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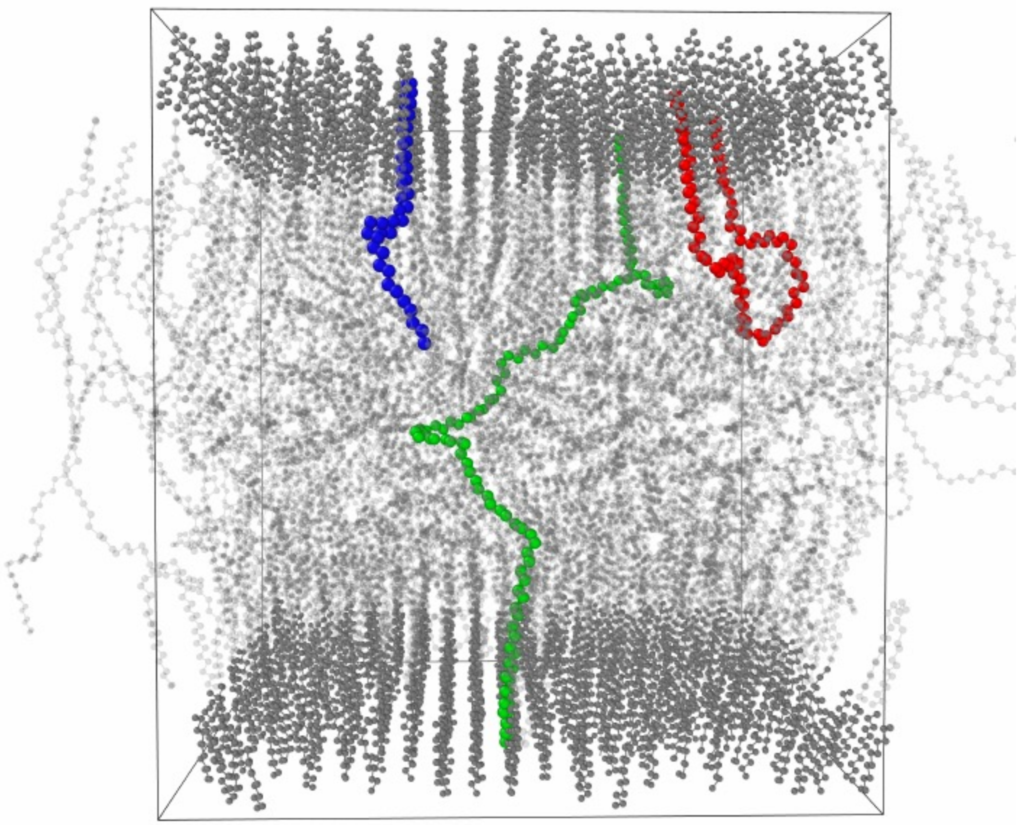
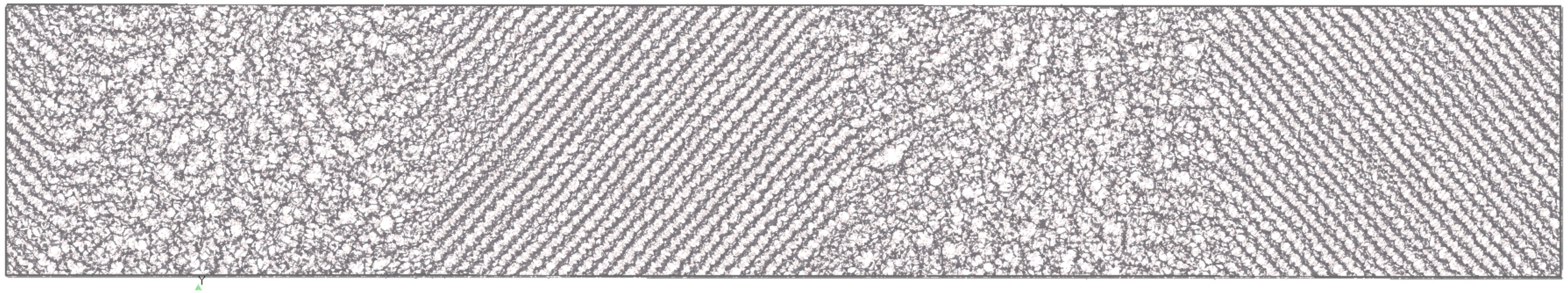
Advancing Molecular-Scale Modeling: A Novel Approach for Semicrystalline Polymers



Speaker: Dr. Boris Belin



February 20th-22nd, 2024

Materials Design Webinar Series

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full screen

during discussion:
raise hand
to speak

Use the raise hand icon to bring attention to your question

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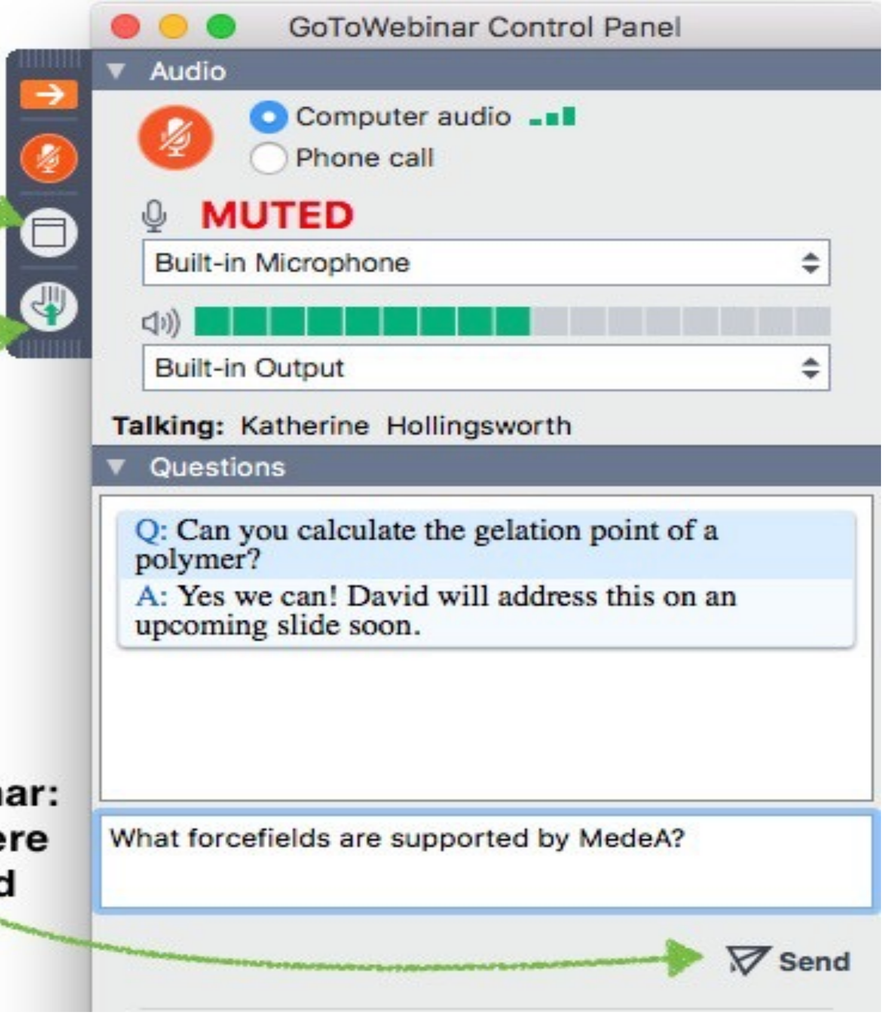

