Mesoscale modeling of hydrated semi-crystalline polymer morphology: A DPD study of structure and entanglement

From soup to structure

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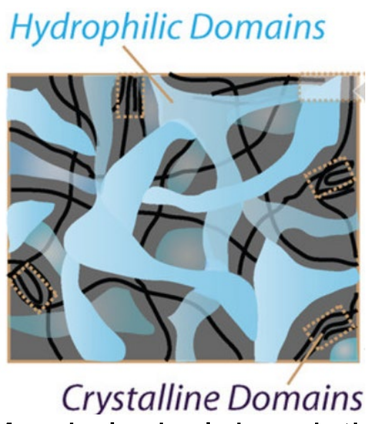
The pasta recipe

Nafion ≡ PASTA + SALT + SAUCE

Proton exchange membranes (PEM) are polymers with exclusive properties. If we take the case of Nafion PEM, they present a high molecular weight, semi-crystalline content, and water clusters under hydration allowing ionic conductivity.
A review of the literature reveals a lack of studies on molecular modeling that adequately address the **crystalline domains** and **mesoscopic-scale entanglement** of Nafion PEMs.



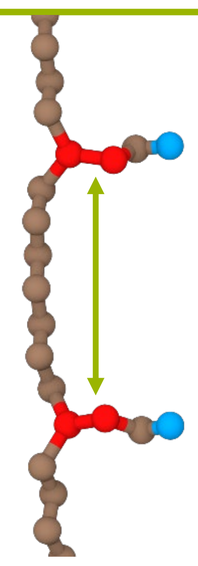
Morphological description of Nafion [1]

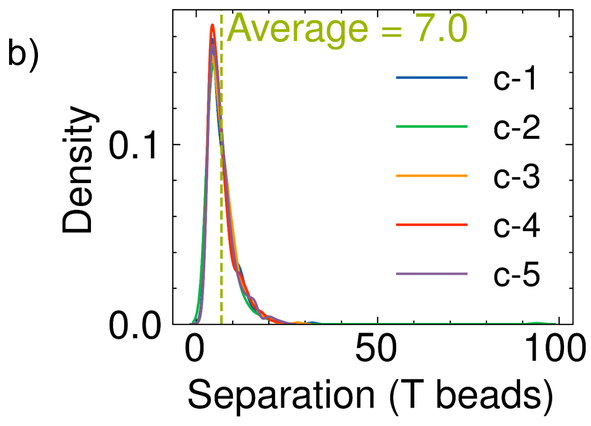
1 Ingredients matter

Start with good spaghettis

- The structure and conformation of polymers will heavily impact the result.
- The **spacing between side chains** is playing a crucial role in the final morphology of crystallites. Nafion is obtained from radical copolymerization which leads to a statistical copolymer with both, short and long runs of backbone between side chains.

a)



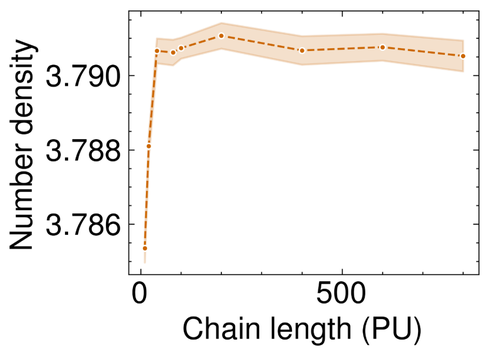


a) Bead representation of Nafion polymer. T/Ts beads are C_2F_4, O bead is C_2F_4O, and H bead is SO_3^-
b) Distribution of side chain spacing for 5 polymer chains of 400 Polymer Units (PU)

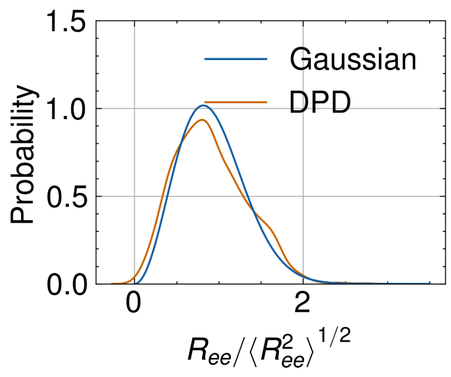
2 Correct conditioning

The spaghettis must entangle in this recipe

- Trust Gaussian chain models to ensure a correct sampling of the space. **Check the distributions** of the end-to-end distance and radius of gyration.[3]
- **Spaghettis must be long enough** to reach the entangled regime, which is easily demonstrated by a density plateau.
- The average molecular weight between entanglements (M_e) was optimized at the creation stage, giving an average of 30 C_2F_4 between entanglements, consistent with experimentally derived value of 34 C_2F_4.



