

Local and Global Order in Two-Dimensional Packings of Semi-flexible Polymers

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1. Introduction

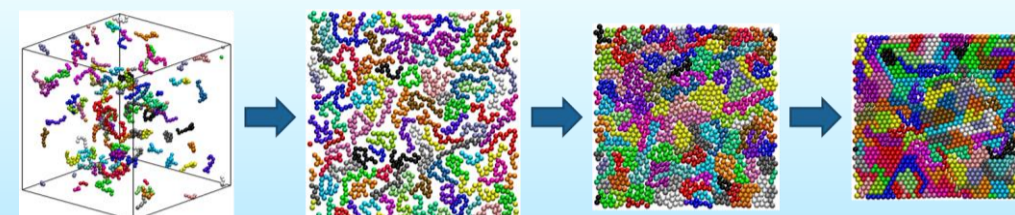
We analyse **dense packings of freely-jointed (FJ) and semi-flexible polymer chains in extremely confined monolayers** [1,2].

- Objectives:**
- ◆ Study the effect of **chain stiffness** on the **packing ability of polymer chains in two dimensions (2D)**.
 - ◆ Explore the **limit of Random Close Packing (RCP)** as a function of **equilibrium bending angle (θ_0)**.
 - ◆ Gauge the **emergence of local and global order** on **monolayer semi-flexible polymer packings**.

2. Method

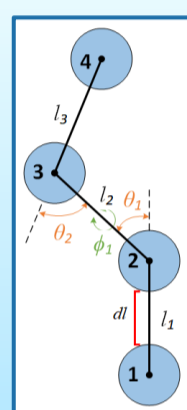
Monte Carlo (MC) Simulations: home-made simulator-descriptor suite, *Simu-D* [3].

- *NVT* ensemble ($T = 1/k_B$).
- Formation of **monolayer by adsorption** process.
- Extreme plate-like confinement (2D film).
- Compression of packings until **RCP limit**.



Process to create the densest 2D polymer thin films [1,2].

3. Molecular Model



Bonded Interactions

Bond Length:

Tangency condition: $dl \rightarrow 0$

Bending Stiffness [4]:

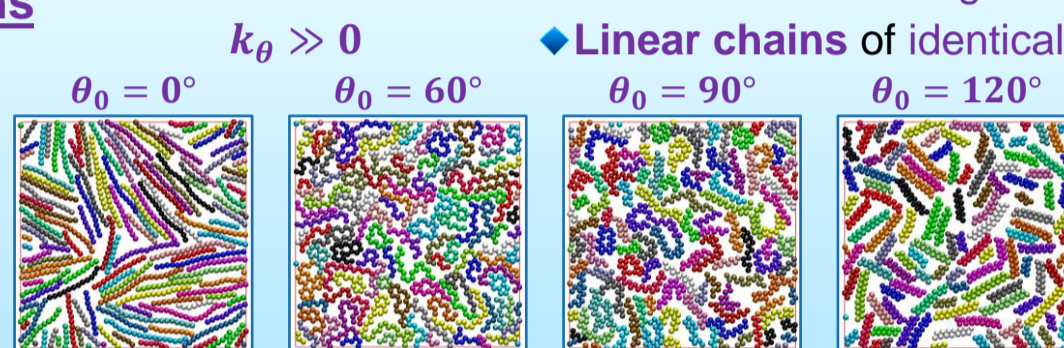
$$U_{bend}(\theta) = k_\theta(\theta - \theta_0)^2$$

- k_θ : Bending constant.
- θ_0 : Equilibrium bending angle.

Non-bonded Interactions

Hard Sphere (HS) Potential

$$U_{HS}(r_{ij}) = \begin{cases} 0, & r_{ij} \geq \sigma \\ \infty, & r_{ij} < \sigma \end{cases}$$