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Webinar Speakers

Katherine Hollingsworth

Dr. Dave Rigby

Dr. Marianna Yiannourakou

Presenter: Dr. Boris Belin

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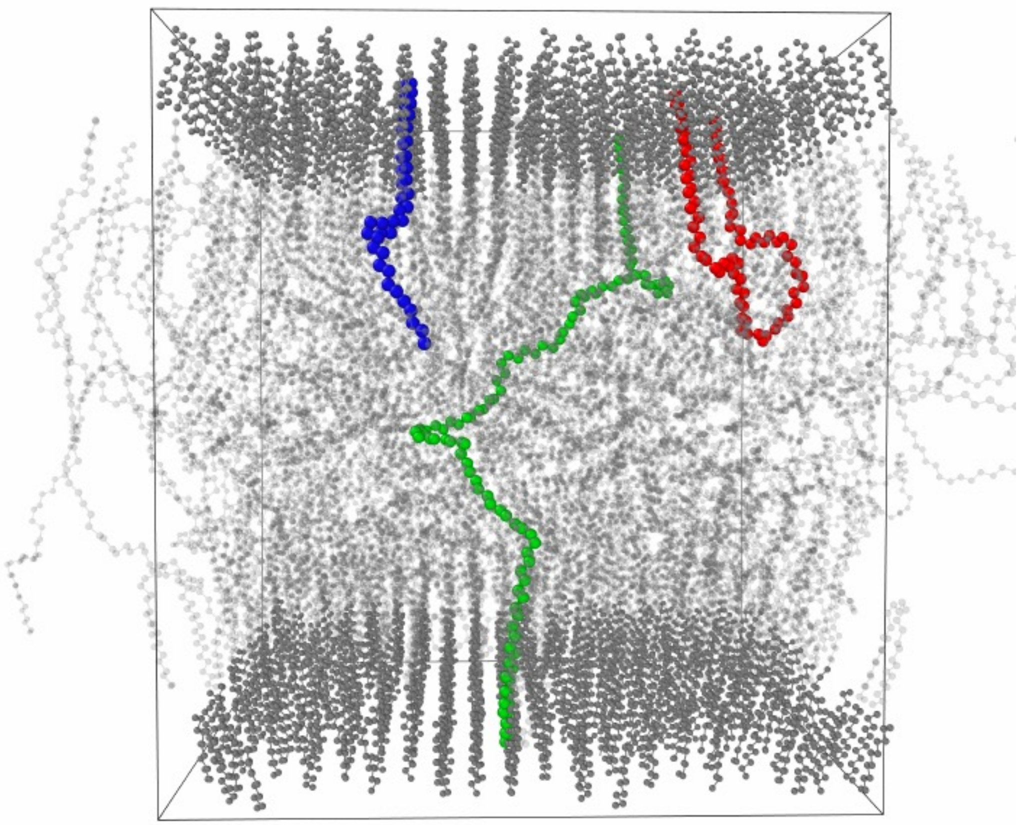
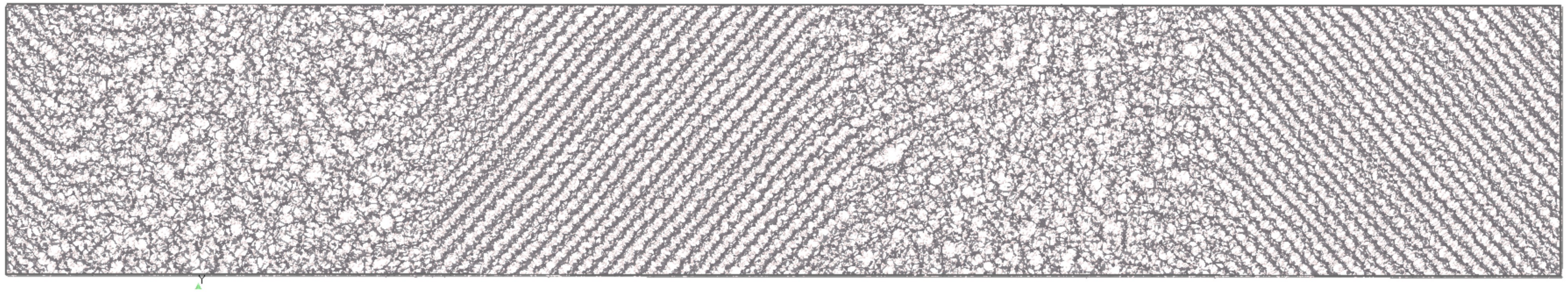


Advancing Molecular-Scale Modeling: A Novel Approach for Semicrystalline Polymers

Speaker: Dr. Boris Belin

February 20th-22nd, 2024



Outline

- **Some elements of semicrystalline morphology.**
  - Experimental
  - Theoretical

- **Building semicrystalline structures in MedeA.**
  - General overview of the building procedure
  - Application to HDPE using statistical polymer physics
  - Characterizations

- **Mechanical properties calculation**
  - Uniaxial elastic coefficients
  - High deformations and stress transmitters

Semicrystalline polymer in industry

Ubiquitous !

Many properties of interest accessible with molecular/atomistic simulation:

- **Mechanical** (molecular dynamic).
- **(non)-permeation** (Monte-Carlo, molecular dynamics).
- **Dielectric/electronic** (density functional theory).

Non-exhaustive industrial uses:

- Replace metals for mechanical properties.
- Protect food and tanks or pipes from corrosion.
- Electric insulator for wires or semiconductor in O-Led TV.

But building models is not trivial!

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Morphology

Experimental and theoretical

Spherulite and shish-kebab

- Semicrystalline polymer composed of amorphous and crystalline phase.

- At the microscale:

spherulite or shish-kebab (films, solidified under strain).

X-ray powder HDPE

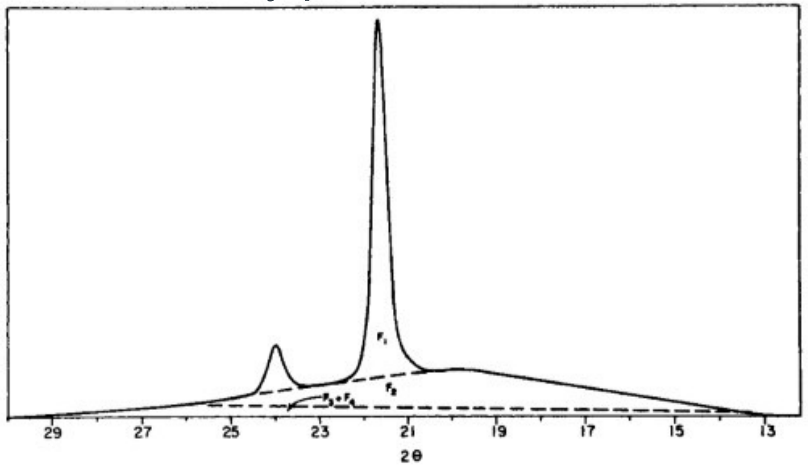
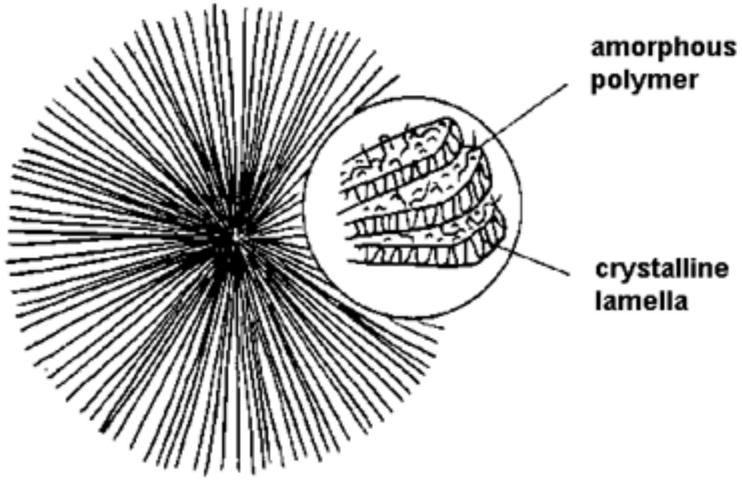
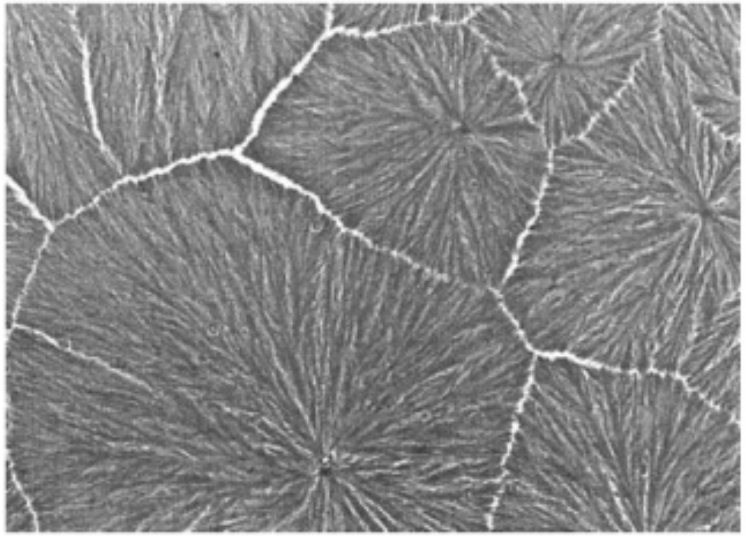


Fig. 1. X-ray diffraction pattern for linear polyethylene at room temperature. $M_\eta = 7 \times 10^6$; density = 0.9309.

