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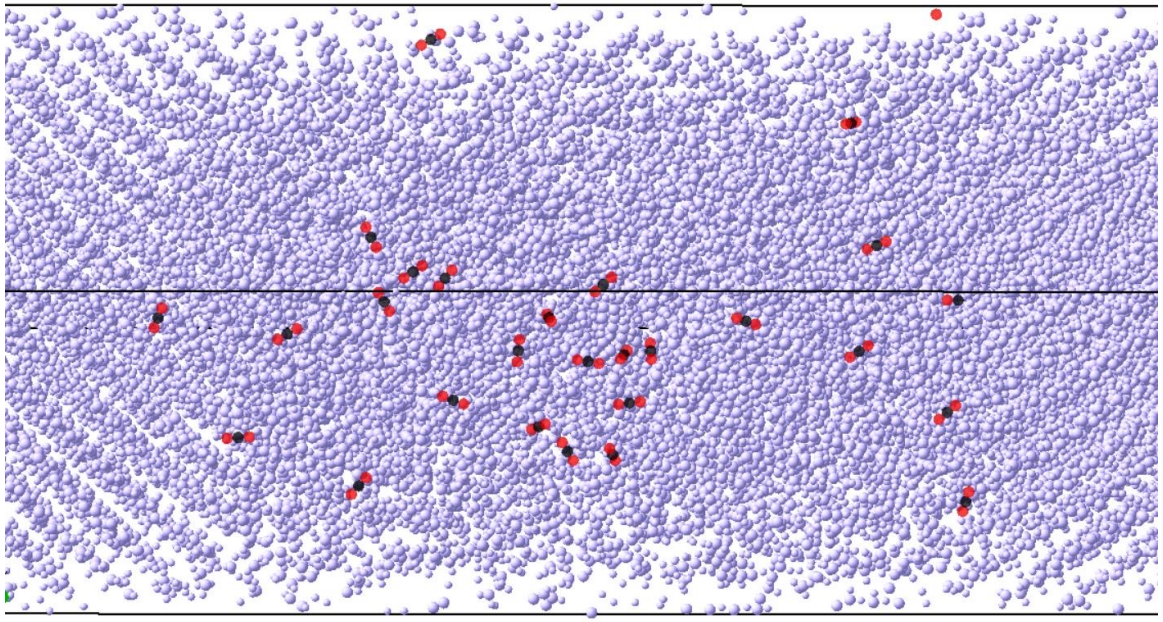
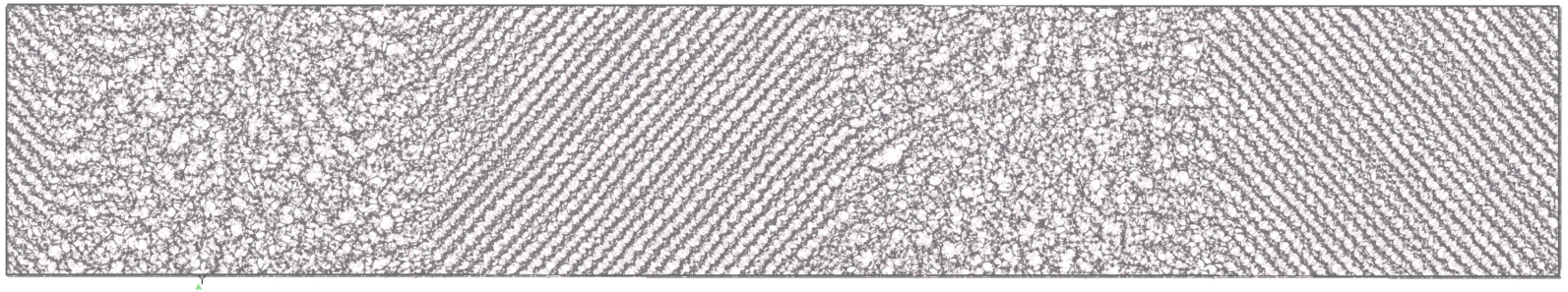
Sorption and Diffusion of Small Gas Molecules in Semicrystalline polymers:

A Molecular-Scale Investigation



Speaker: Dr. Boris Belin

March 5th-7th, 2024



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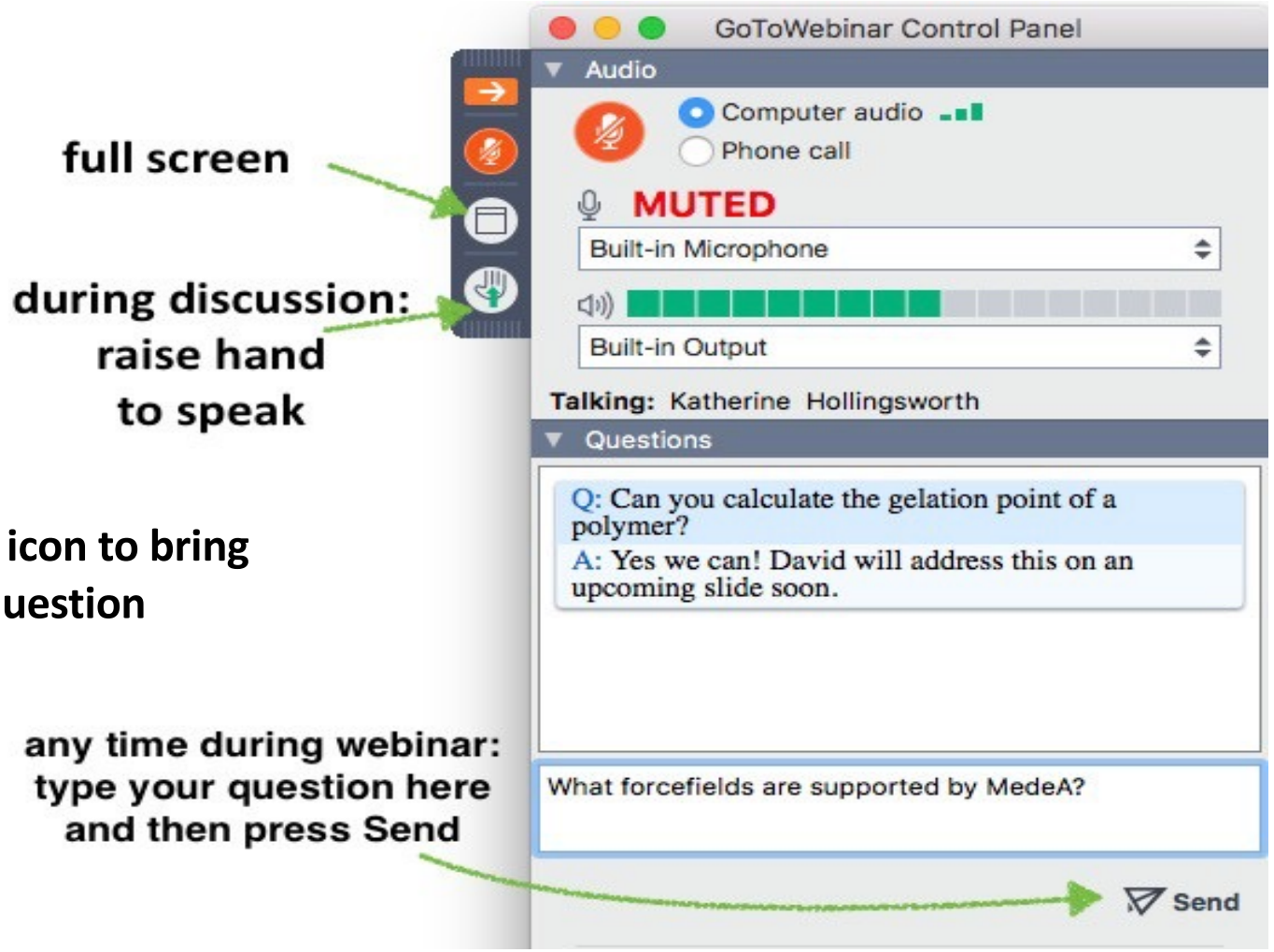

Use the raise hand icon to bring attention to your question

any time during webinar: type your question here and then press Send

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Webinar Speakers

Katherine Hollingsworth

Dr. Dave Rigby

Dr. Marianna Yiannourakou

Presenter: Dr. Boris Belin

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Sorption and Diffusion of Small Gas Molecules in Semicrystalline polymers:

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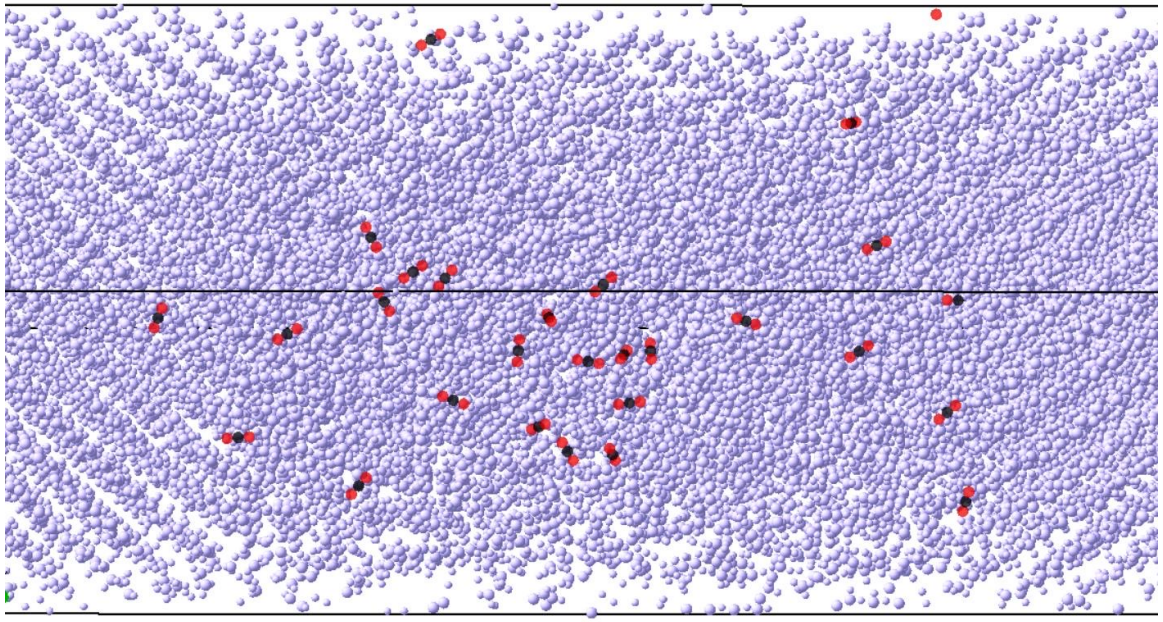