Surface Coverage

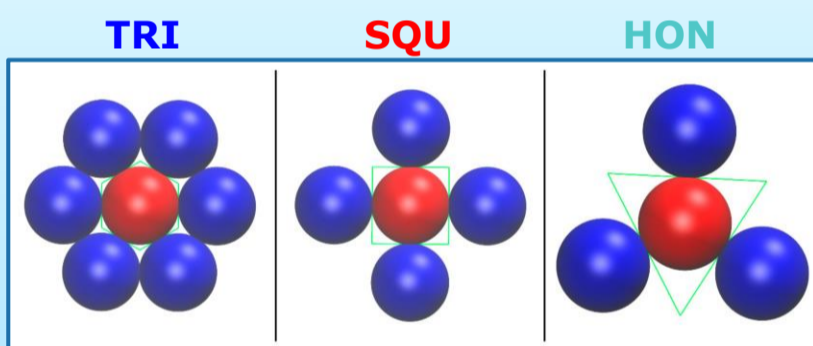
$$\varphi^* = \frac{\pi N_{at}}{4S_{cell}} \sigma^2$$

4. CCE Norm

The **Characteristic Crystallographic Element (CCE) Norm** [5] descriptor (ε_i^X) quantifies the **orientational and radial similarity** of a local environment for a given site i with respect to a **reference crystal X**.

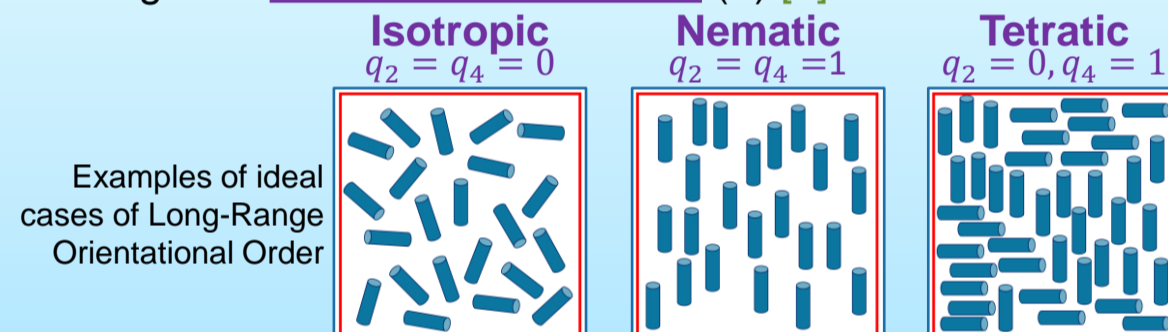
Local environment i is identified as a **X-type crystal**:

$$\varepsilon_i^X \leq \varepsilon^{thres} = 0.245$$



5. Long-Range Order Parameter

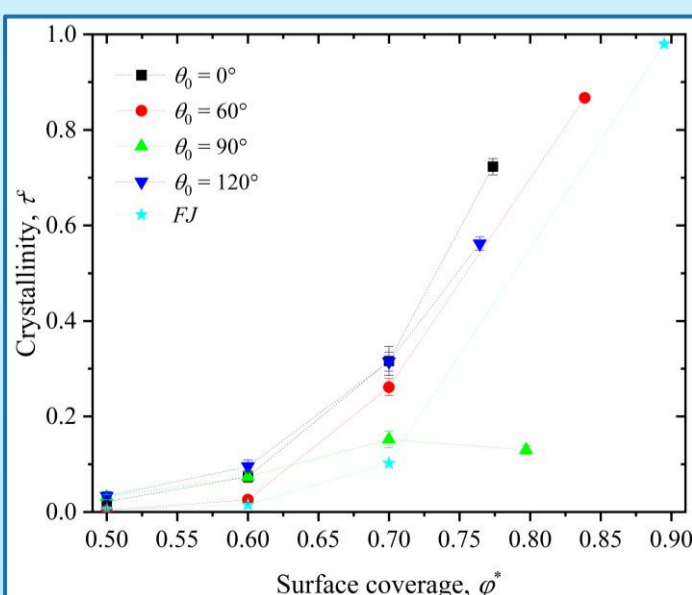
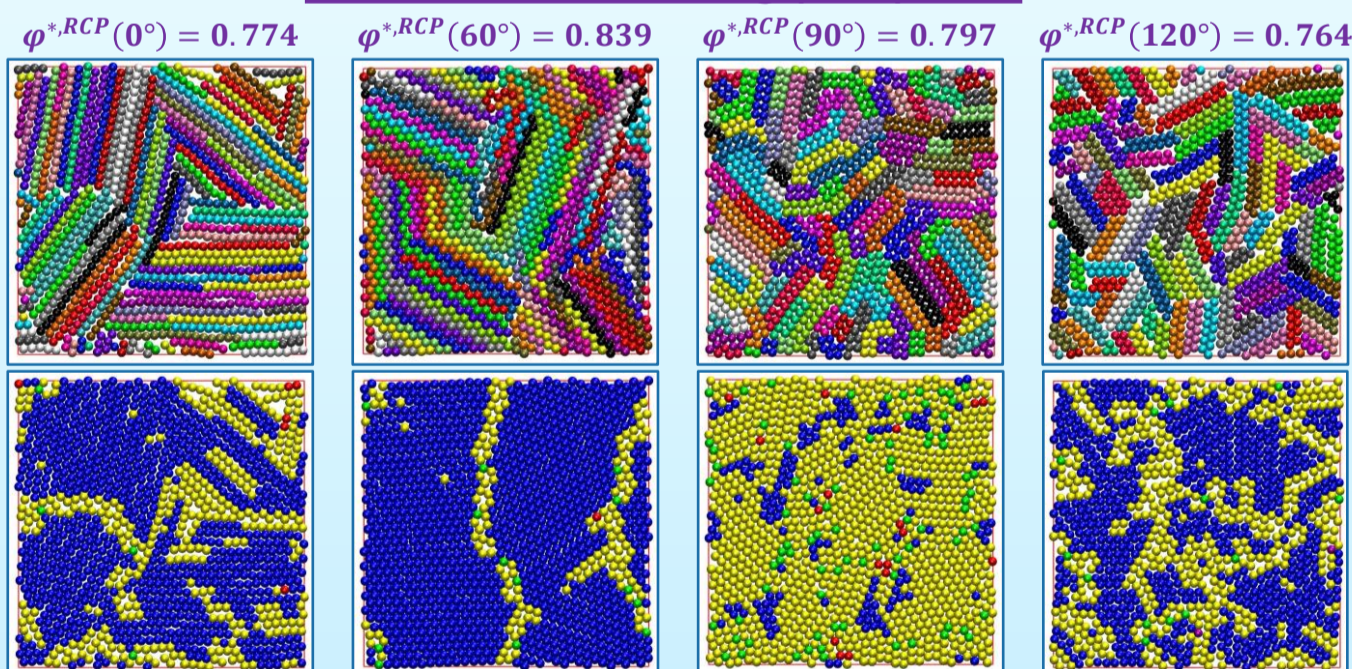
The **Long-Range Orientational Order** is measured by two parameters [2]: the **nematic order parameter (q_2)** with the **2nd-order tensor (Q)** [6] and the **tetratic order parameter (q_4)** through the **4th-order tetratic tensor (T)** [7].