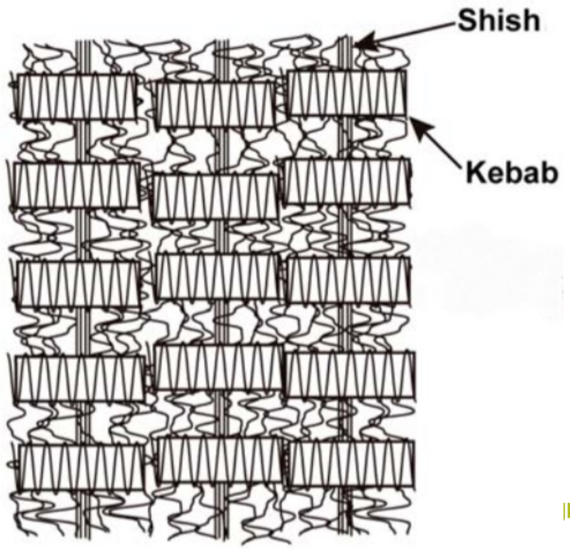
Spherulite



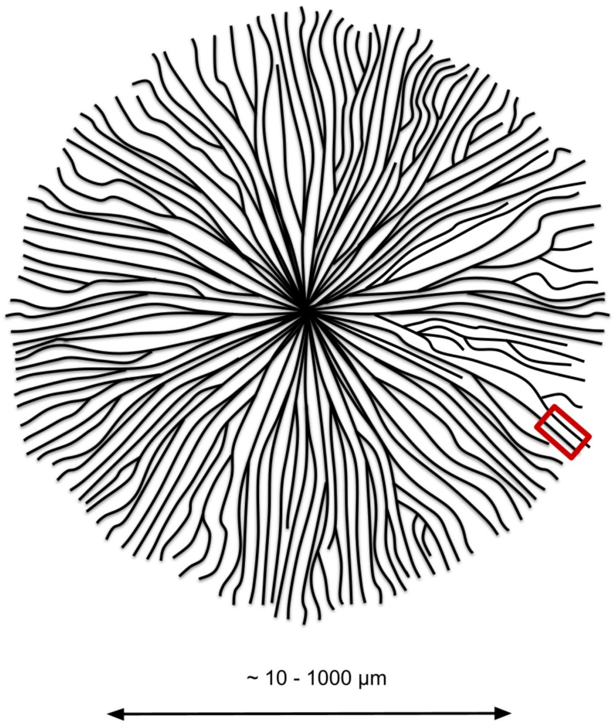
Spherulite under microscopy

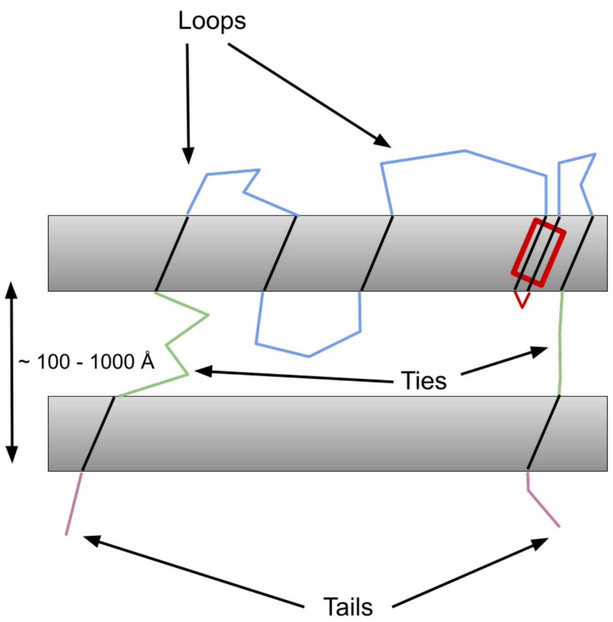


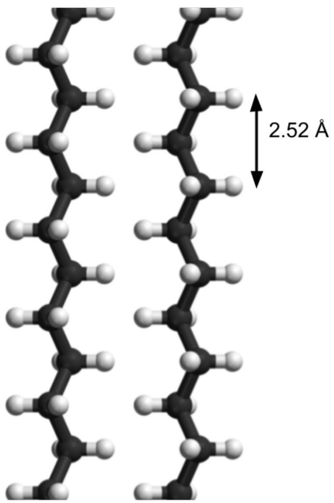
Shish Kebab



Morphological characterization

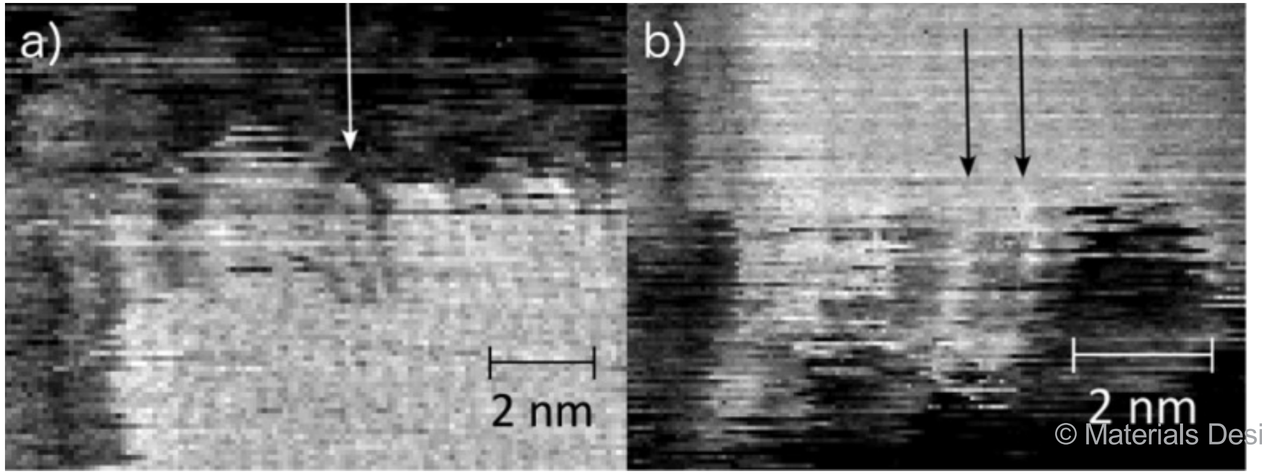






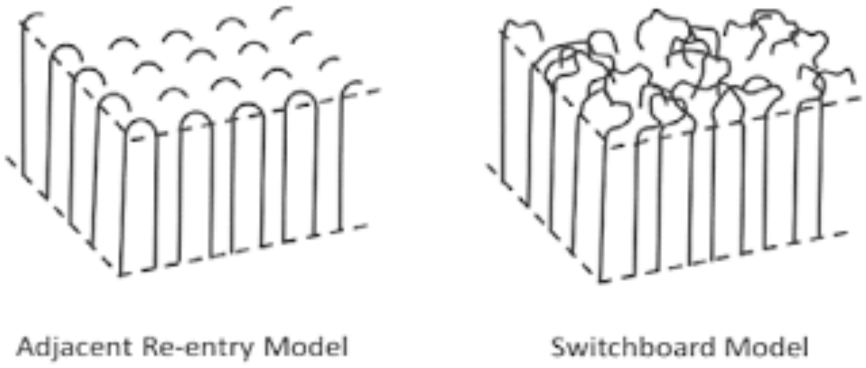
Characterization

- Density, long period, degree of crystallinity (χ), molecular weight.
- Tilt angle.
- Characterization of the amorphous section (tie chains, loops, tails).
- Characterization of the interphase (perfect foldings or not).



AFM study of the interphase.
R. C. Savage, N. Mullin, and J. K. Hobbs, Macromolecules (2015)

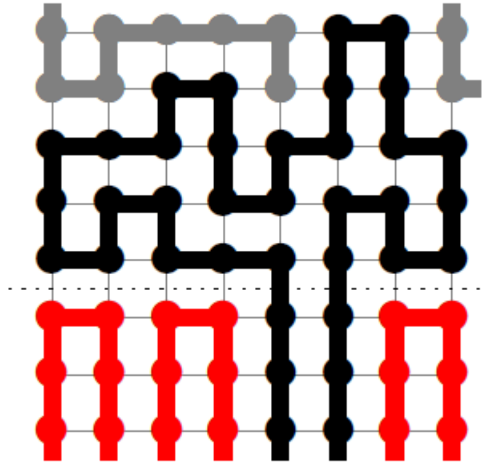
Theoretical treatment : folding in the interphase



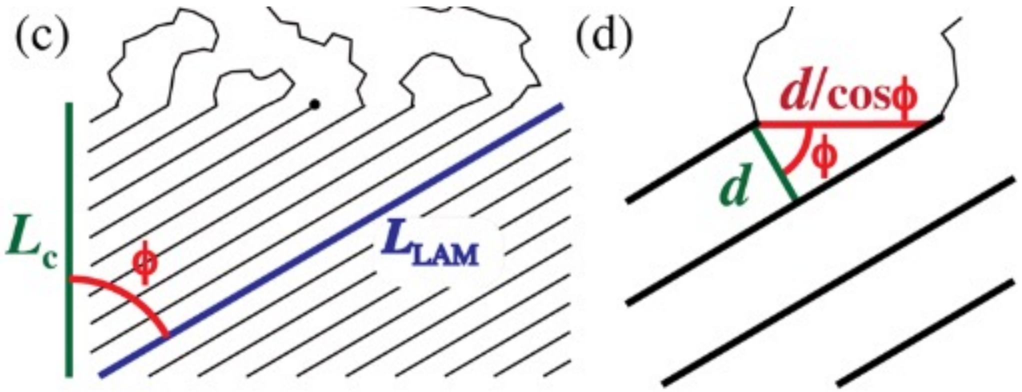
Flory et al. (1984) with $\rho_{amorph} = \rho_{crystal}$
- Orthogonal stems: 70% adjacent reentries:
  Adjacent reentry model
- Tilt angle: low proportion of adjacent reentries:
  Switchboard Model

Fritzsching et al. with $\rho_{amorph} < \rho_{crystal}$:
Switchboard Model
- Tilt angle
- Tails in the interphase
- Low proportion of adjacent reentries

Necessity of the adjacent reentries with orthogonal
with a 2D semicrystalline on a square lattice.



The tilt angle dissipates the density



Flory, P. J.; Yoon, D. Y.; Dill, K. A. *Macromolecules* **1984**, *17* (4), 862–868
Yoon, D. Y.; Flory, P. J. *Macromolecules* **1984**, *17* (4), 868–871.
Fritzsching, K. J.; Mao, K.; Schmidt-Rohr, K. *Macromolecules* **2017**, *50* (4), 1521–1540.