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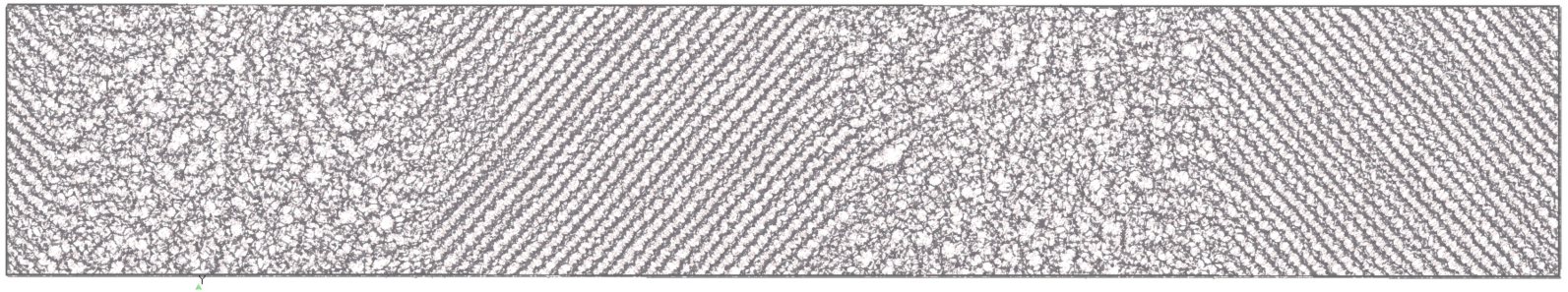


Outline

- **Building semicrystalline polymer structures (reminder of the last webinar)**

- **Sorption of CH_4 and CO_2**
  - Methods
  - Results
  - Comparison with experiments with Michael's theory of sorption in S-C

- **Diffusion of CH_4 and CO_2**
  - Methods
  - Results

Semicrystalline polymers in industry

Ubiquitous !

Many properties of interest accessible with molecular/atomistic simulation:

- **Mechanical** (molecular dynamics).
- **(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.

Morphology

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

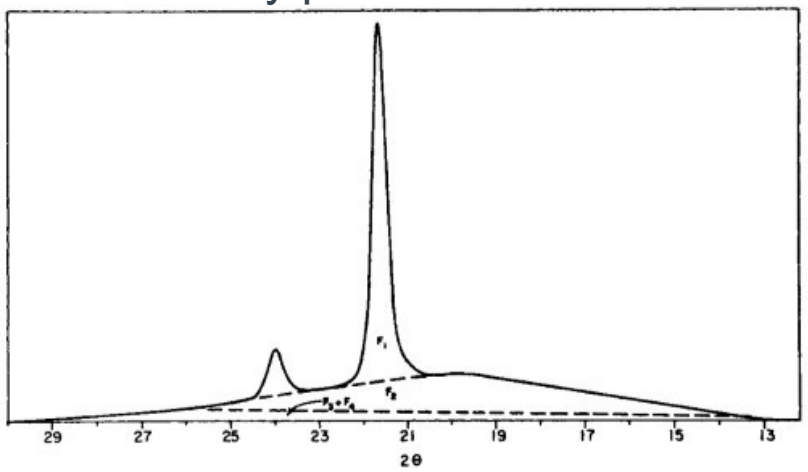
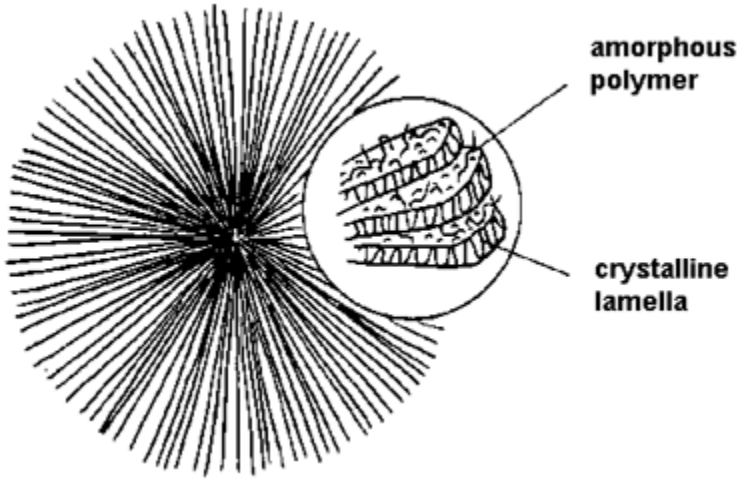
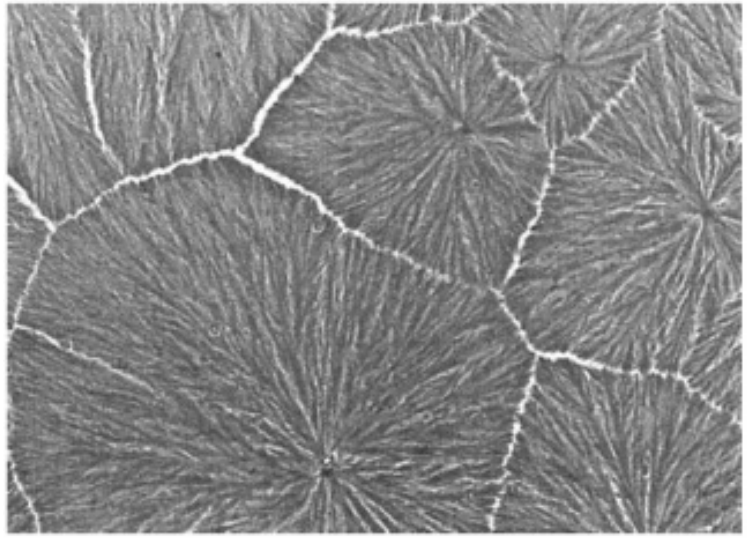


Fig. 1. X-ray diffraction pattern for linear polyethylene at room temperature. $M_\eta = 7 \times 10^6$; density = 0.9309.

