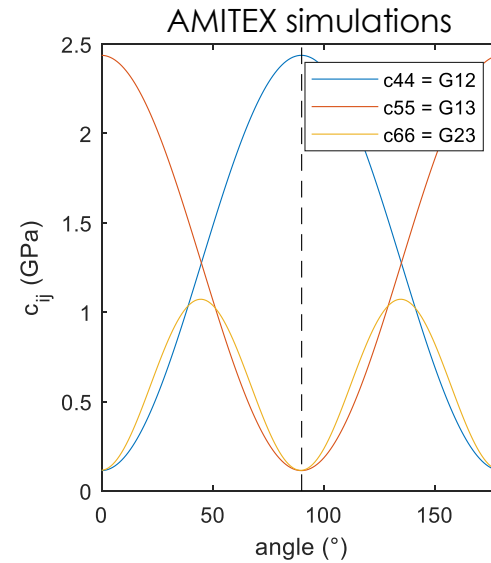
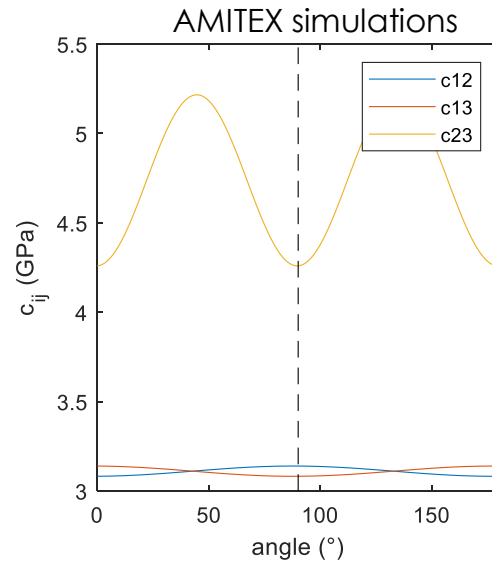
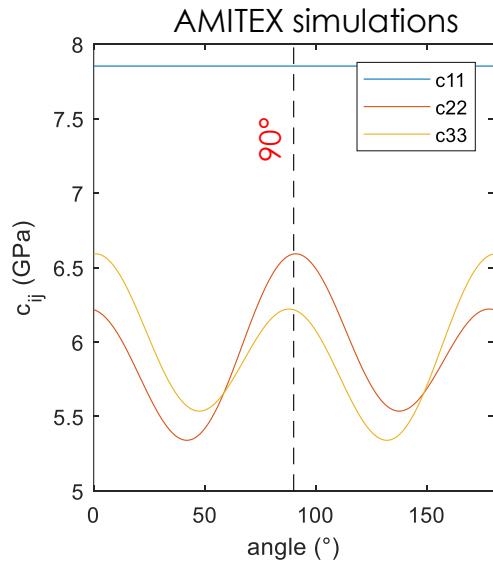
$$\langle \bar{\mathbf{C}} \rangle_{\theta} = \begin{bmatrix} 7.8524 & 3.1108 & 3.1108 & & & & \\ 3.1108 & 5.9257 & 4.7377 & & & & \\ 3.1108 & 4.7377 & 5.9257 & & & & \\ & & & 1.2755 & & & \\ & & & & 1.2755 & & \\ & & & & & & 0.5940 \end{bmatrix} \text{ GPa}$$

+ same procedure for long times

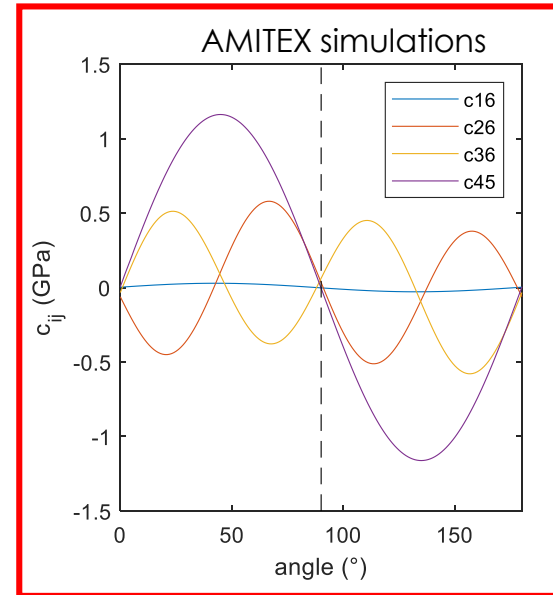
2 development of a viscoelastic behavior law