An new approach to generate semicrystalline models:

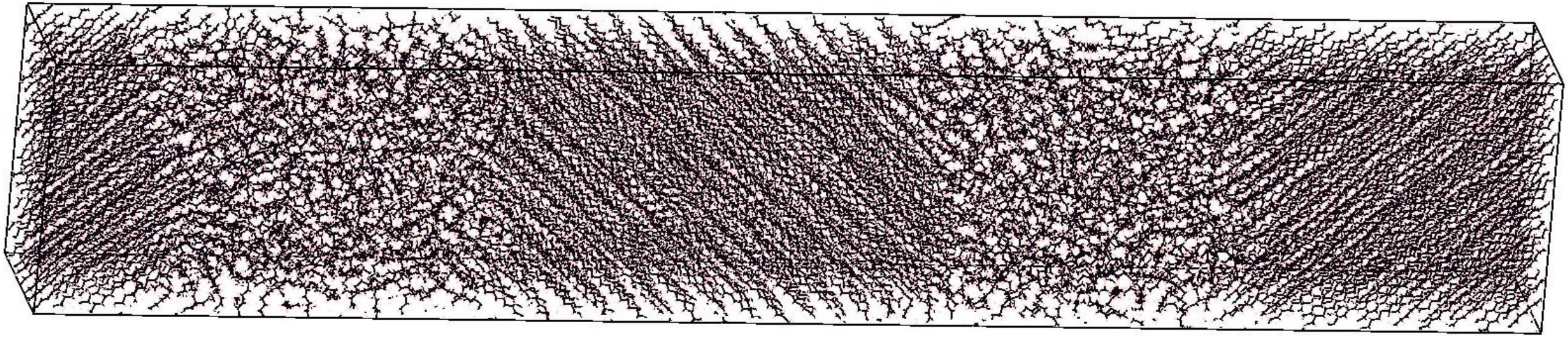
Modeling Method for Semicrystalline Polymers Controlling Aspects of the Morphology at the Molecular Scale for the Study of Mechanical and Physicochemical Properties

Boris Belin, Marianna Yiannourakou, Véronique Lachet, and Bernard Rousseau

The Journal of Physical Chemistry B **2022** *126* (46), 9673-9685

Overview of the method: general idea (1)

HDPE semicrystalline model with periodic boundary conditions

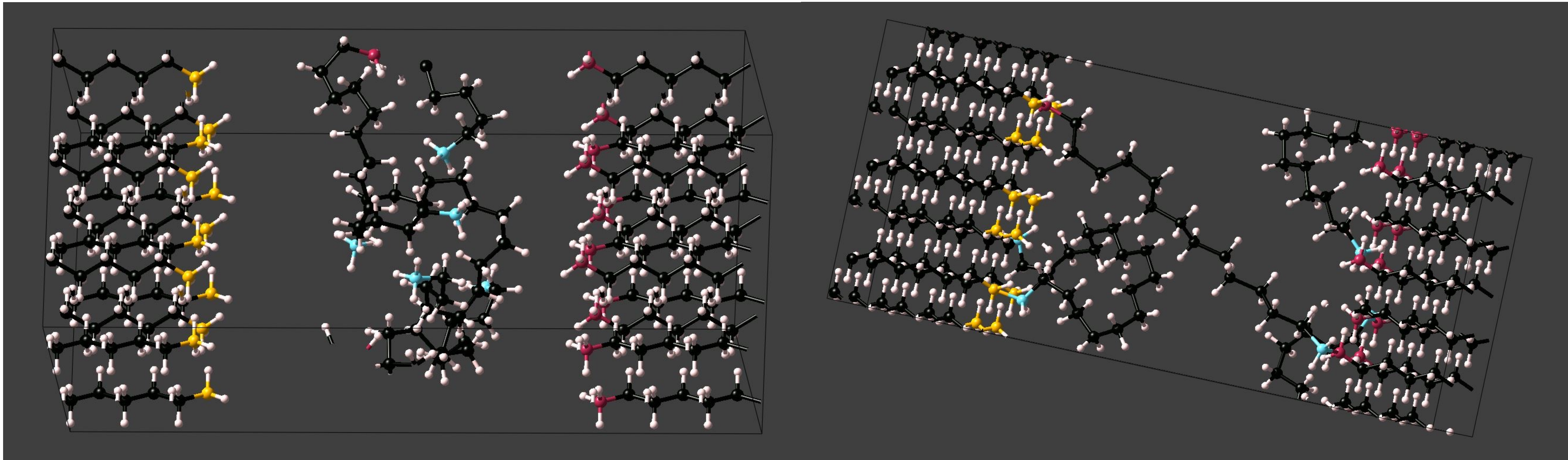


Goals: Build realistic semicrystalline structures at the scale of the long period.

Means: Connect an amorphous and a crystalline phase.

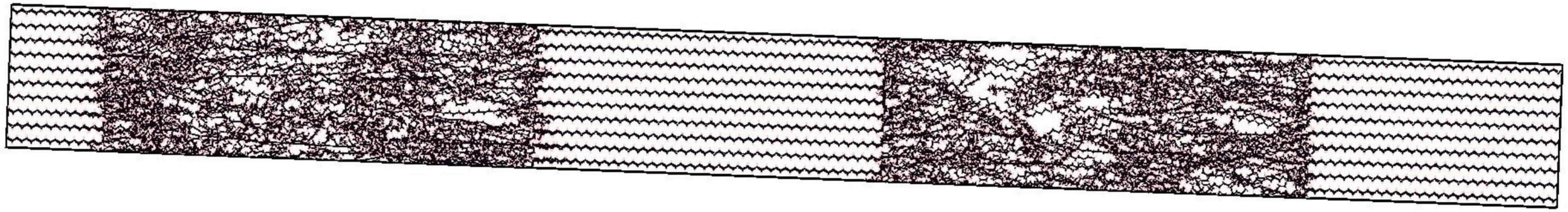
Overview of the method: toy model for the connection procedure (2)

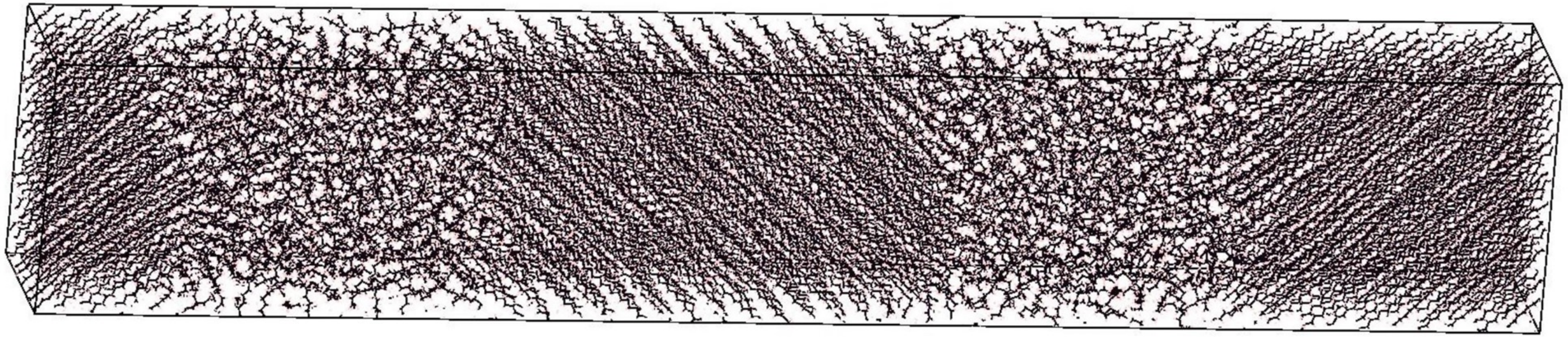
- Build a crystal layer (supercell from the primitive cell with crystallographic data).
- Build an amorphous layer with the *MedeA Amorphous Builder*.
- Labelling of the chain ends of the crystal layer and the amorphous chain.
- Stack the amorphous chains and the crystal.
- Connection with the *MedeA Thermoset Builder* according to a connection matrix.



Overview of the method (3) : Realistic HDPE system.

- **Hypothesis** : We know the distribution of size and type of the amorphous chain sections (tie chains, loops, tails), from experimental data or from a statistical polymer physics theory.
- With the **MedeA Amorphous Builder**, build an amorphous layer correctly labelled (depending of types). Build a supercell layer of the crystal with labelled chain ends.
- Connection and long relaxation (100 ns, ff TraPPE-UA), (AFTER Connection only two long chain left with realistic molecular weight : ~10 000 CH_2 groups, Mw 140 000 g/mol (30 000 to 6 000 000 g/mol in exp.).