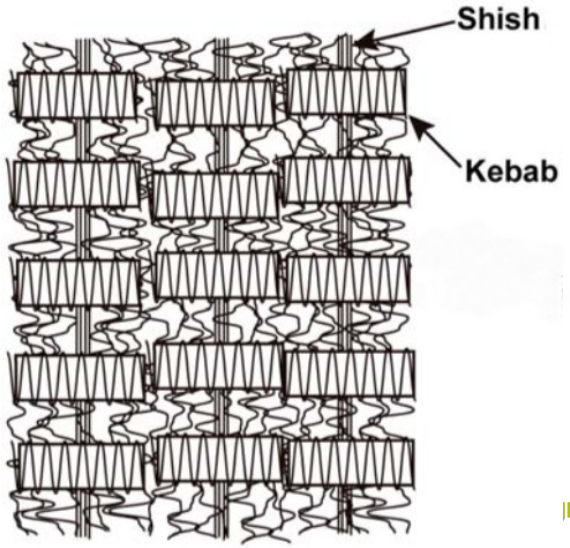
Spherulite



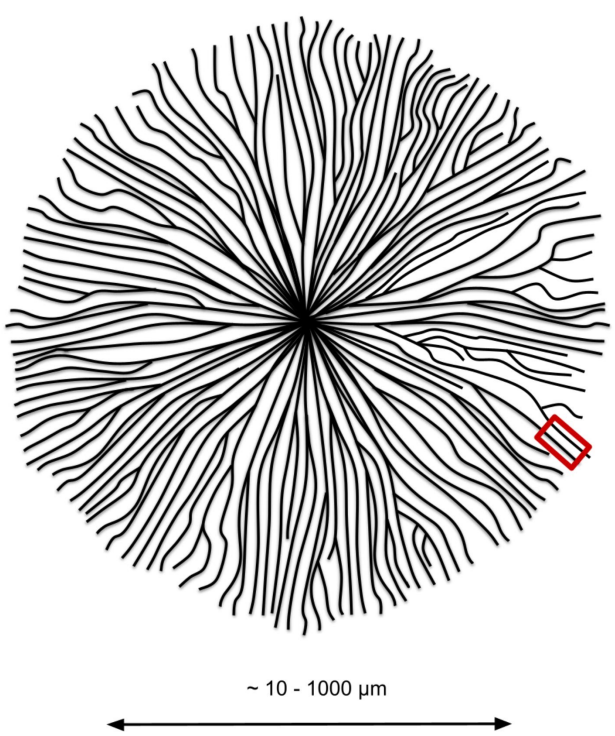
Spherulite under microscopy

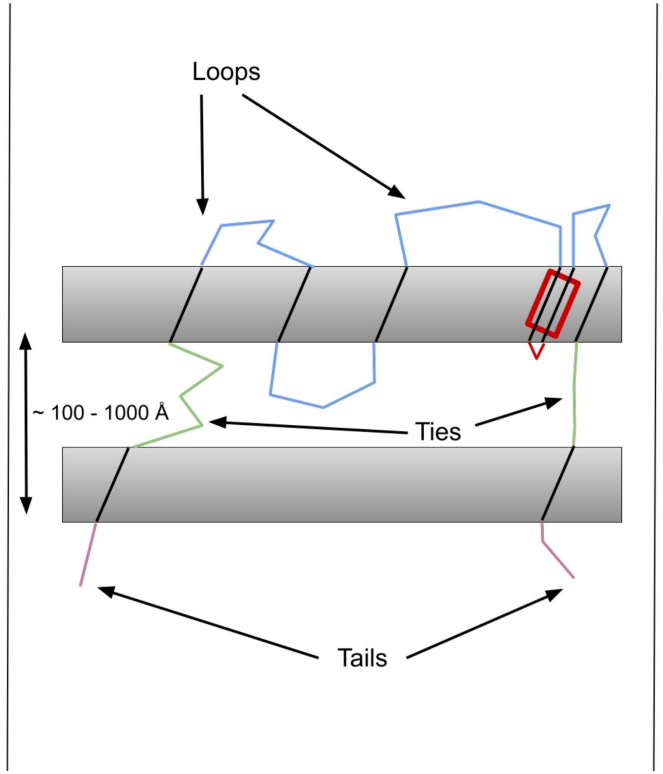


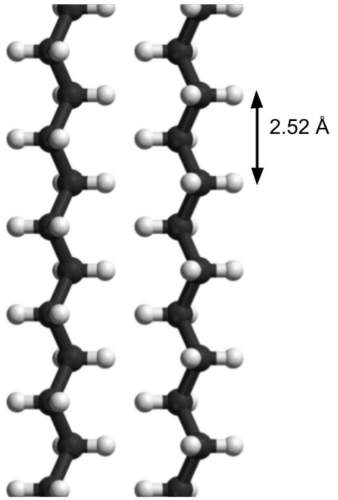
Shish Kebab



Morphological characterization

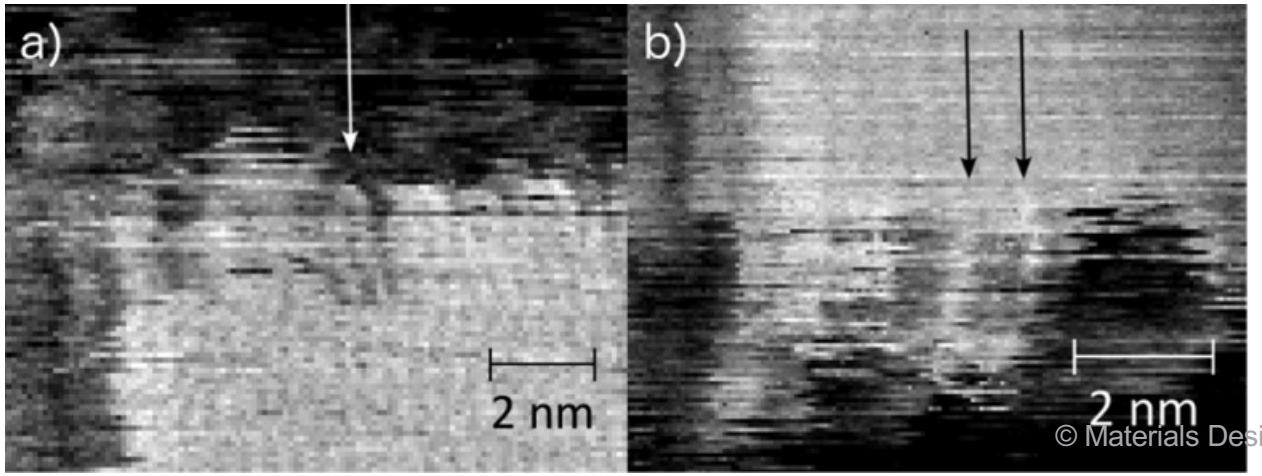






Characterization

- 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)

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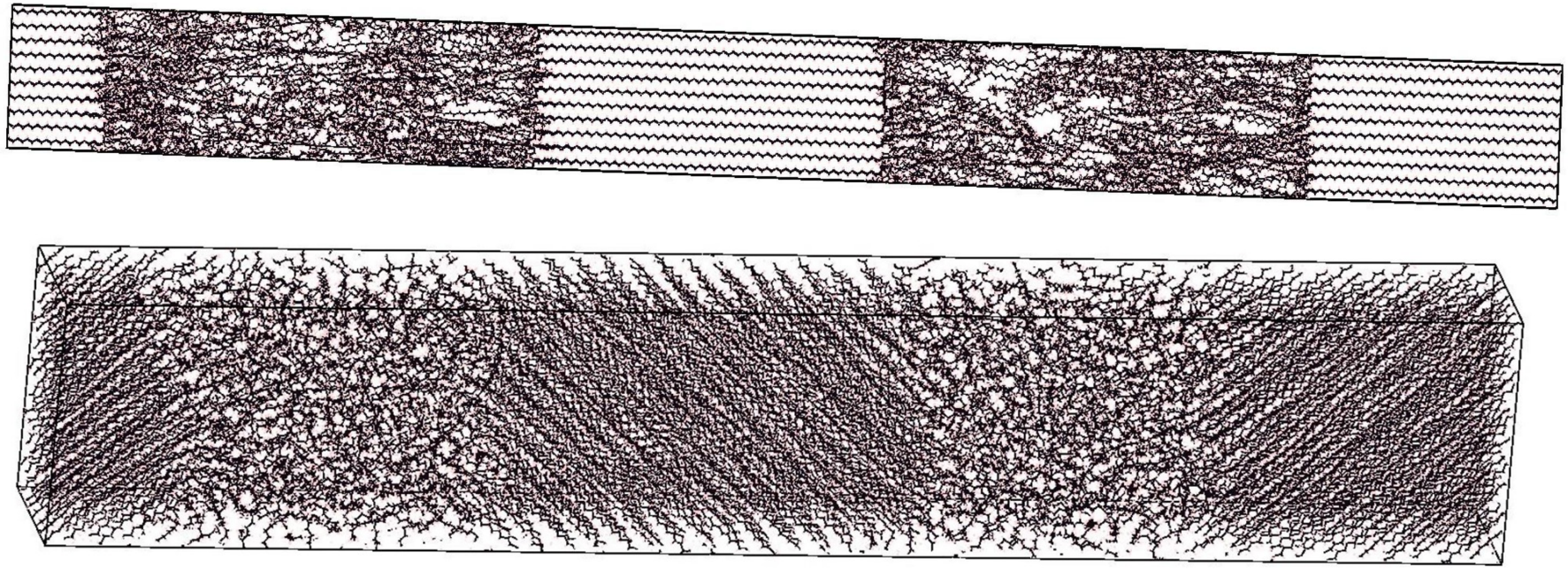
Building structure reminder

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

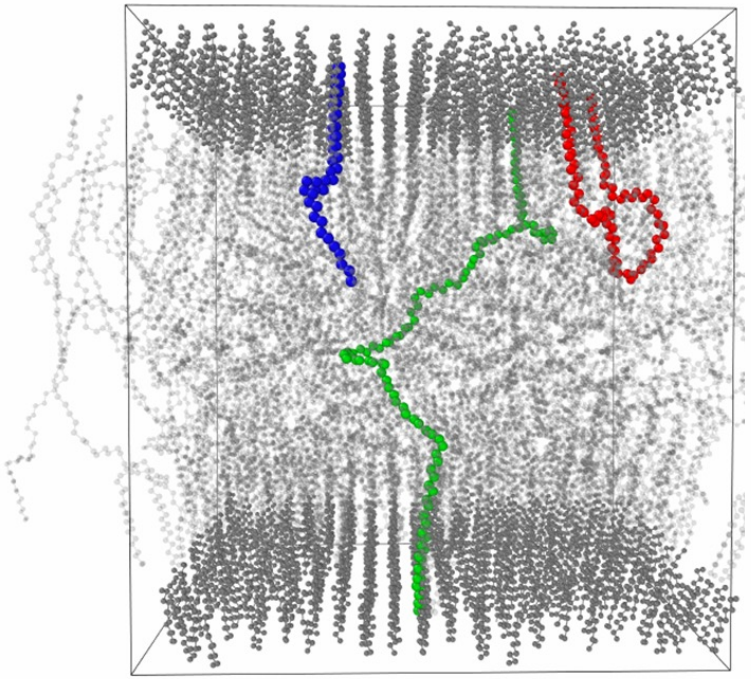
- **Hypothesis** : We know the distribution of size and type of the amorphous chain sections (tie chains, loops, tails), from experimental data or from a statistical polymer physics theory.
- With the **MedeA Amorphous Builder**, build an amorphous layer correctly labelled (depending of types). Build a supercell layer of the crystal with labelled chain ends.
- Connection (**MedeA Thermoset Builder**) 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.).

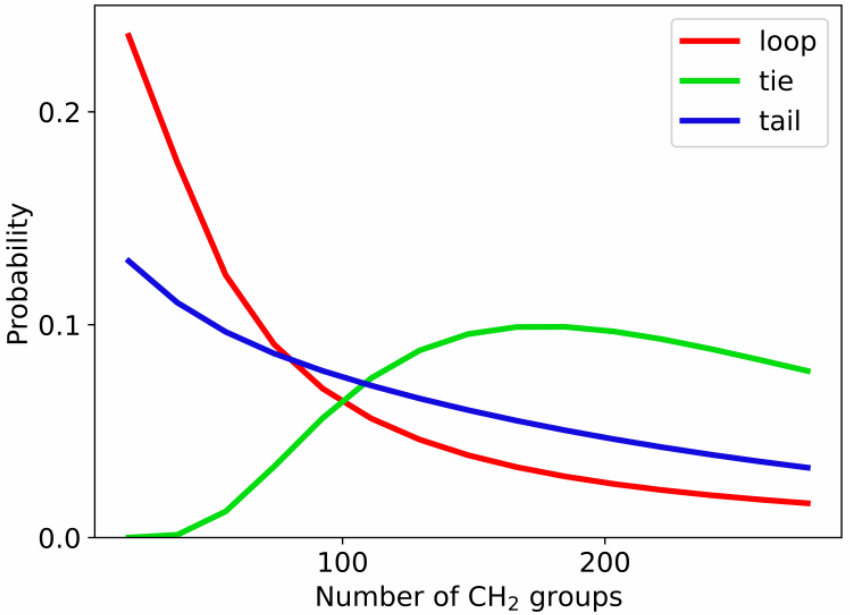


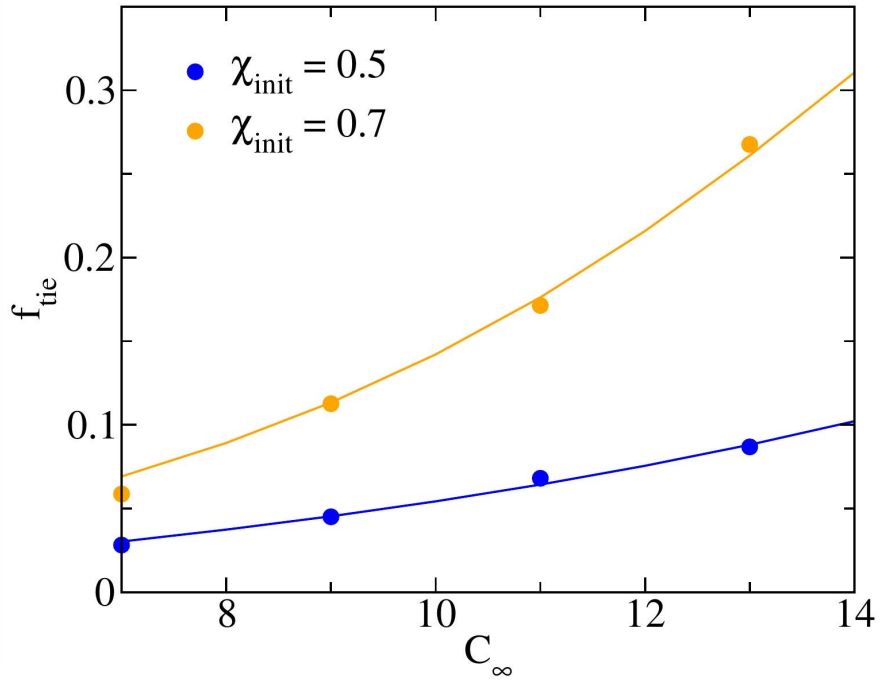
Fraction and size distribution of **loops**, **ties** and **tails**.