... viscoelastic transversal isotropic law : **parameters ?**

HDPE Lamella
70% crystal + 30% amorphous



Average = 0



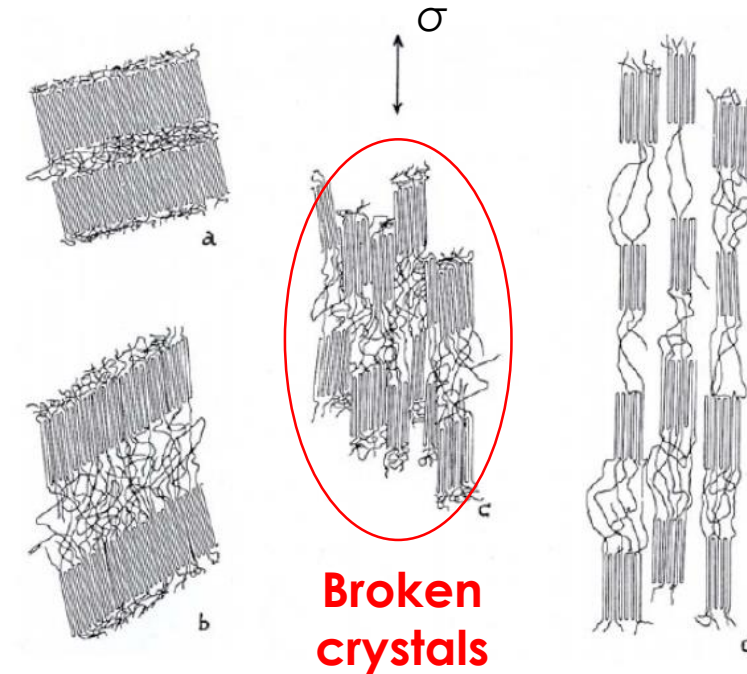
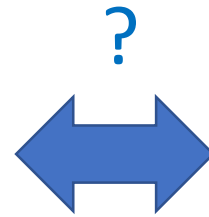
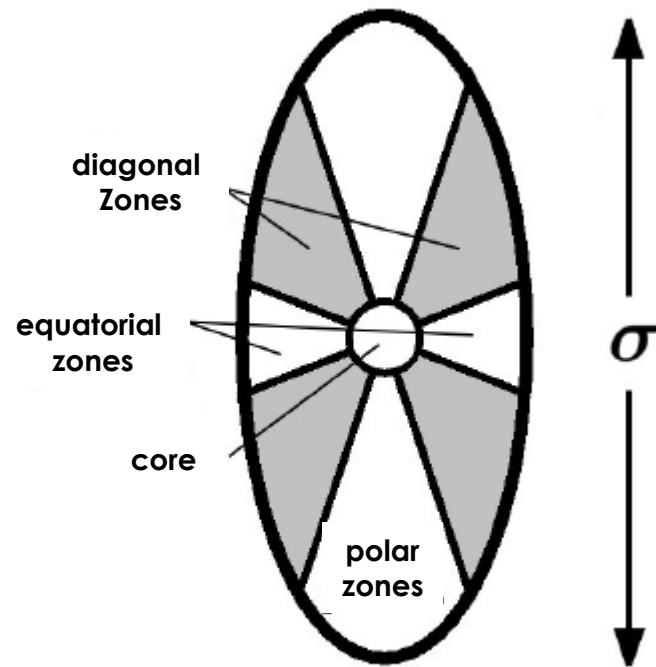
C_{ij} Stiffness 6x6 matrix as a function of angle θ of strain load (details)

$$\langle \bar{C} \rangle_{\theta} = \begin{bmatrix} 7.8524 & 3.1108 & 3.1108 & & & \\ 3.1108 & 5.9257 & 4.7377 & & & 0 \\ 3.1108 & 4.7377 & 5.9257 & & & \\ & & & 1.2755 & & \\ & & & & 1.2755 & \\ & & & & & 0.5940 \end{bmatrix} \text{ GPa}$$

3

toward the mechanical/phase-field coupling

Deformation of a spherulite



J.M. Schultz. Review : Deformation mechanisms in crystalline polymers. *Polym.Mat.Sci.*, pages 2034-51, 1974.