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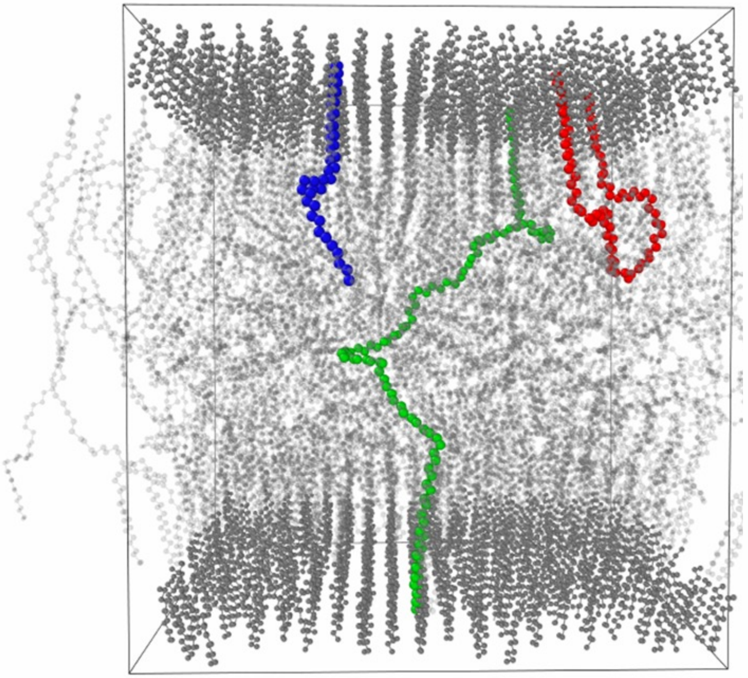
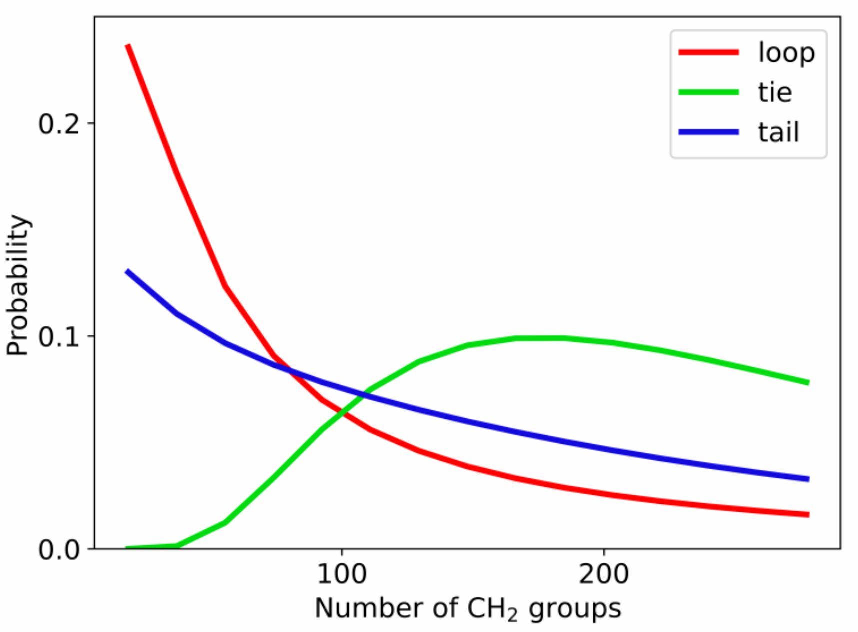
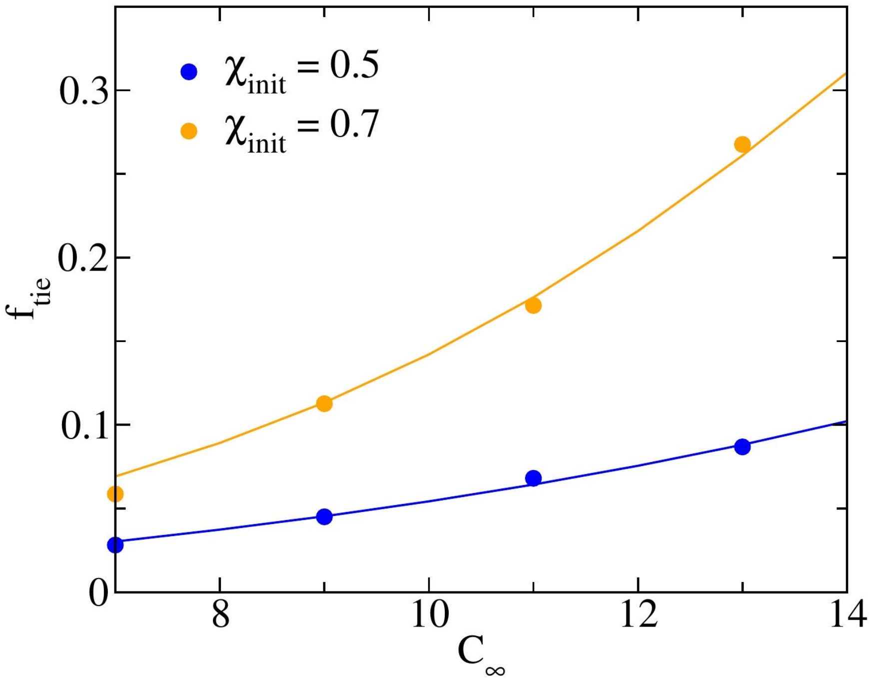
Fraction and size distribution of loops, ties and tails.

THEORY I USED : **Theory of statistics of ties, loops, and tails in semicrystalline polymers** FREE

Sabin Adhikari ; Murugappan Muthukumar







In my work, I used a new theoretical freely jointed chain statistics, which allowed me to control the fraction of tie chains f_{tie} (end others as a result), controling the conversion between real chain and ideal chain with the Kuhn length.
It also gave the probability distribution of amorphous chain section sizes.

(1) Adhikari, S.; Muthukumar, M. *J. Chem. Phys.* **2019**, *151* (11), 114905

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Characterization (1): Density and degree of crystallinity

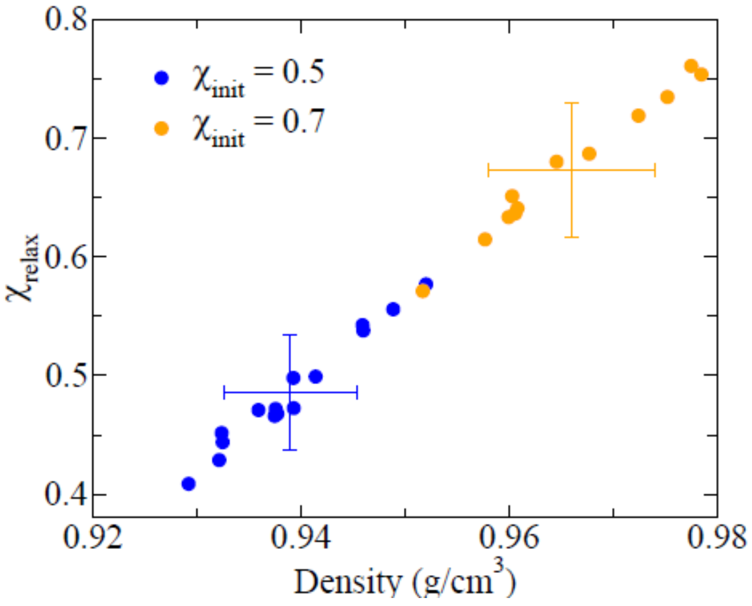
χ_{init}	0.5	0.7
$C_\infty = 7$	3	3
$C_\infty = 9$	6	3
$C_\infty = 11$	3	3
$C_\infty = 13$	3	3

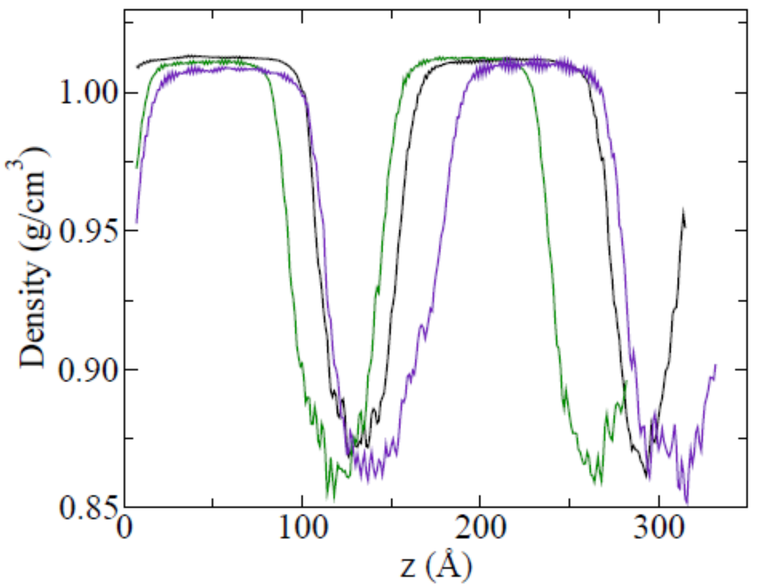
χ_{init}	0.5	0.7
$\overline{\chi}_{relax}$	0.49	0.67
$\sigma_{\chi relax}$	0.05	0.06
$\overline{\rho}_{relax}$ g/cm^3	0.939	0.966
$\sigma_{\rho relax}$	0.008	0.006

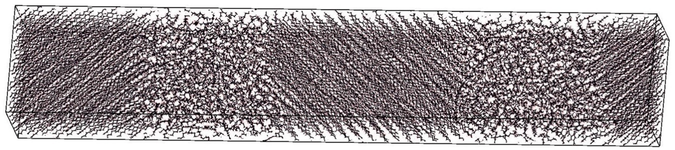
27 structures varying the initial degree of crystallinity χ_{init} and f_{tie} ($\leftrightarrow C_\infty$).