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

Sabin Adhikari ; Murugappan Muthukumar







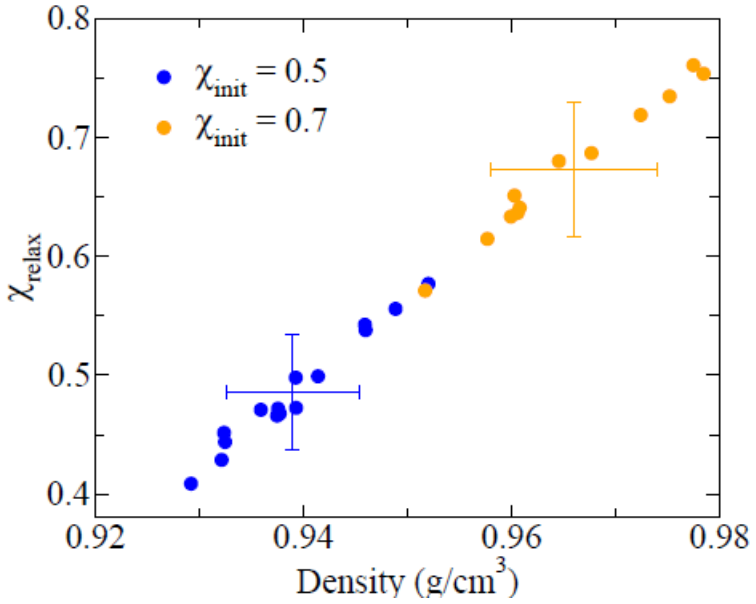
In my work, I used a new theoretical freely jointed chain statistics, which allowed me to control the fraction of tie chains f_{tie} (end others as a result), controling the conversion between real chain and ideal chain with the Kuhn length.
It also gave the probability distribution of amorphous chain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

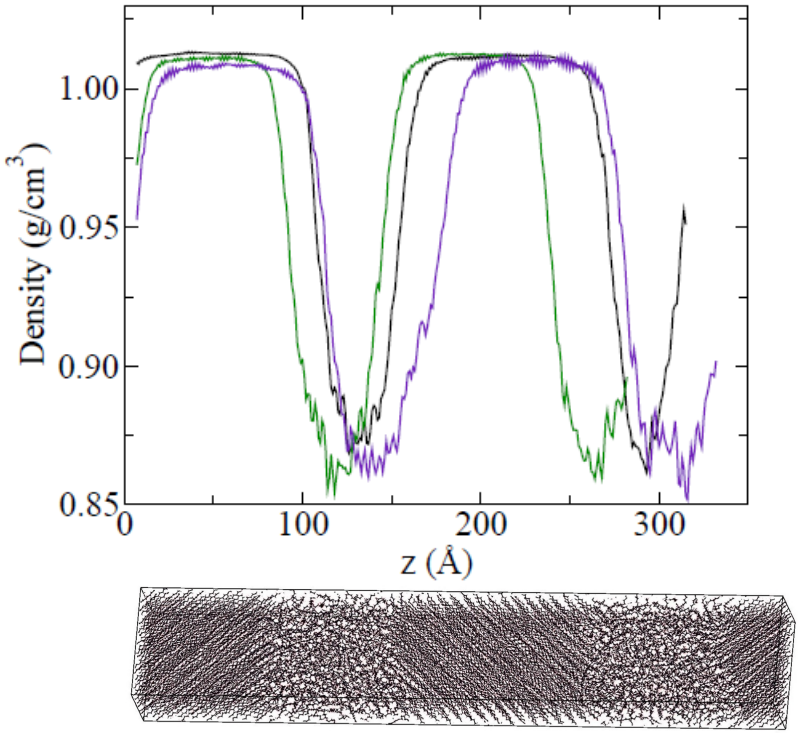
Adhikari, S.; Muthukumar, M. *J. Chem. Phys.* **2019**, *151* (11), 114905

Characterization : 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

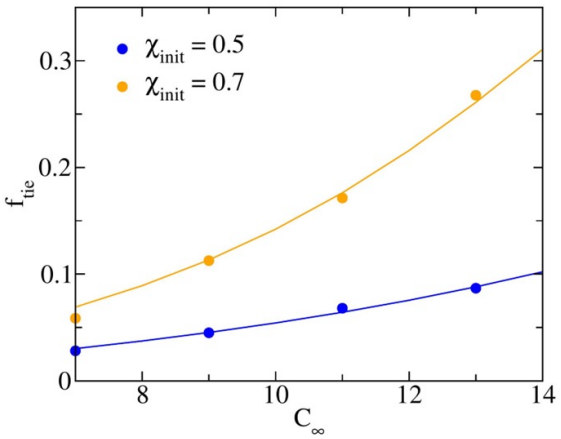




27 structures varying the initial degree of crystallinity χ_{init} and f_{tie} ($\leftrightarrow C_\infty$).

Spread of degree of crystallinity and density.

Tilt angle apparition (in agreement with exp.)

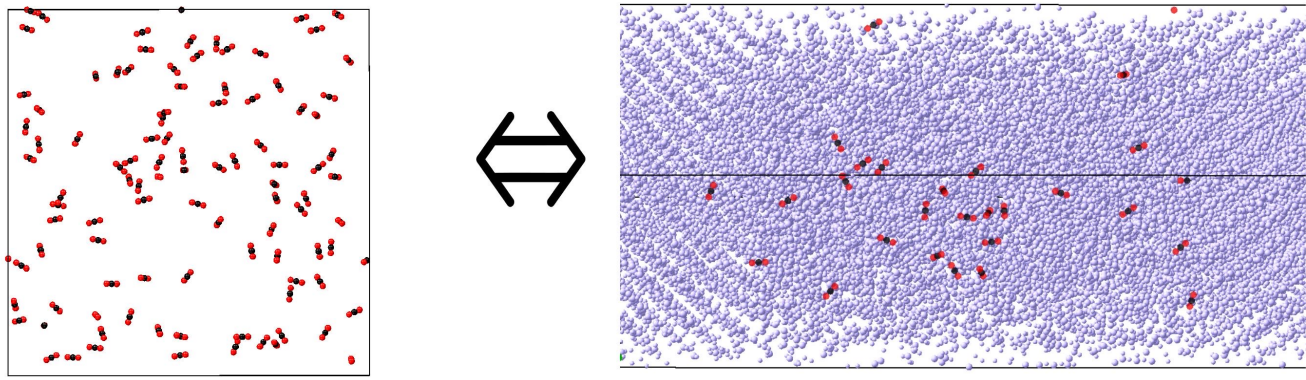


Sorption computations with CH_4 and CO_2

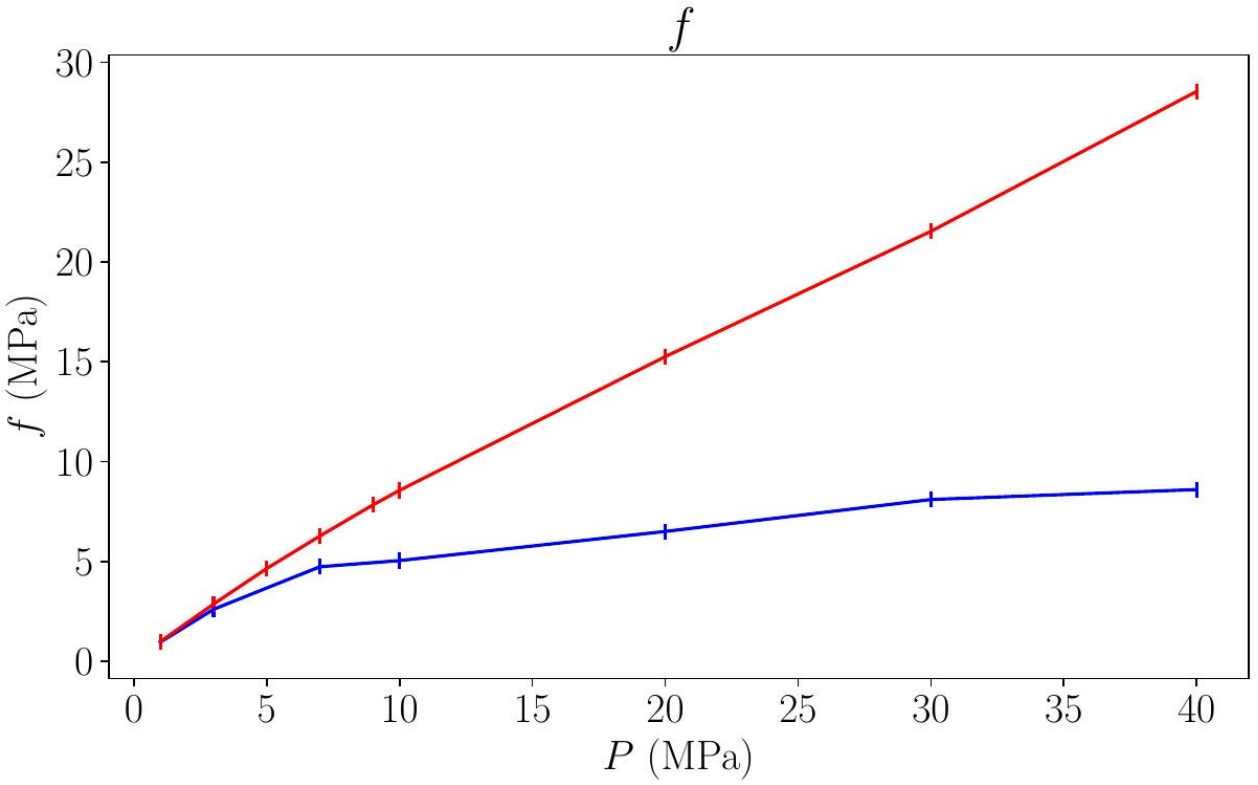
Fugacity computations

$$(\mu_{CO_2}(P,T))_{bain} = \mu = (\mu_{CO_2}(P,T))_{poly}$$

$$\mu - \mu^0 = RT \ln f/P^0$$



Chemical equilibrium



Fugacity of CO_2 in blue and CH_4 in red

- Goal: We want to do sorption computations in: **$\mu_i VT$ ($f_i VT$)** , the grand canonical ensemble where **μ_i** is the chemical potential.
- Chemical equilibrium: **$(\mu_i)_{poly} = (\mu_i)_{bath.}$**
- Widom insertion tests at P and T=300 K.