Density plateau indicating entangled regime for long chains



Distribution of end-to-end distances

3 Good seasoning

The salt is missing

- Electrostatic interactions between ionic species is not to be underestimated. Still skeptical? Check out our latest paper, we show how adding NaCl boosts surfactant aggregation.[2] Nafion's side chains love water, they point right at the water channels. Why? Their sulfonic acid groups are hydrophilic and negatively charged, making them proton and water magnets.
- **Charged sulfonates and counterions** → Slater type Coulombic interactions.
- **Repulsive parameters** come from optimized systems which reproduced the **CMC of charged perfluoroalkyl surfactants**. [2]

4 Perfect cooking

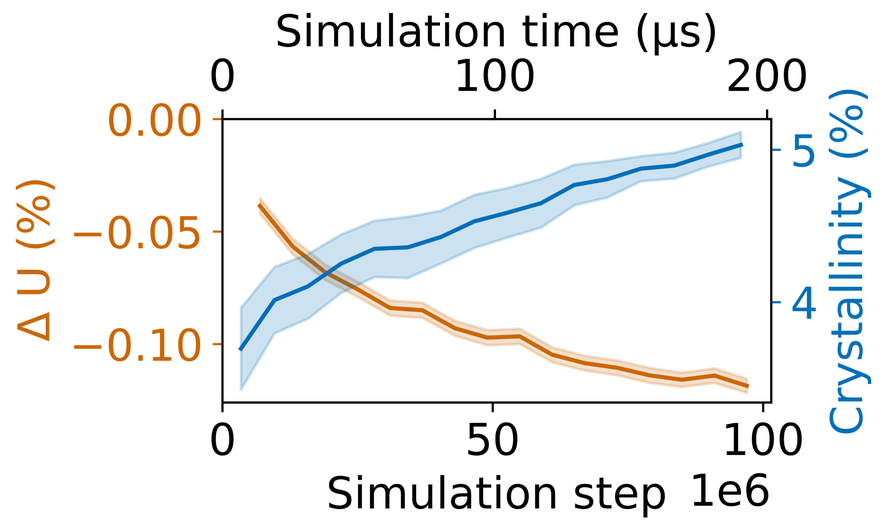
The soup needs energy

- **Annealing cycles** speed up equilibrium by giving extra energy. This separates water from the amorphous matrix and favor chain alignment for crystallization.
- Traditional MD too slow for long polymers ? We use Dissipative Particle Dynamics (**DPD**) to efficiently study polymer conformation and dynamics. We also developed a new GPU-accelerated pair style for **LAMMPS** to speed up our simulations.[4]

5 Resting time

To develop its flavor

- Let your **polymers relax**, reorder, and **align** for crystallization. Reptation is slow, so this relaxation takes time!
- A minimum cell edge of **40 nm ensures space** for multiple crystallites (~ 5 nm).



Evolution of crystalline content (blue) and potential energy variation (orange).

6 Taste it

Prepare your taste buds

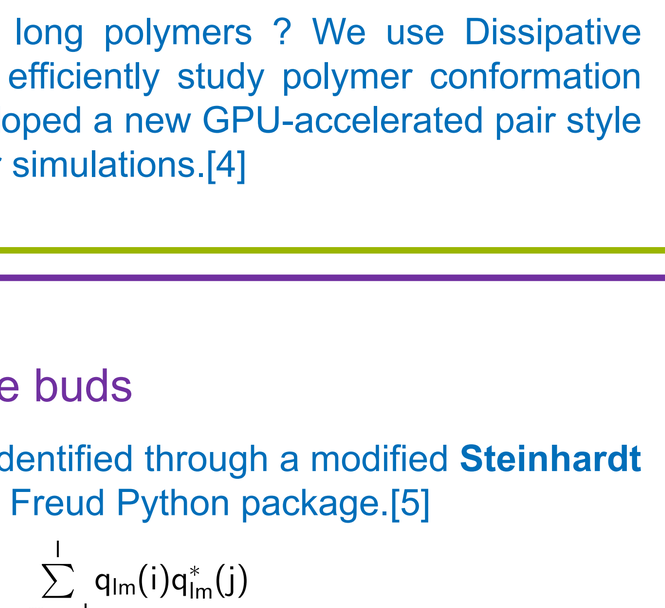
- The crystallite clusters were identified through a modified **Steinhardt order parameter** available in Freud Python package.[5]

$$d_l(i,j) = \frac{\sum_{m=-l}^{l} q_{lm}(i) q_{lm}^*(j)}{\sqrt{\sum_{m=-l}^{l} |q_{lm}(i)|^2} \sqrt{\sum_{m=-l}^{l} |q_{lm}(j)|^2}}$$

- The **structure factor** is generated through the **Fourier transform** of the **scattering length density** for direct comparison with **SAXS** intensity profiles.