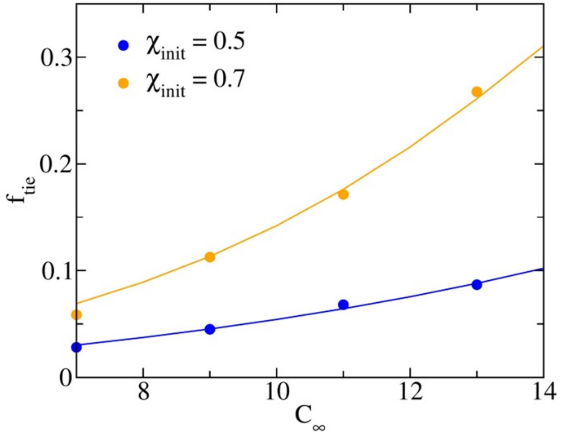
Spread of degree of crystallinity and density.

Tilt angle apparition (in agreement with exp.)



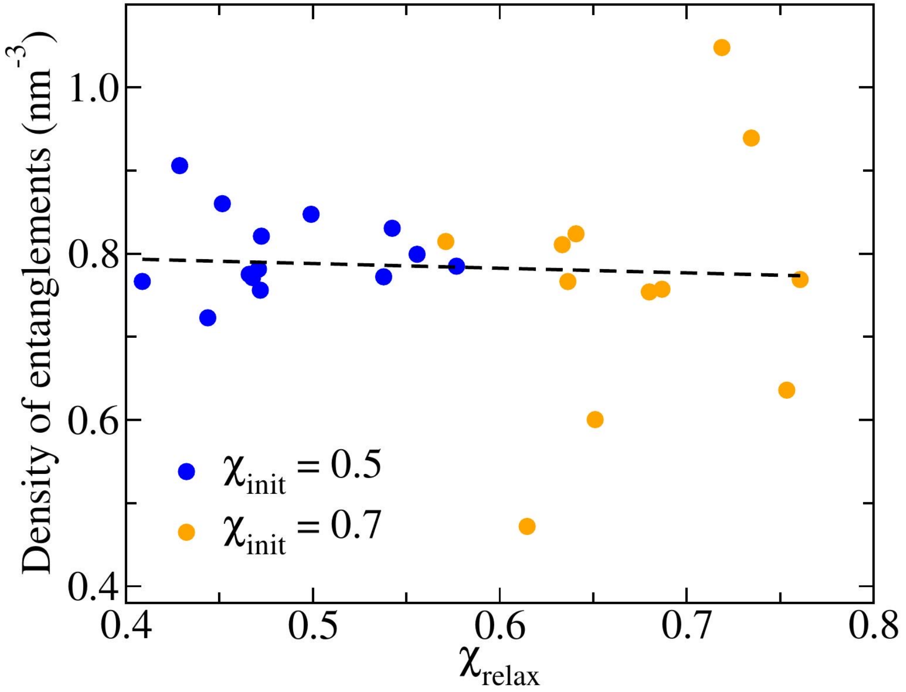






Characterization (2): Entanglements in the amorphous phase – with Martin Kröger Z1-code.

Primitive path of an amorphous phase:
Shortest path without chain crossing



According to Flory and Yoon, all the entanglements in the melt are trapped in the amorphous phase.
Flory, P. J. & Yoon, D. Y. Nature (1978)
Hoffman, J. D. & Miller, R. L. Polymer (1997)

Entanglements density controls the crystallization.

Density of entanglements in the S-C amorphous =
2 or 3 times entanglements in the melt .

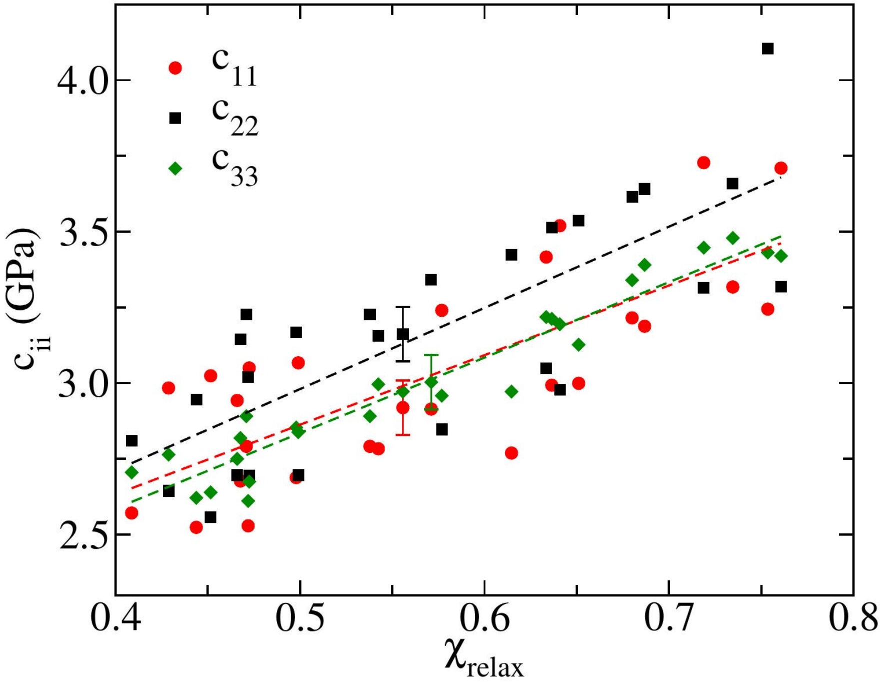
Some mechanical properties

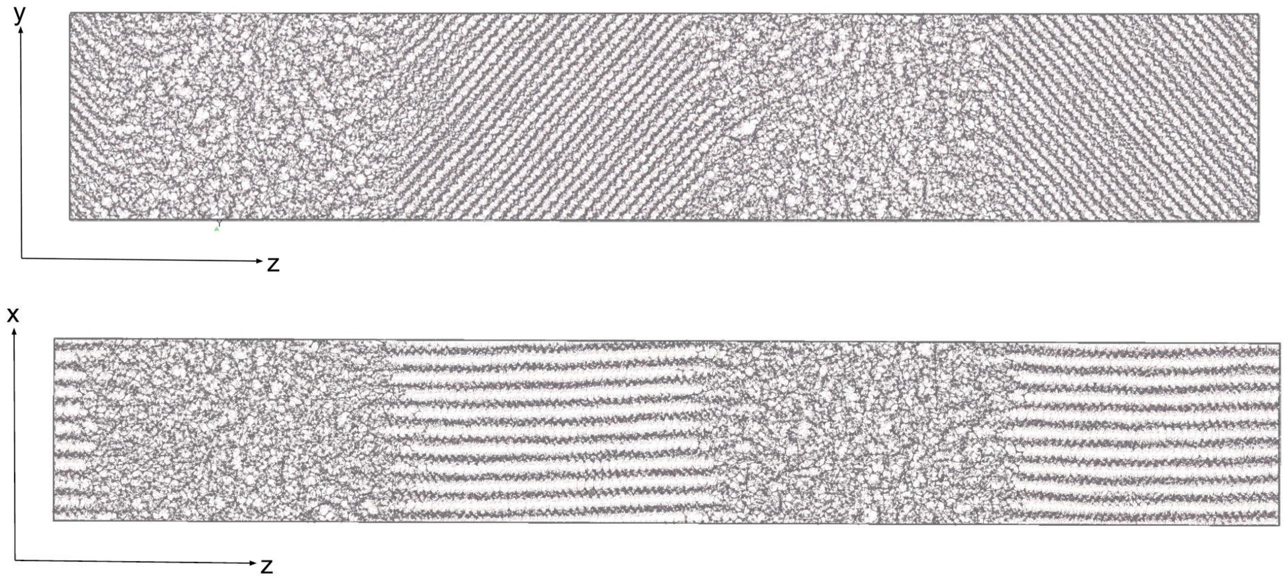
Uniaxial elastic coefficients C_{ii}

- With MedeA LAMMPS, deformation (ϵ_{ii}) and minimization (to obtain pressure σ_{ii})

Hook's Law : $\sigma_{ii} = C_{ii}\ \epsilon_{ii}$

- Evolution with degree of crystallinity (χ_{relax}) with a bit of anisotropy
- No influence of entanglements, nor the tie chain fraction (small strain, only crystallinity matter).