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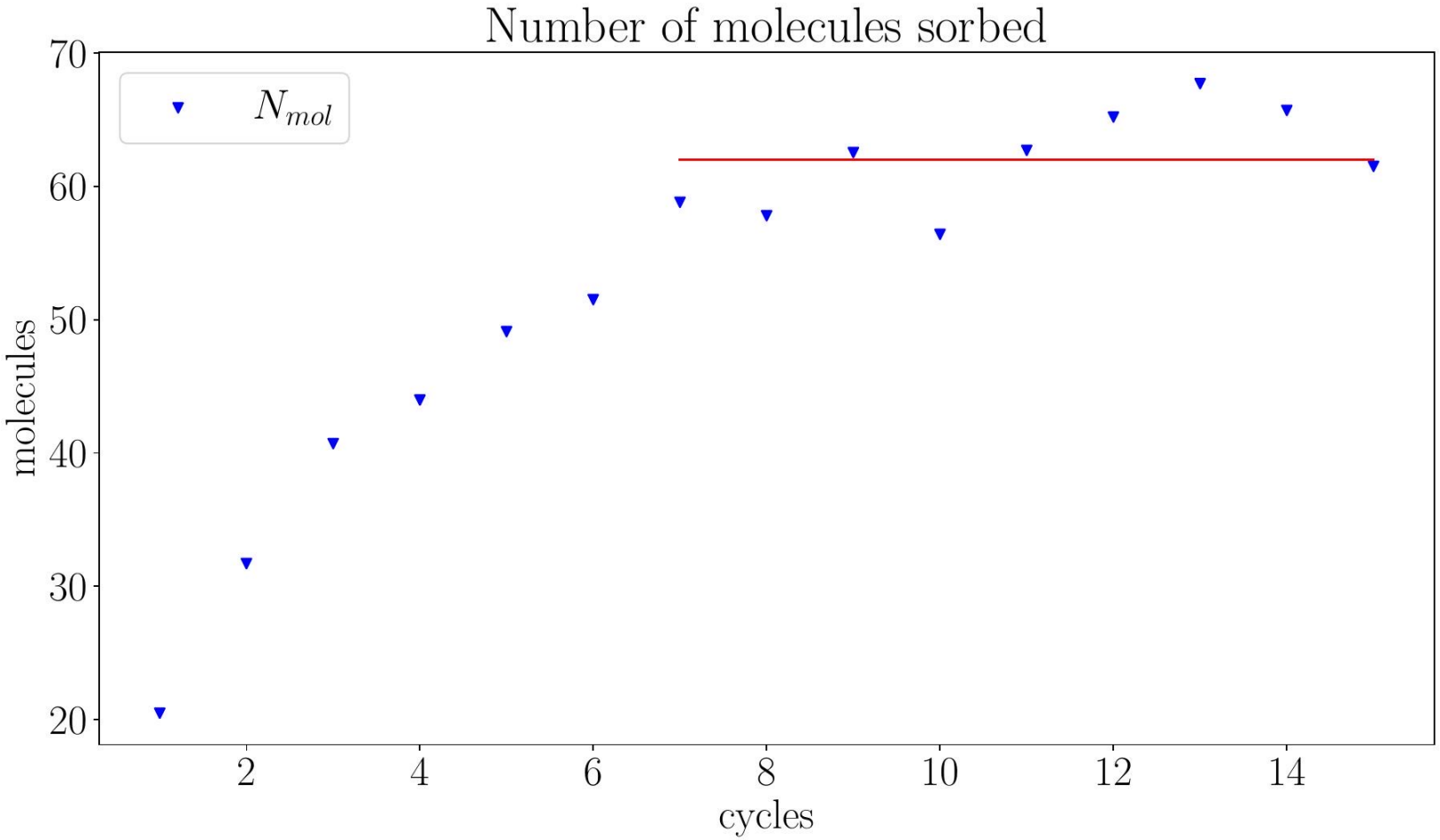
MC/MD cycles method

- **MC-MD cycle**: iteration of Monte Carlo ($\mu_i VT$) + MD in NPT until convergence.
- **Monte Carlo run (grand canonical):** frozen polymer
- **Molecular dynamics run (NPT):** account for the chain mobility and swelling.
- **Iteration until convergence**



Velioglu, S. et al. Journal of Membrane Science (2012)
Abedini, A. et al. Langmuir (2017)
Velioglu, S. et al. Journal of Membrane Science (2018)
Kupgan, G. et al. Journal of Membrane Science (2018),
Balcik, M. & Ahunbay, M. G. Journal of Membrane Science (2018)

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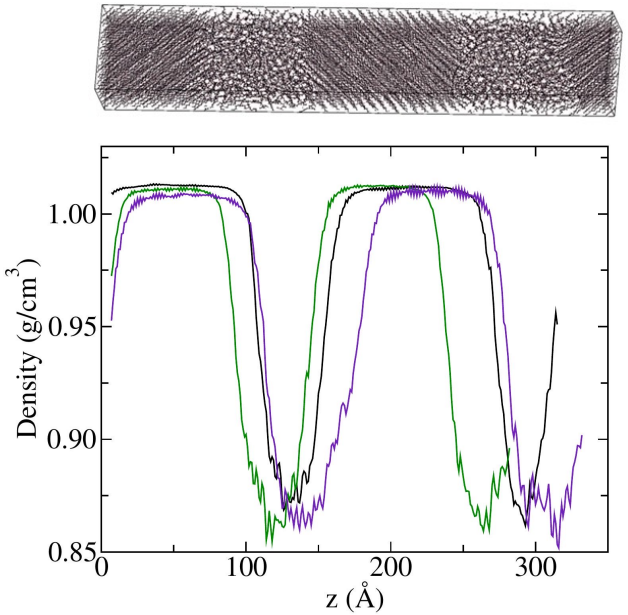
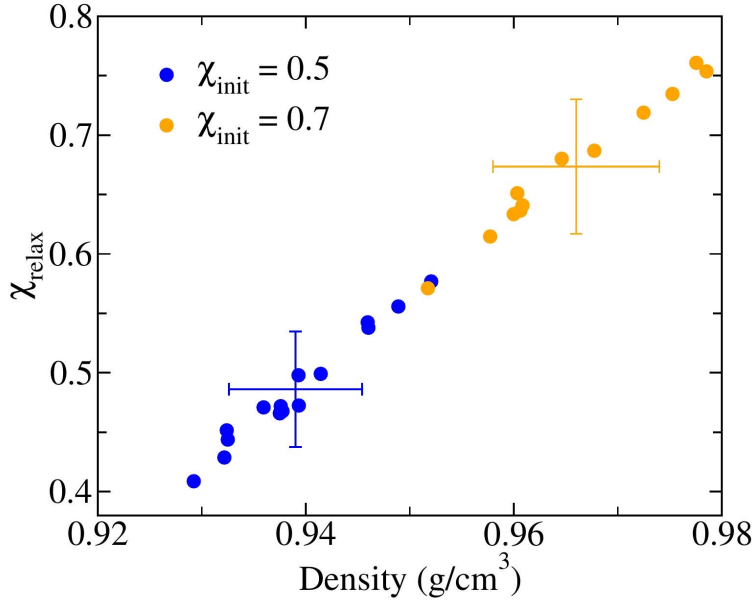
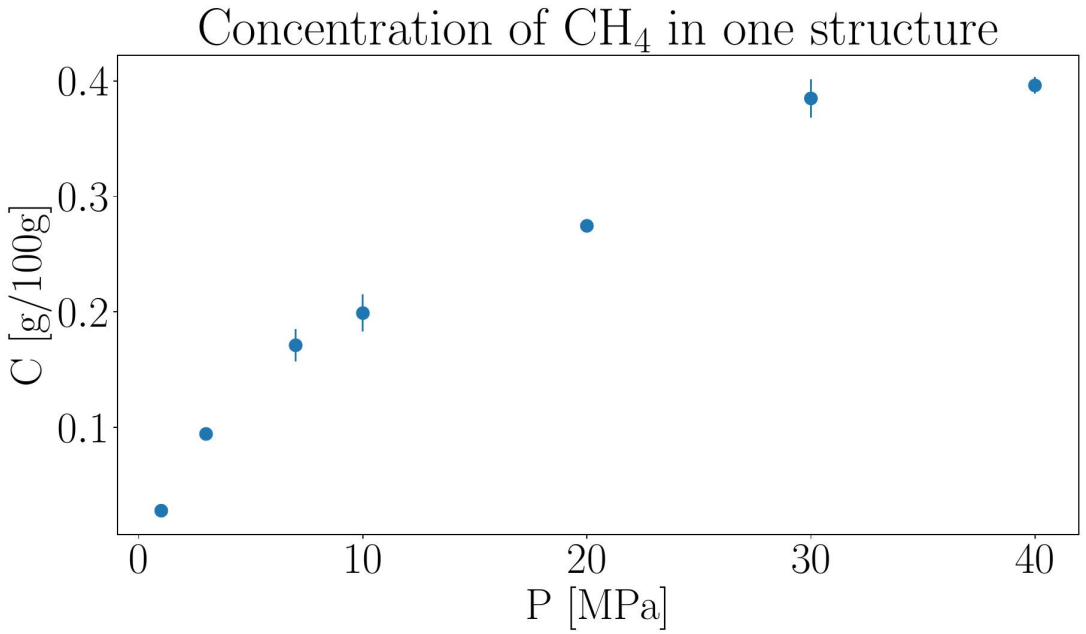
Michaels' Law

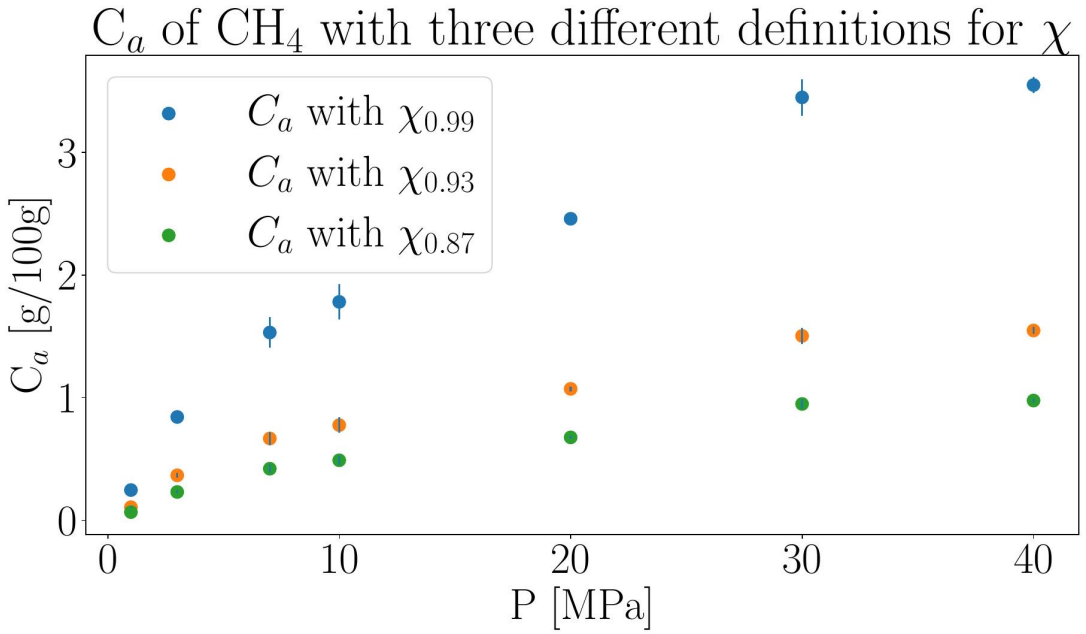
- Michaels' Law, to compare results : $C_a = C/\Phi_a$ (Φ_a is the volumic amorphous fraction).
- $\rho_a = 0.86$ g.cm^{-3} $\rho_c = 1$ g.cm^{-3}