3

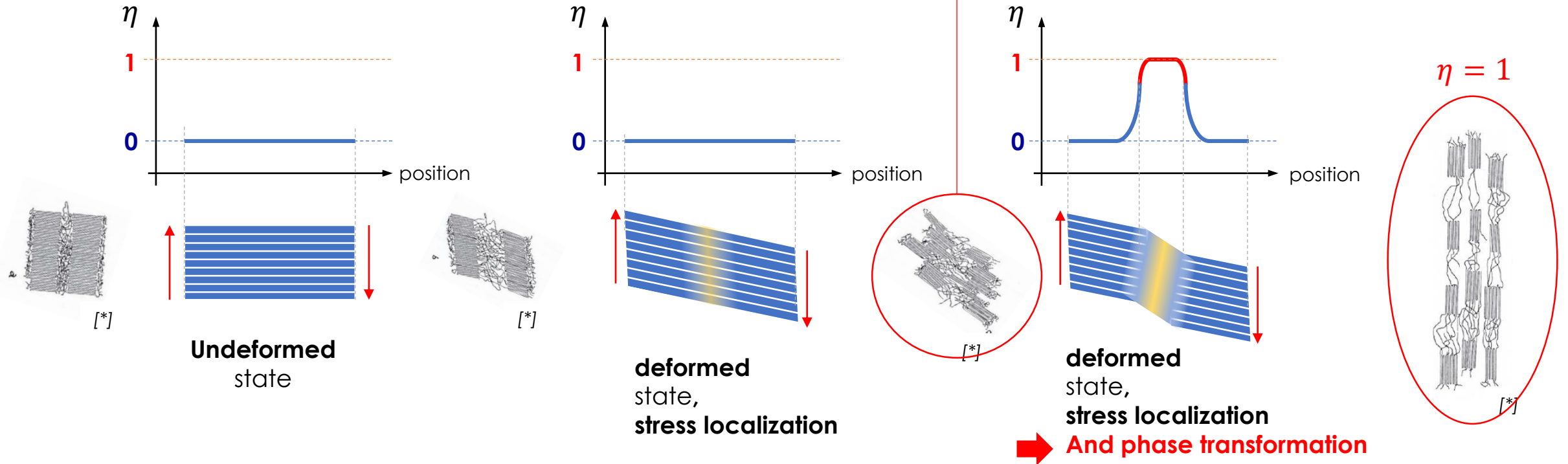
toward the mechanical/phase-field coupling

Definition of **1 state variable** reflecting the **damage** of the crystals at the scale of **several lamellae**

$$\eta \in [0,1]$$

$\eta = 0$ Viscoelastic transversal isotropic

$\eta = 1$ **“Amorphous”** viscoelastic isotropic + **“Broken”** crystals



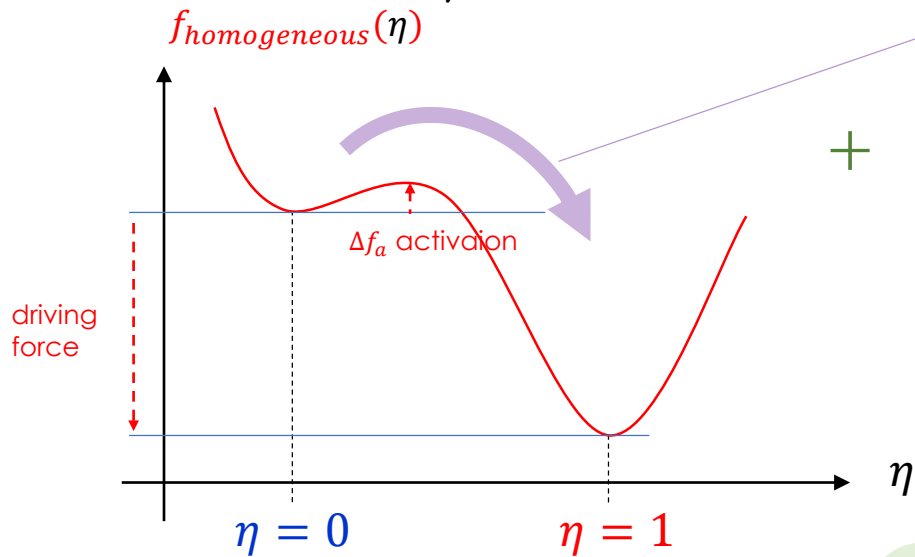
3

toward the mechanical/phase-field coupling

Development of the energy model: **Free Energy F**

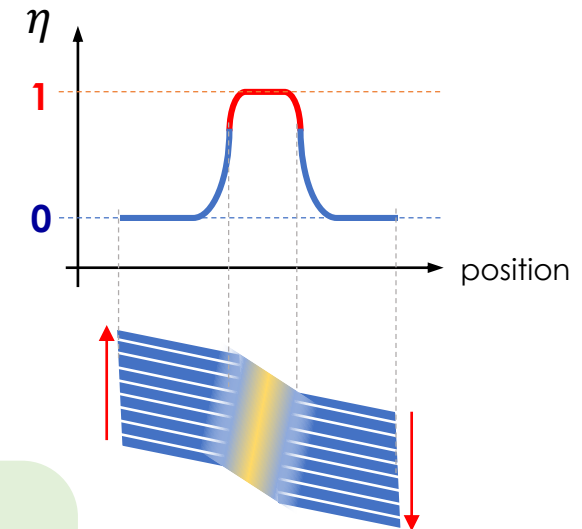
$$F = F_{total} = \int_V \{ f_{homogeneous} + f_{interface} + f_{mechanical} + \dots \} dV$$

1 voxel



+ Kinetic law
Ginzburg-Landau

$$\frac{\partial \eta}{\partial t} = -L \frac{\delta F}{\delta \eta}$$



usually $f_{homogeneous}$ is approximated with a polynôme

AMITEX

TODO ! under Development

...



Thank You !