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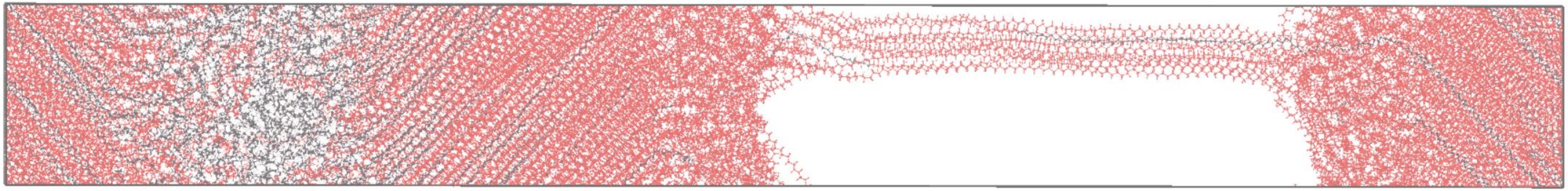
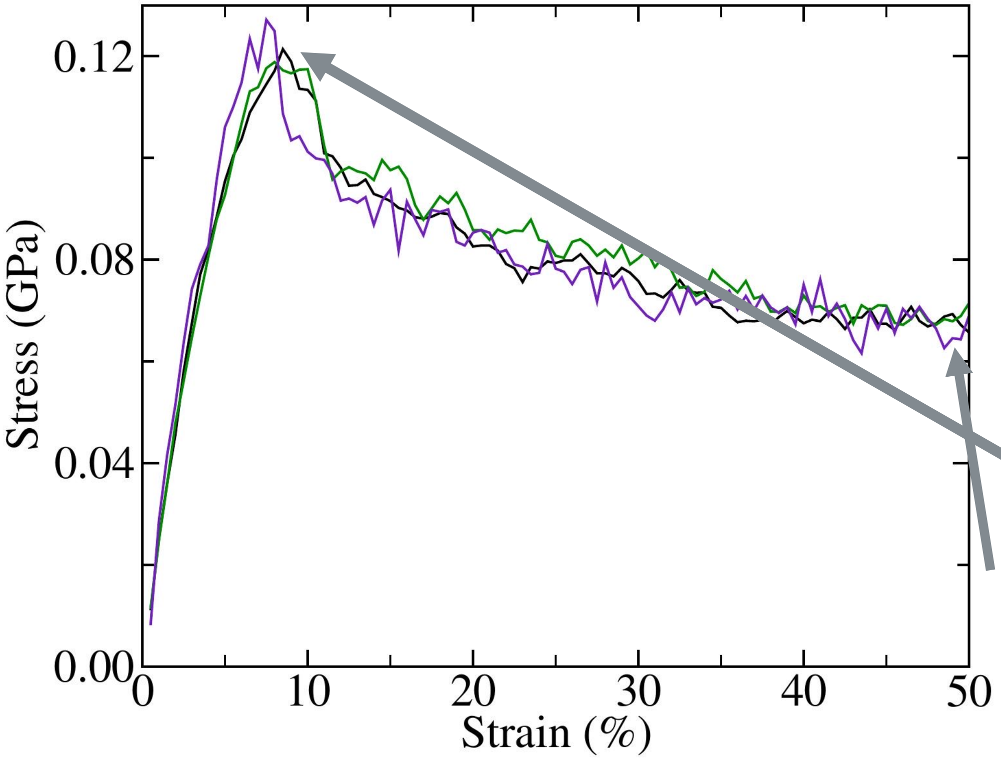
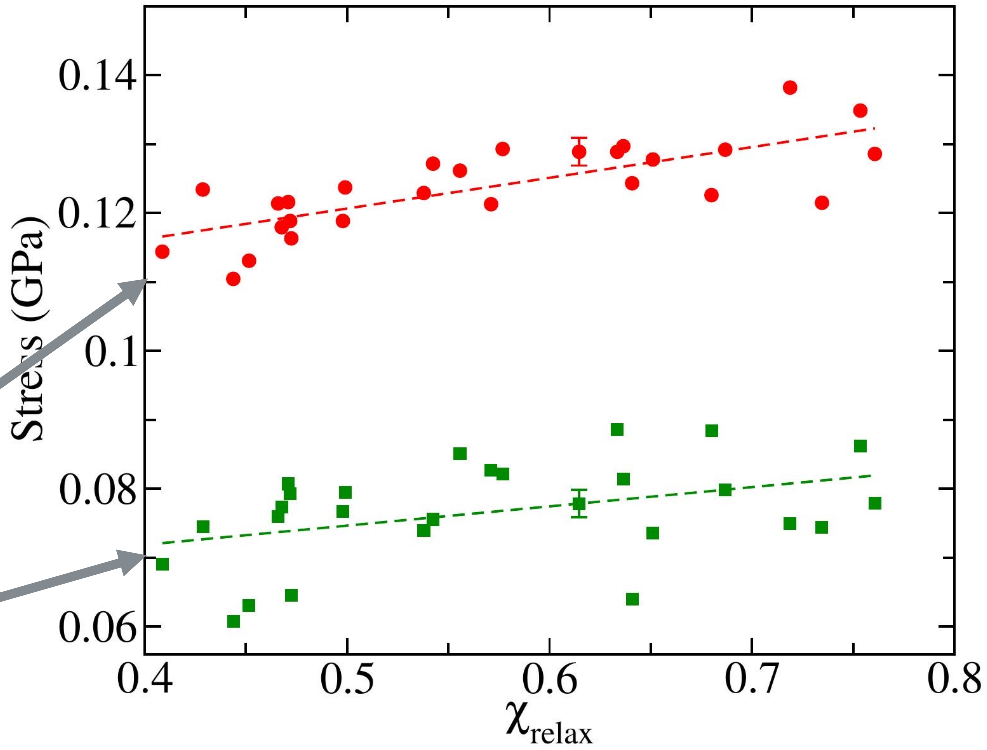
High deformation along the long period direction





- $\frac{d\epsilon}{dt} = 2.5\ 10^{-3}\ ns^{-1}$ along z (long period with 0.5 % step followed by NVT relaxation.
- σ_{US} : max stress (peak)
- σ_{45-50} : average stress between 45 and 50%



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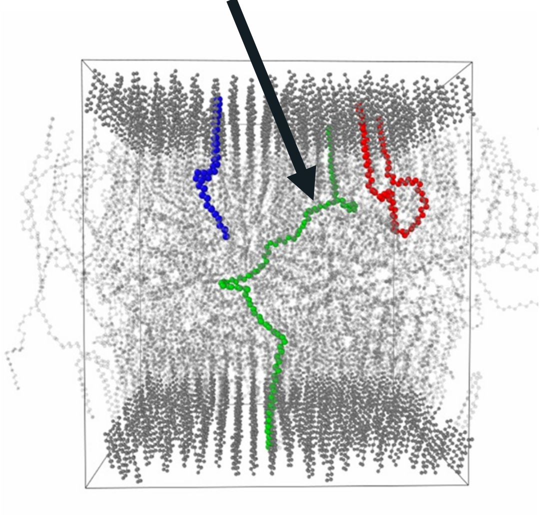
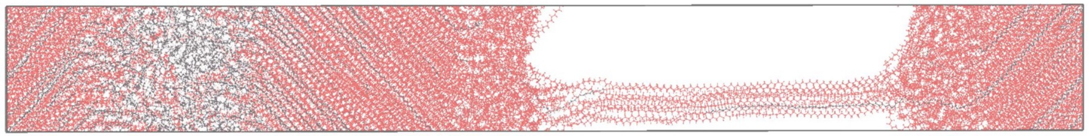
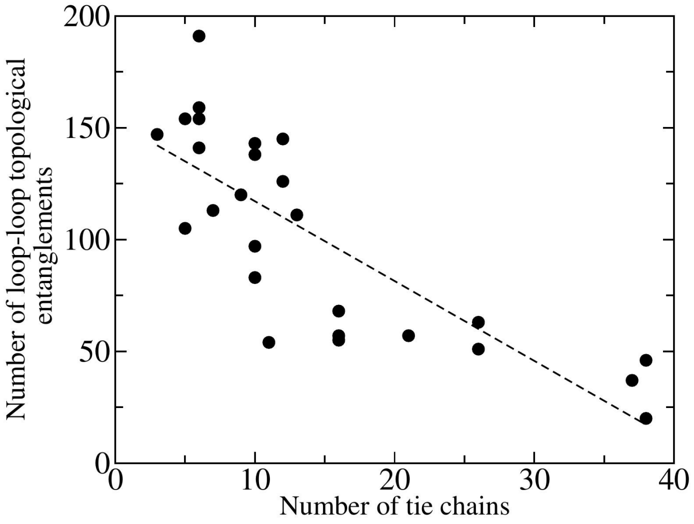
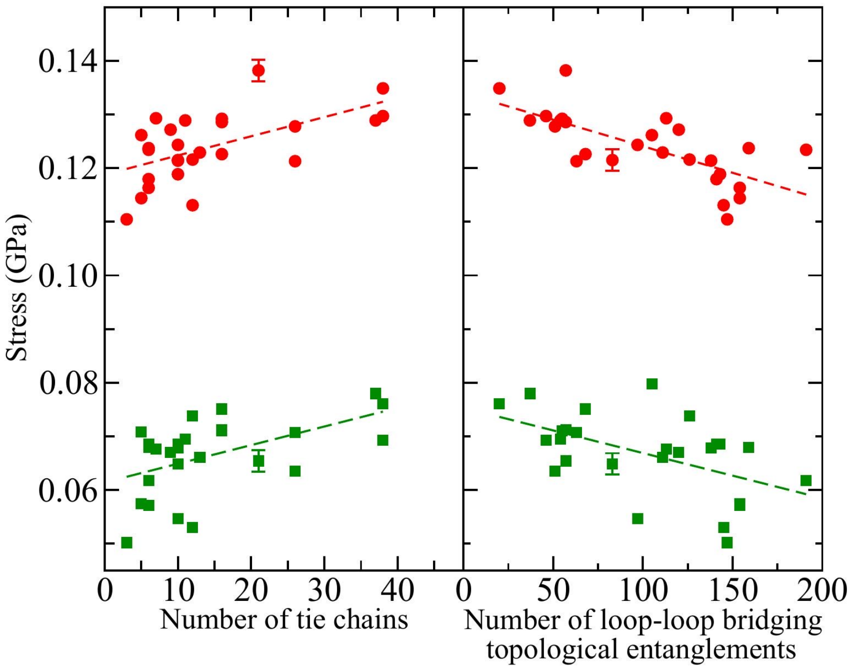
Investigations of the stress-transmitters

- Tie chains and bridging entanglements are believed to be the **stress-transmitters.**









- The tie chains are the most important morphological conformations to act as stress transmitter.
- But it’s always the amorphous phase with the least trapped entanglements which is the most strained (fibrils).
- Tie chains have the top priority, then the trapped entanglements.