Example of absorption isotherm



CH4 absorption isotherm in the amorphous

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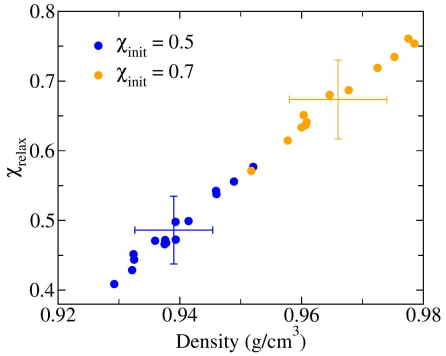
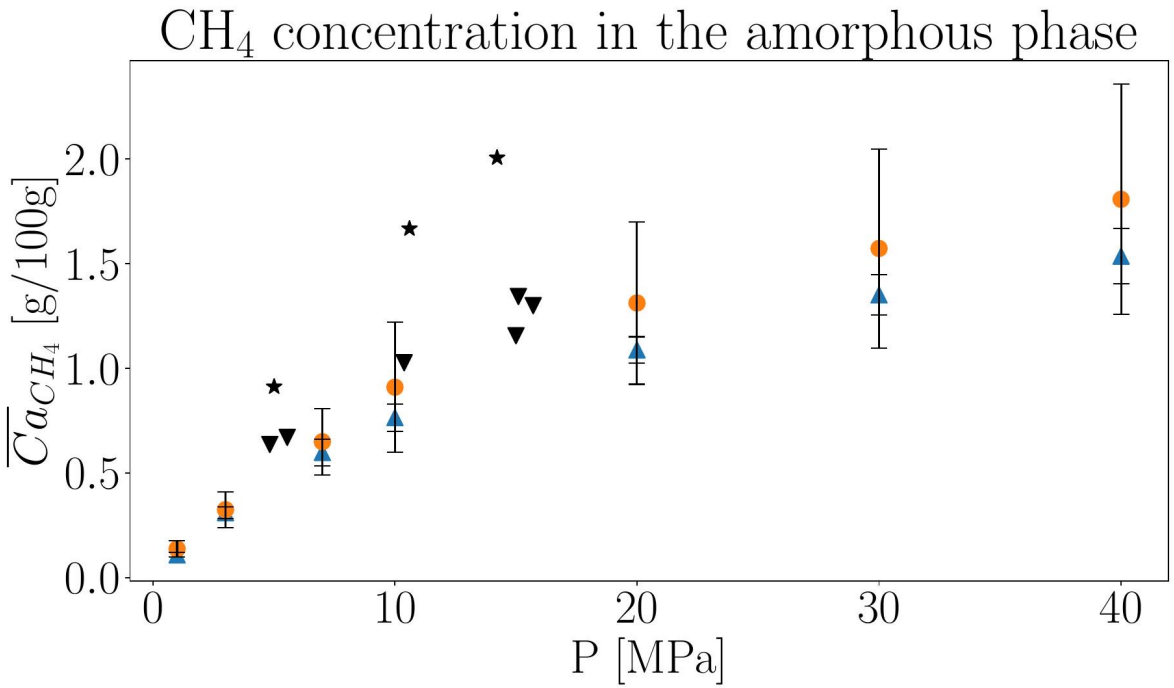
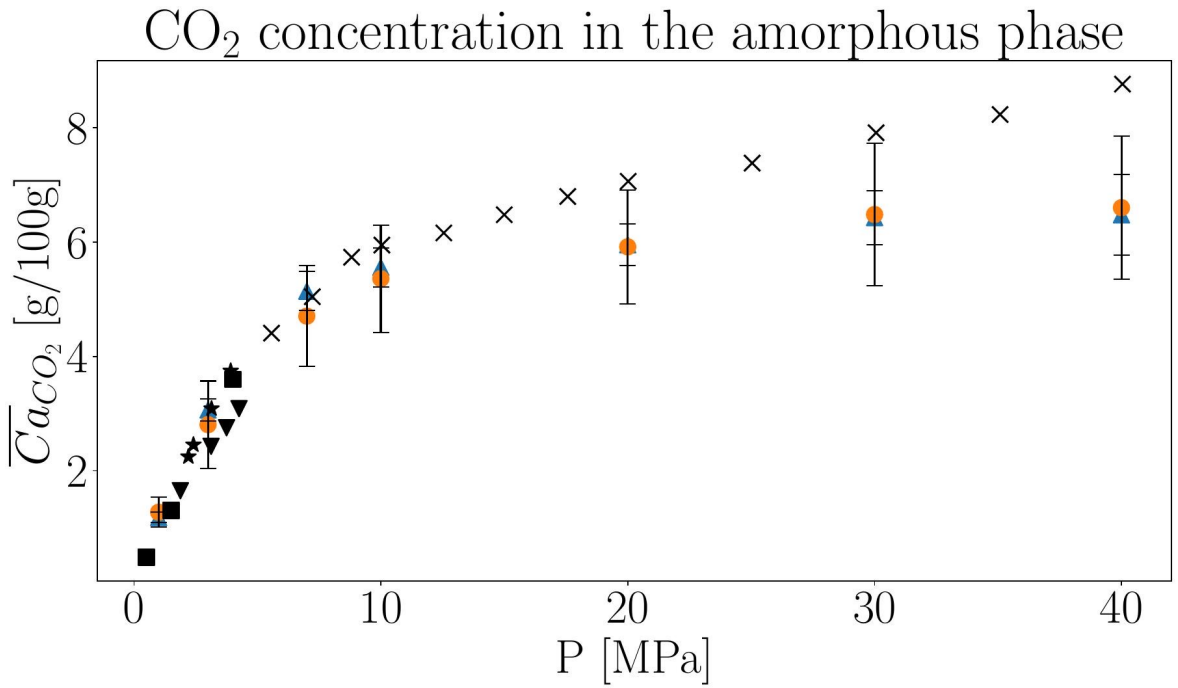
Results averaged over all the structures

Michaels' law is verified, and predictions are in agreement with experiments.
No influence of tie chains or entanglements.





Concentration of CH_4 in the amorphous (blue triangles χ_{init} =50%) and (orange dots χ_{init} =70%) at T=300 K. Von Solms' measurements (▼,T=305 K) and (★, T=298 K).



Concentration of CO_2 in the amorphous fraction (blue triangles χ_{init} =50%) and (orange dots χ_{init} =70%) at T=300 K. Von Solms' measurements (▼,T=305 K) and (★, T=298 K). Flaconnèche et al. squares (■, T=298 K), and Hu cross (✖, T=298 K).

Von Solms, N. et al. Journal of Applied Polymer Science (2004)
Flaconneche, B. et al. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles (2001)
Hu, T. Permeation of High Pressure CO2 in Semicrystalline Polymers. Phd Thesis. (Imperial College London, 2021)

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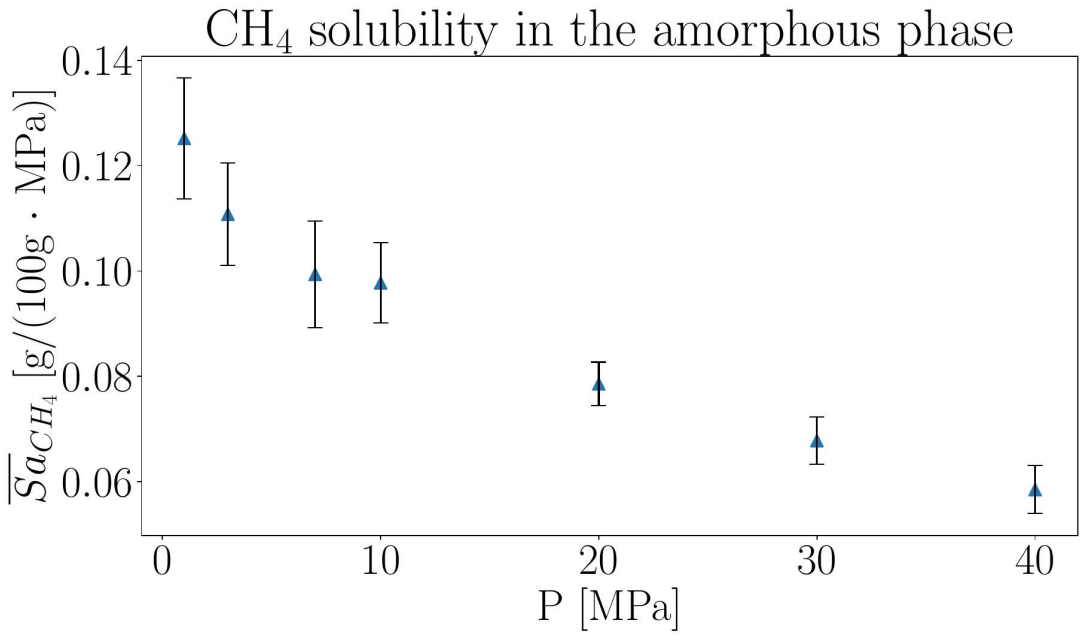
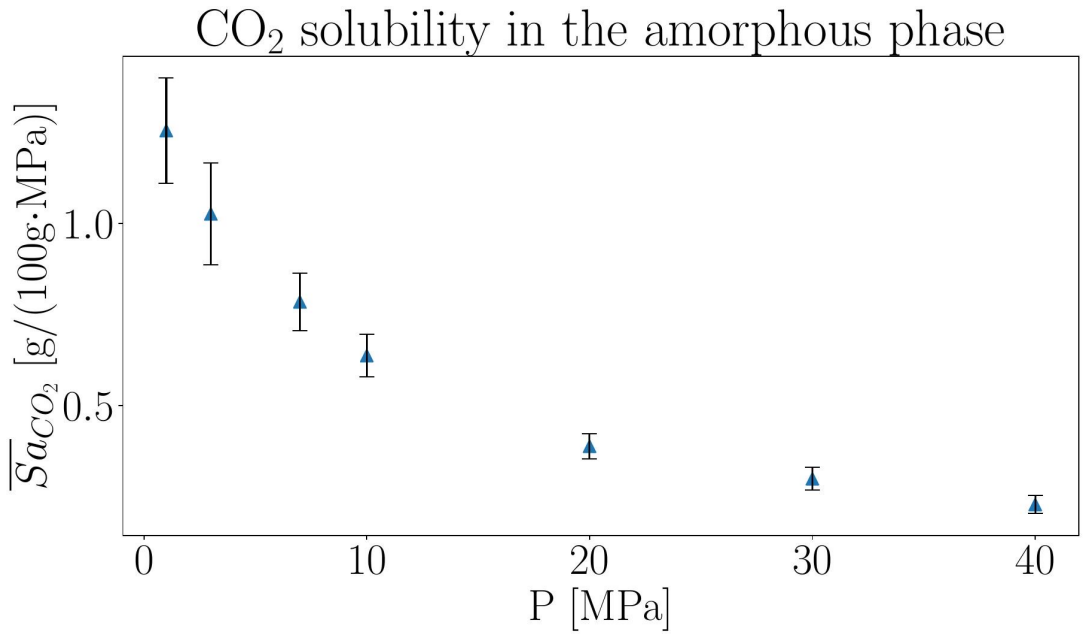
Solubility coefficients