Examples of ideal cases of Long-Range Orientational Order

6. Local Order

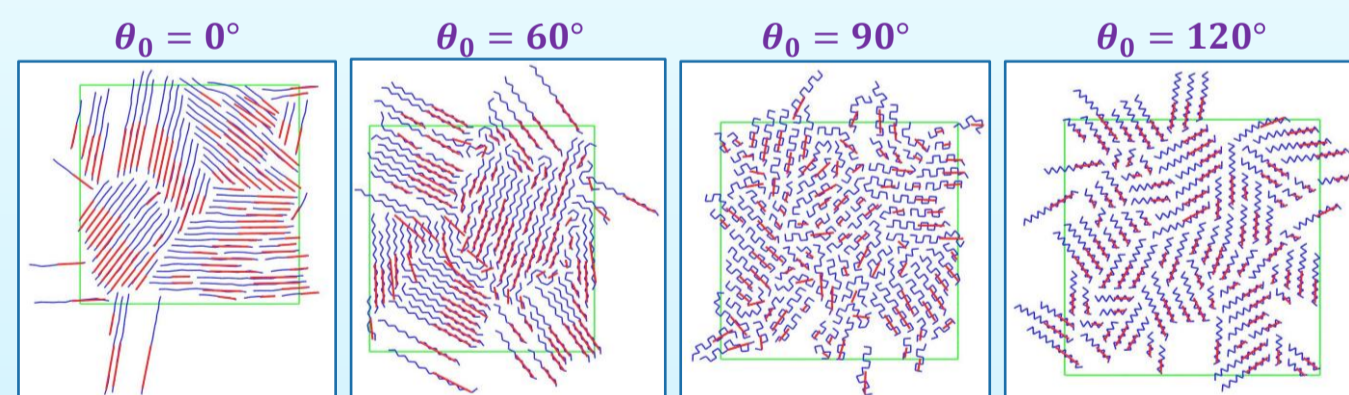
Random Close Packing (RCP) Limit



Universal behaviour for semi-flexible polymers:

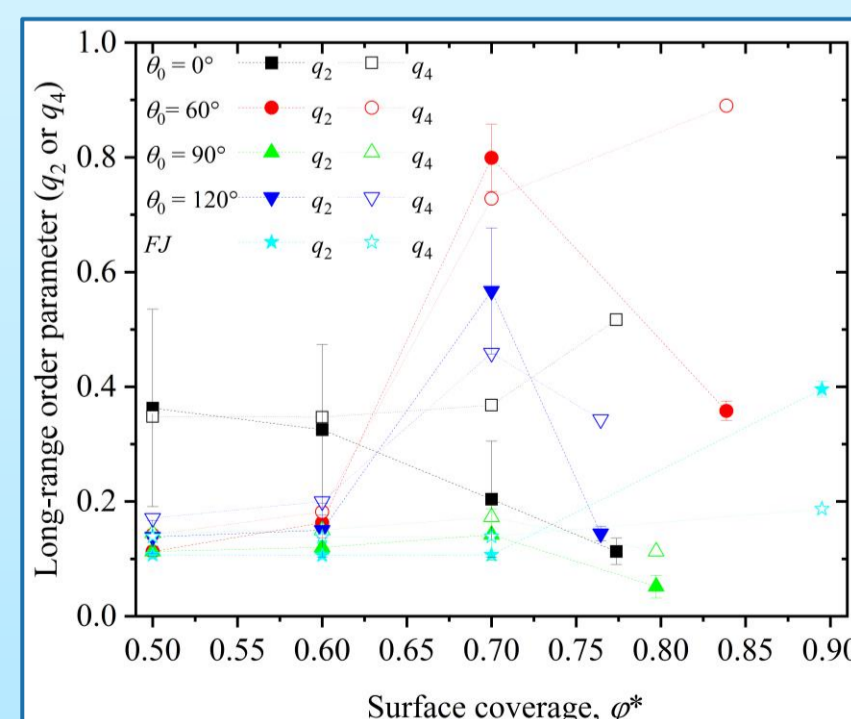
- ◆ **Crystallinity increases significantly** as concentration increases.
- ◆ **Highest local order** is reached at the RCP limit.
- ◆ **EXCEPTION:** Packings of $\theta_0 = 90^\circ$ remain **locally amorphous** because of geometric incompatibility with TRI crystal. Resulting packing is a tiling pattern of intramolecular squares and intermolecular triangles.

7. Global Order



Semi-flexible polymer chains at the RCP limit ($\varphi^{*,RCP}(\theta_0)$) represented by **blue lines**. Also **red lines** represent the **chain orientations** (vectors of the largest semiaxis of the inertia ellipsoids).

- ◆ As **surface coverage increases**, there is a **transition of isotropic \rightarrow nematic \rightarrow tetratic order**.
- ◆ **Tetratic order** is the prevailing state at the RCP limit.
- ◆ For rod-like (0°) polymers, **nematic phase is highly unstable** due to the small chain lengths.
- ◆ **EXCEPTION:** Packings of $\theta_0 = 90^\circ$ remain **isotropic** at all concentrations.



References

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- [2] D. Martínez-Fernández *et al.*, *J. Chem. Phys.* **161**, 034902 (2024).
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- [5] P.M. Ramos *et al.*, *Crystals* **10**, 1008 (2020).
- [6] D. Frenkel and R. Eppenga, *Phys. Rev. A* **31**, 1776-1787 (1985).
- [7] J. Geng and J.V. Selinger, *Phys. Rev. E* **80**, 011707 (2009).

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