Similar to:

McDermott, A. G.; DesLauriers, P. J.; Fodor, J. S.; Jones, R. L.; Snyder, C. R. Measuring Tie Chains and Trapped Entanglements in Semicrystalline Polymers. *Macromolecules* **2020**, *53* (13), 5614–5626.

Other polymers

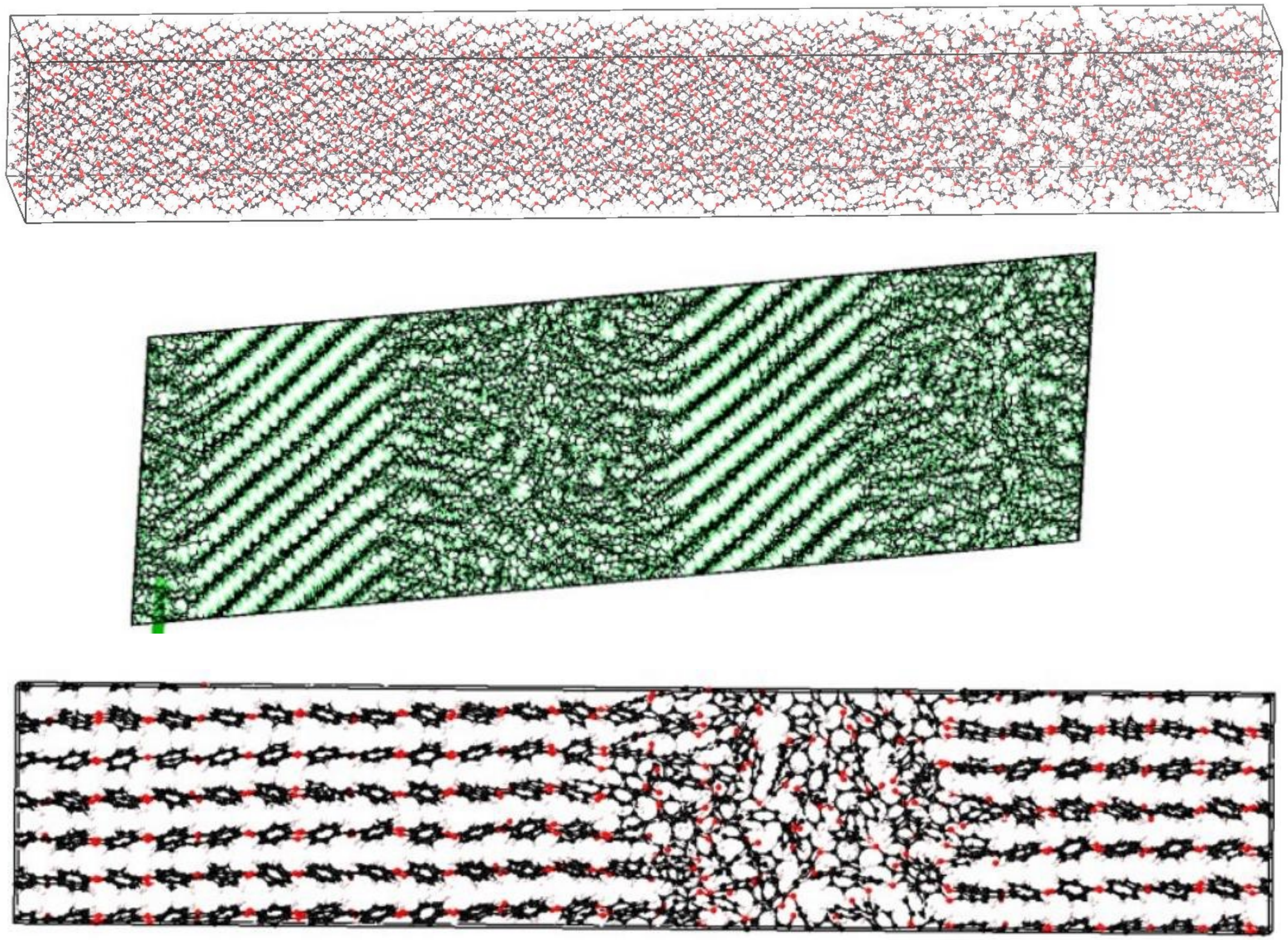
PEEK, PEG, TEFLON

Below high deformation for mechanical properties, for sorption and diffusivity (**next Webinar**), for electronic properties (with DFT), there is not influence of type of chains (tie chains…).

Beyond controversies, still in debate, theoretical and experimental consensus for a strictly decreasing size probability distribution (lot of small amorphous sections, few large ones).

It’s possible to use simple exponential, or half-normal probability of size distributions.

Amorphous chain sections smaller than the width of the amorphous zone, have to connect on one side or the other, the rest may be left to create loops or ties randomly.



PEG

Teflon

PEEK

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Highlighted *MedeA* Modules

***MedeA* Environment:** with high productivity integrated tools, property prediction using application-specific property modules in conjunction with state-of-the-art simulation engines, reproducible workflows as graphical flowcharts for multi-stage protocols

***MedeA* JobServer & TaskServer:** central unit to manage, monitor, and archive your calculations efficiently and consistently. highly flexible workflow maximizes productivity, on systems with heterogeneous hardware, and different operating systems.

***MedeA* Amorphous Materials Builder:** lets you efficiently create condensed phase models based on system chemical composition and target density. It eliminates the need for lengthy mixing and amorphization simulations through realistic sampling of the translational, rotational, and conformational degrees of freedom of component species.

***MedeA* Polymer builder:** Creates models of isolated polymer chains, providing a foundation for building more complex models. Examples include bulk polymers, blends, solutions, or multiphase systems incorporating one or more interfacial regions.

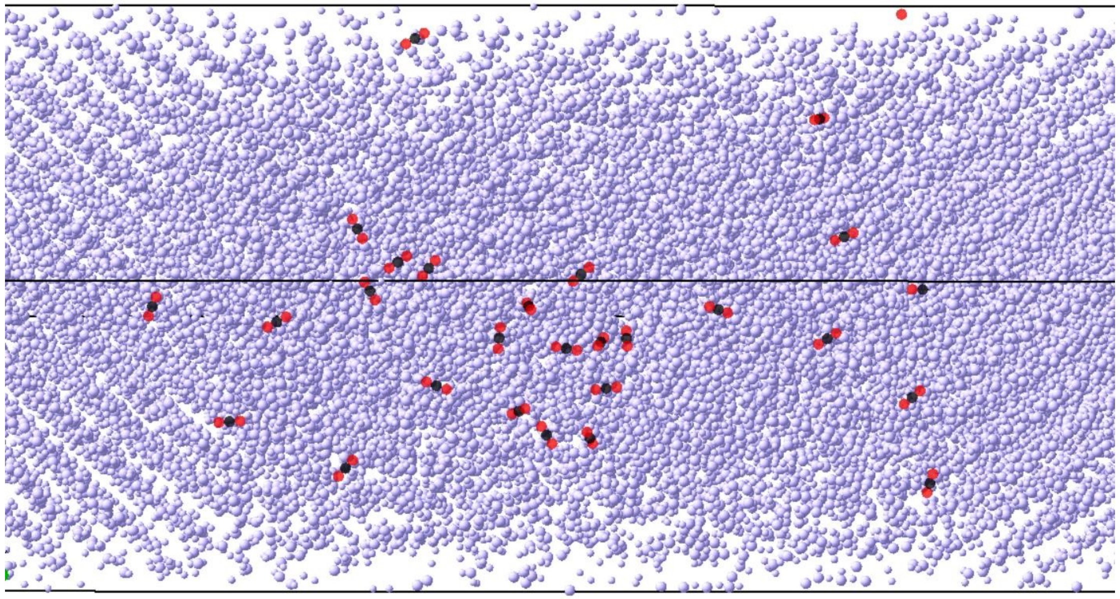
***MedeA* Thermoset Builder:** Applies state-of-the-art methods for creating complex topologies of polymer networks in order to create strain-free molecular models with experimentally observed crosslink densities.

***MedeA* LAMMPS:** Provides flexible calculation setup and analysis capabilities to unlock the power of LAMMPS.

Upcoming Webinar

Sorption and Diffusion of Small Gases in Semicrystalline Models: A Molecular-Scale Investigation

Abstract: Expanding on the work from this webinar, our study employs these structures to conduct sorption computations for CO2 and CH4 across pressures ranging from 1 MPa to 40 MPa, employing a combination of Monte Carlo and Molecular Dynamics techniques iterated in cycles. Through molecular dynamics simulations, the diffusion coefficients of gas molecules within the polymer matrix is computed with Einstein's equation.



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Question and Answer Session

Dr. Marianna Yiannourakou

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Dr. Boris Belin

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Dr. Dave Rigby

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Questions about Materials Design Webinars

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MedeA

Innovation by Simulation