Average CH_4 sorption coefficient in the amorphous fraction

$$C_a = S_a \times f$$



Average CO_2 sorption coefficient in the amorphous fraction

Henry's constant CH_4 : 0.10 to 0.14 g/(100g.Mpa)
Henry's constant CO_2 : 0.8 to 1.4 g/(100g.Mpa)

Michaels, A. S. & Bixler, H. J. Journal of Polymer Science (1961)
Naito, Y. et al. Journal of Applied Polymer Science (1996)
Von Solms, N. et al. Journal of Applied Polymer Science (2004)
Togawa, J. et al. Journal of Membrane Science (2001)
Ash, R. et al. Polymer (1970)
Flaconneche, B. et al. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles (2001)

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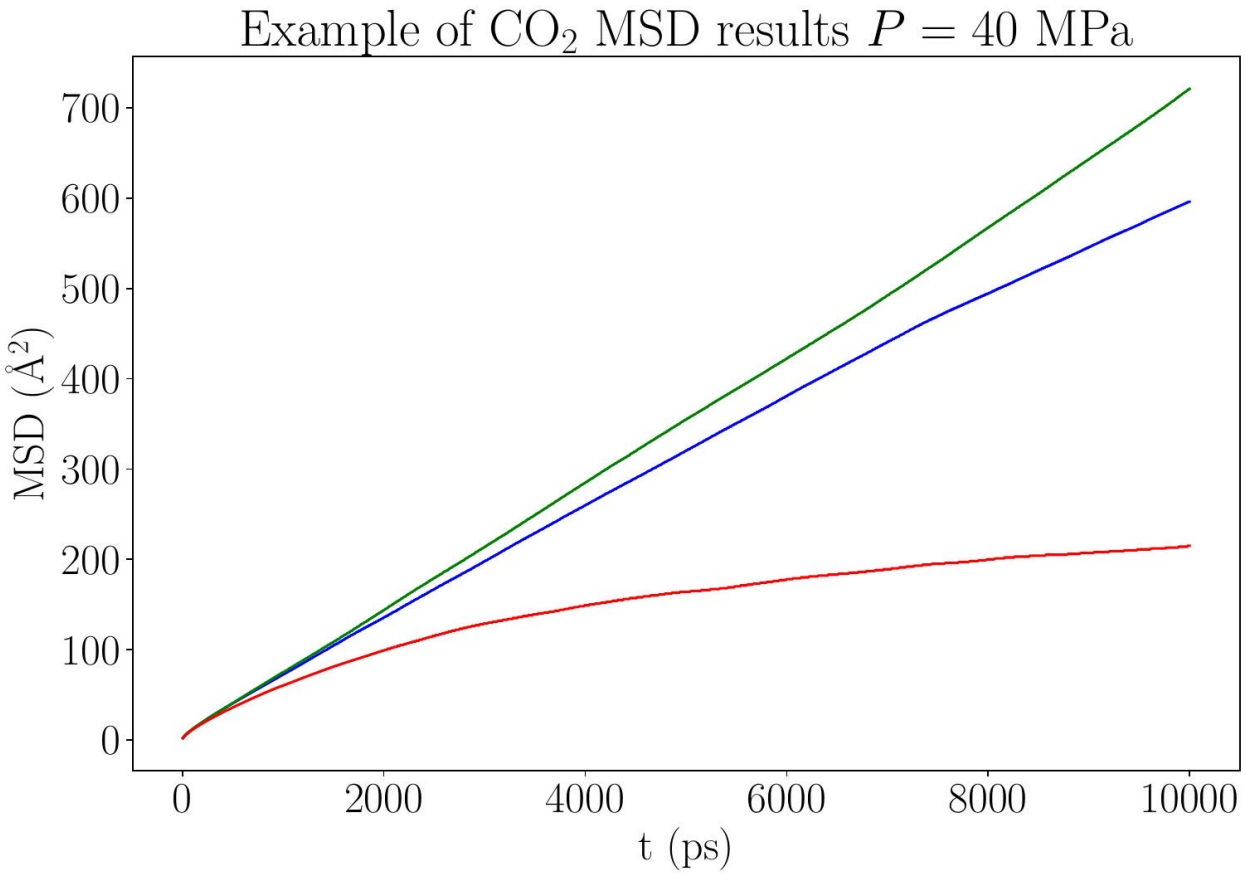
Diffusion

Diffusion: method

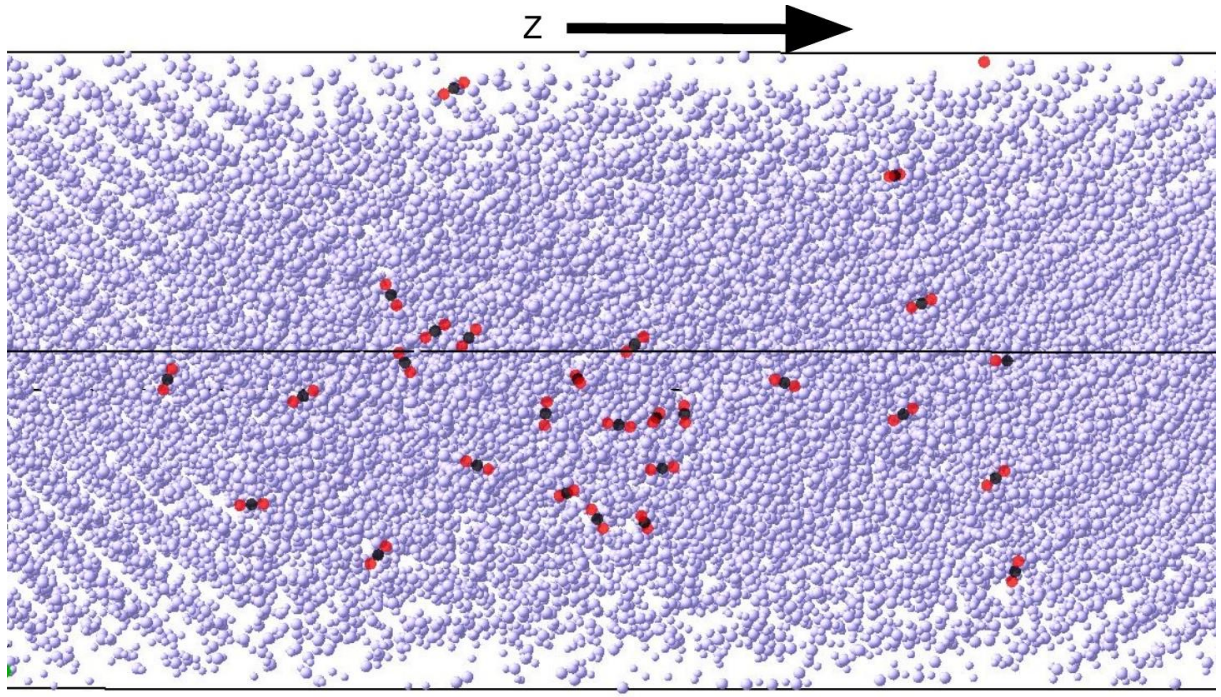
Only the x and y directions are taking into account.

Slope of the msd and Einstein relation $D_{self} = \frac{1}{4} \lim_{1 \to \infty} \frac{d}{dt} msd(t)$

$$D_{self} = D_{MS}, \qquad D = QD_{MS} \ and \ Q = \frac{\delta \ln(f)}{\delta \ln(C)}$$



MSD, in blue and green the x and y directions, in red the z direction



CO_2 dissolved in the amorphous region

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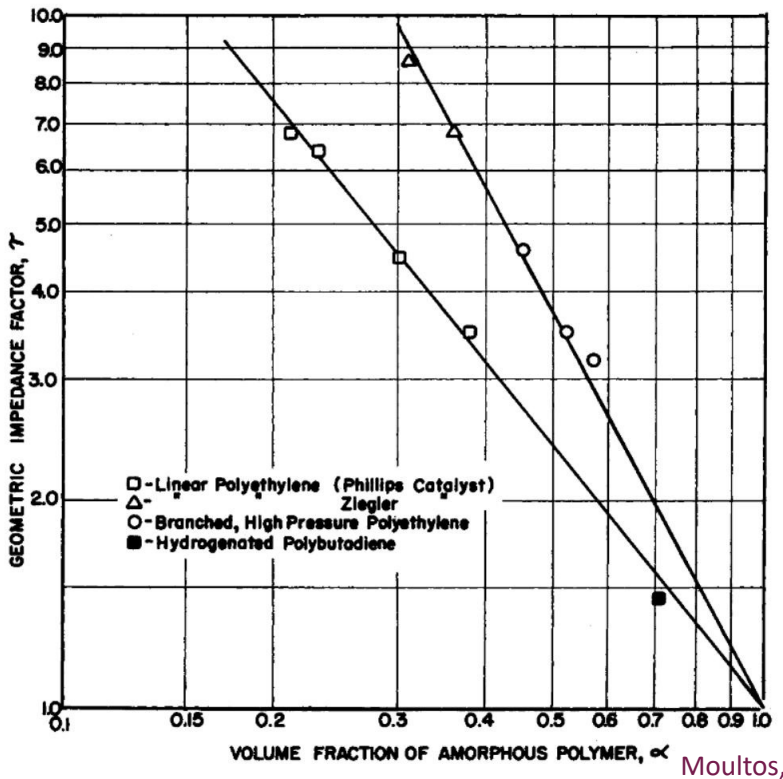
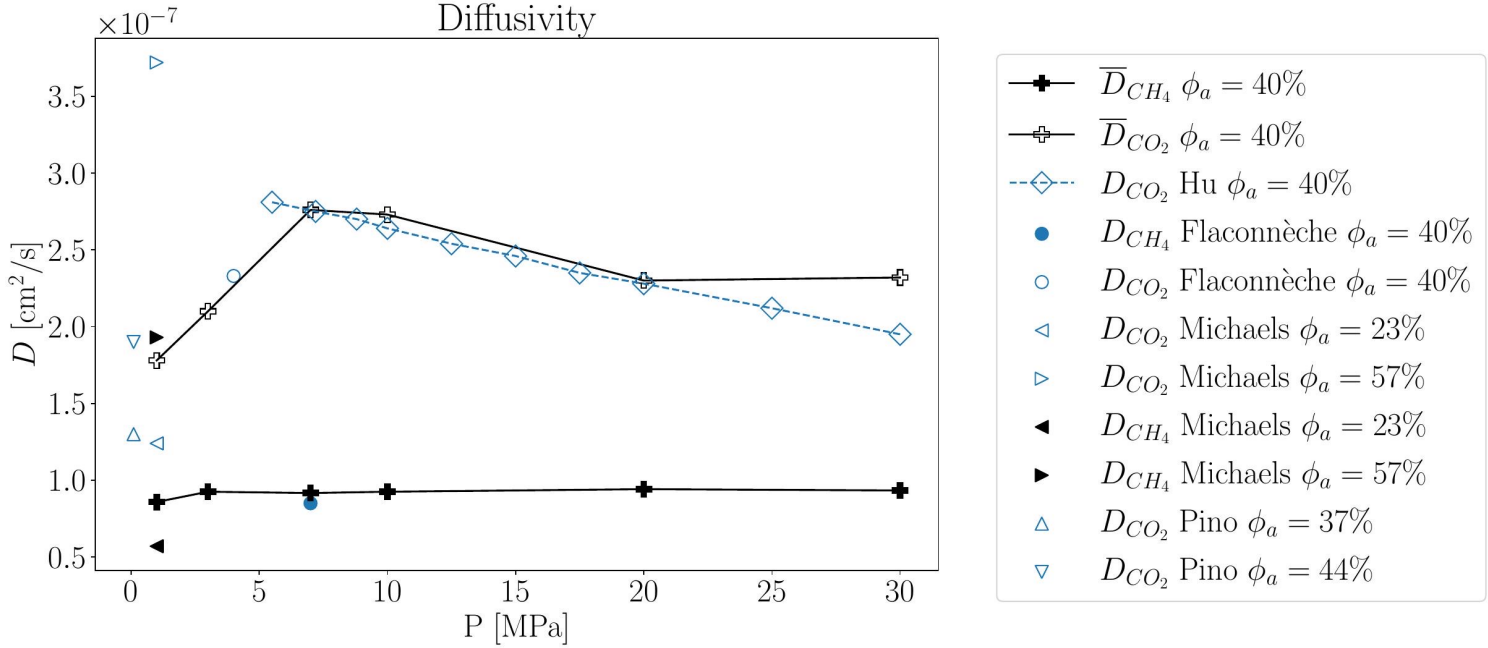
Diffusion: result