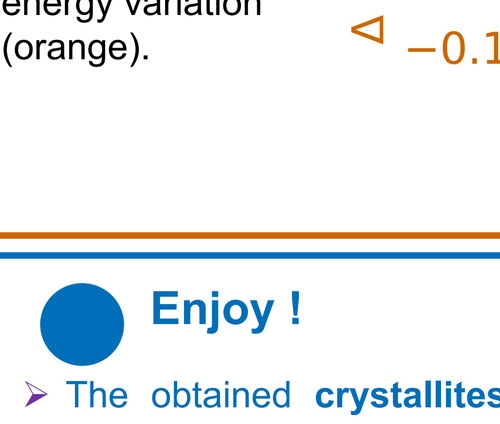
$$A(\vec{q}) = \int_V \rho(\vec{r}) e^{-i\vec{q}.\vec{r}} d^3\vec{r}$$

$$S(|\vec{q}|) = \frac{1}{N} \left\langle |A(\vec{q})|^2 \right\rangle$$

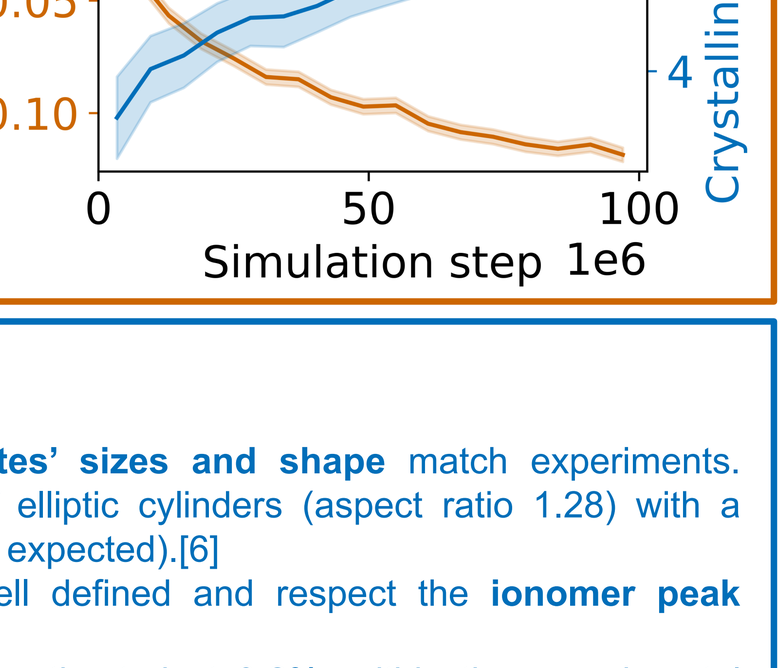


Enjoy !

- The obtained **crystallites' sizes and shape** match experiments. They mainly consist of elliptic cylinders (aspect ratio 1.28) with a **height of 3 nm** (2-5 nm expected).[6]
- **Water clusters** are well defined and respect the **ionomer peak** position upon hydration
- **Crystalline content** is estimated at **9,2%,** within the experimental range (7–20%)[1]. This result enables new applications, including advanced polymer formulations, improved proton transport, precise osmotic pressure control, and solid polymer electrolytes.



Example of crystallite



Snapshot of equilibrated membrane, with crystallites in black

References:

[1] Kusoglu, A .; *et al.* Chemical Reviews **2017**, 117 (3), 987–1104
[2] Barraud, E.; *et al. Langmuir*, **2025**, 41 (11), 7272–7282
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[4] Github. LAMMPS. github.com/lammps/lammps/releases/tag/patch_27Jun2024
[5] Ramasubramani, V.; *et al. Computer Physics Communications*, **2020**, 254, 107275.
[6] Schmidt-Rohr, K.; *et al. Nature Materials*, **2008**, 7 (1), 75–83