- Michaels theory : $D = \frac{D_a}{\beta\tau}$, β is taking account by the model, so $D = \frac{D_{model}}{\tau}$.
- Michaels is giving τ with the amorphous than an equivalent amorphous polymer is natural rubber.
- τ is calibrated with Flaconnèche results, $\tau_{cal.} = 8$ (Michaels is predicting $\sim 3.5 < \tau < 6$, but TraPPE-UA overestimates D (more than 50 %), which gives $4.25 < \tau_{eff} < 9$).



τ proposed by Michaels



CO_2 and CH_4 diffusion coefficients with ϕ_a = 40 %

Moultos, O. A.; Tsimpanogiannis, I. N.; Panagiotopoulos, A. Z.; Trusler, J. P. M.; Economou, I. G.. J. Phys. Chem. B 2016, 120 (50), 12890–12900

Michaels, A. S. & Bixler, H. J. Journal of Polymer Science (1961)

Flaconneche, B. et al. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles (2001)

Hu, T. Permeation of High Pressure CO2 in Semicrystalline Polymers. Phd Thesis. (Imperial College London, 2021)

Pino, M.; Duckett, R. A.; Ward, I. M. Polymer 2005, 46 (13), 4882–4890. https://doi.org/10.1016/j.polymer.2005.02.118.

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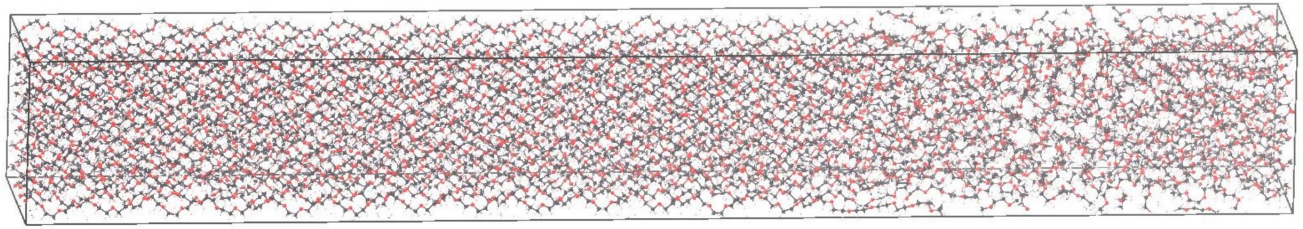
Conclusion

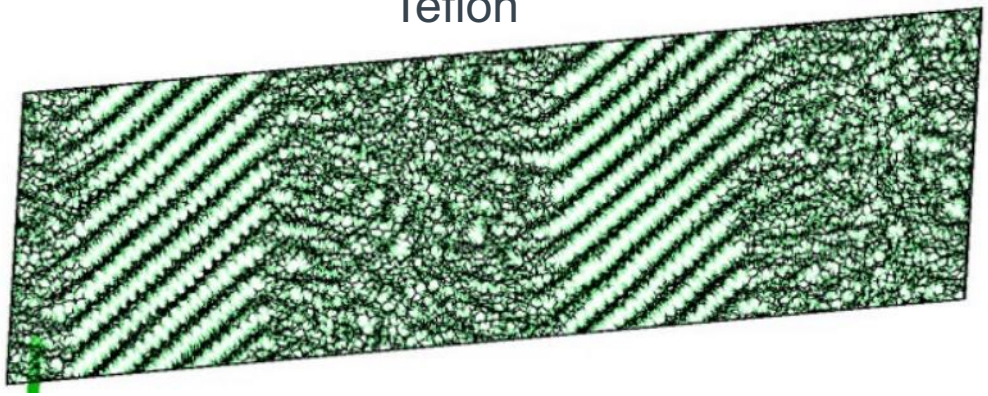
Sorption and diffusion

- **Sorption is well predicted** with the MC/MD cycles' method.
- **Diffusivity is predicted but need one correction factor** (taking into account how the geometry of the amorphous phase in the material and maybe the forcefield). **The correction factor is species-independent.**
- **Only the crystallinity matters! (Same for elastic properties in previous webinar).**

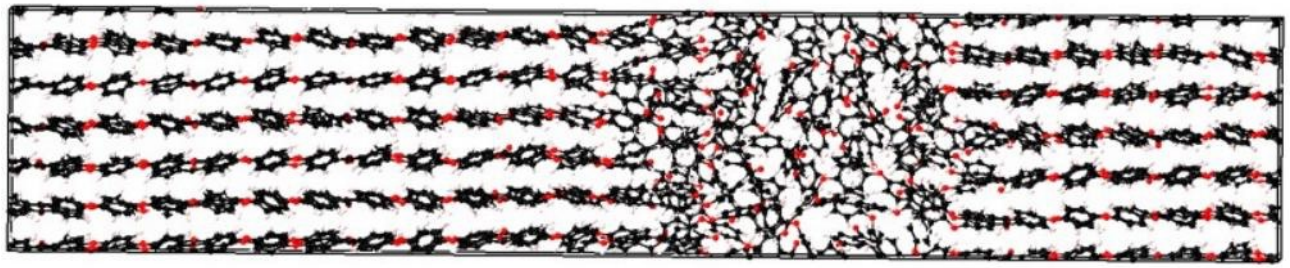
PEG



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.

***MedeA* Gibbs:** The reference approach for fluid properties and sorption.

Question and Answer Session

Dr. Marianna Yiannourakou

Materials Design

Dr. Boris Belin

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Dr. Dave Rigby

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Questions about Materials Design Webinars

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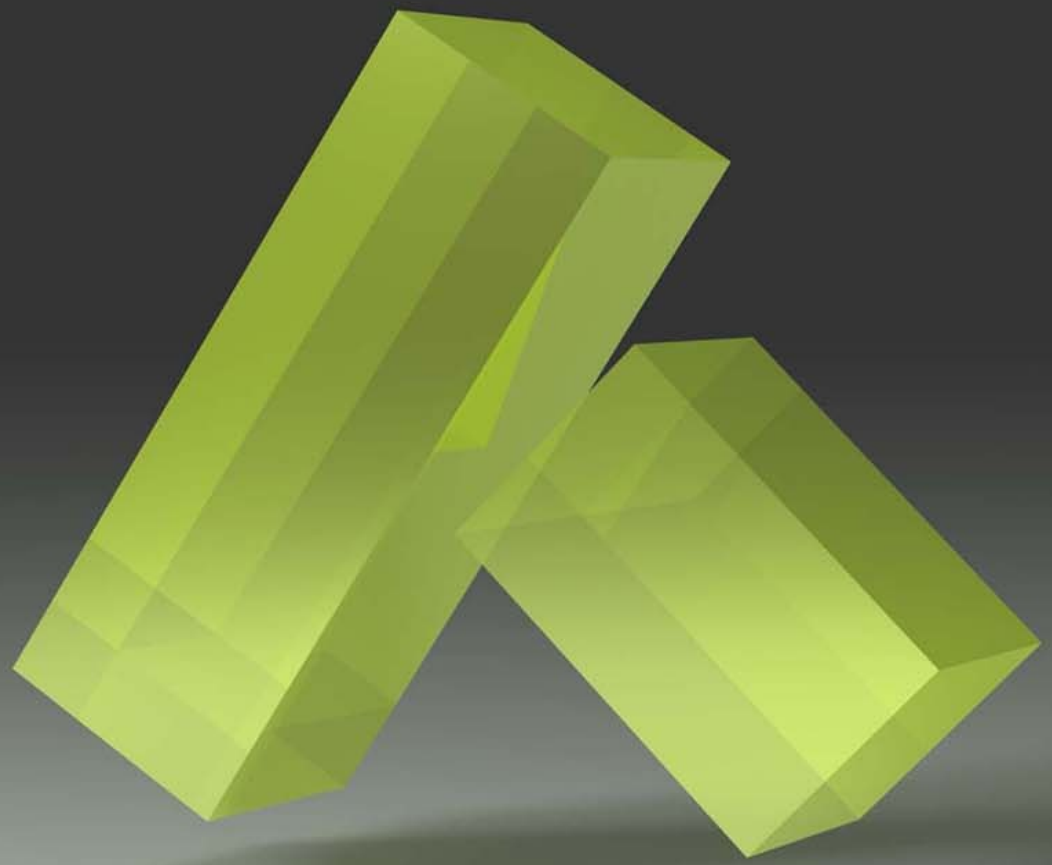

MedeA

Innovation by Simulation