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ETSI de Ingenieros Industriales

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ISOM Institute for Optoelectronic Systems and Microtechnology

Molecular Simulation of the Phase Behaviour of Attractive Rod-like Polymers

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1. Introduction

(shape, size and interactions)

Fine tuning of selected parameters can lead to the **design of materials with controlled structural behaviour**.

Objectives:

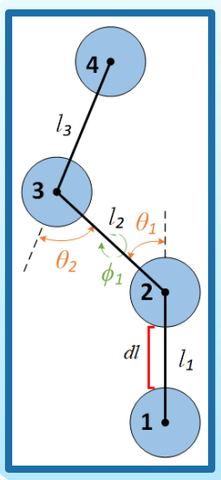
- Predict the **crystal morphologies** of **attractive rod-like polymers** through a simple **geometric neighbour model** [1].
- Study the effect of **interaction range** and **chain stiffness** on the phase behaviour of **colloidal polymer crystals**.
- Determine a **phase diagram of distinct crystal morphologies of attractive rod-like polymers** [1,2].

2. Method

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

- *NVT* ensemble ($T = 1/k_B$, $\varphi = 0.05$ or $\rho_n = 0.0262$).
- Dilute bulk conditions (3D).

3. Molecular Model



- 100 chains of average chain length $N_{av} = 12$.
- Linear chains of identical hard spheres.

Bonded Interactions

Bond Length:
Tangency condition: $dl \to 0$

Bending Stiffness [4]:

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

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

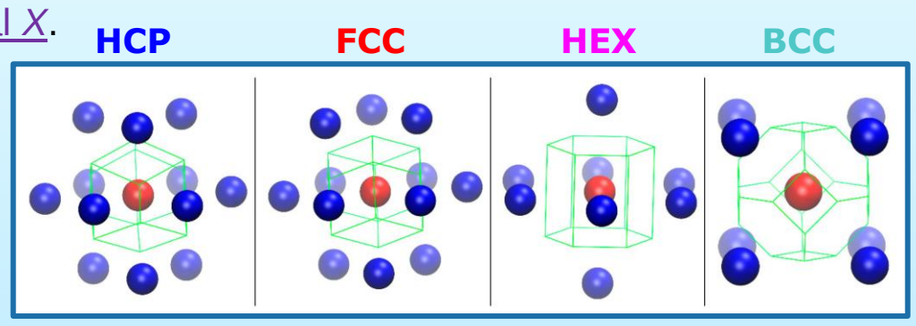
Non-bonded Interactions

Square-Well (SW) Potential

$$U_{SW}(r_{ij}) = \begin{cases} 0, & r_{ij} \geq \sigma_2 \\ -\varepsilon, \sigma_1 \leq r_{ij} < \sigma_2 \\ \infty, & r_{ij} < \sigma_1 \end{cases}$$

4. CCE Norm

The **Characteristic Crystallographic Element (CCE) Norm** [5,6] 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:** → $\varepsilon_i^X \leq \varepsilon^{thres} = 0.245$

CCE Order Parameter, S^X

$$S^X = \int_0^{\varepsilon^{thres}} P(\varepsilon^X) d\varepsilon^X$$

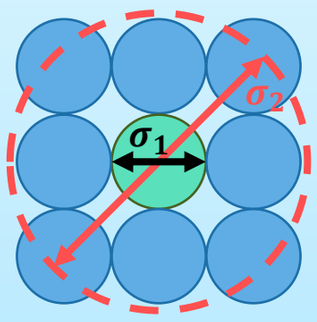
Degree of total crystallinity, τ^c

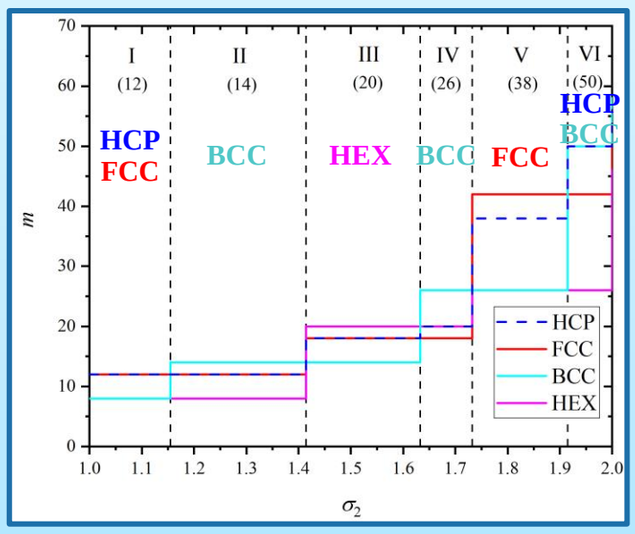
$$\tau^c = \sum_{k=1}^{N_{s,d}} S^X = \sum_{k=1}^{N_{s,d}} \int_0^{\varepsilon^{thres}} P(\varepsilon^X) d\varepsilon^X$$

5. Geometric Neighbour Model

Geometric Neighbour (GN) Model [1]: Given the entirely attractive SW potential, **the thermodynamic stability of the crystal is primarily dictated by the number of neighbours that can fit within a range** [7].

More neighbours within σ_2 → **More stable the corresponding crystal**

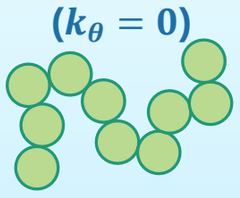


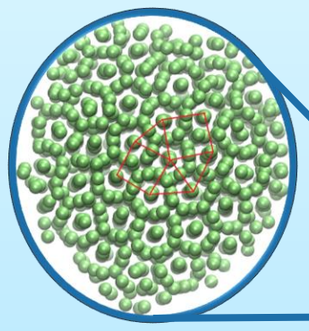


Number of neighbours (*m*) as a function of distance from a reference site (σ_2) for the **HCP**, **FCC**, **BCC**, and **HEX** crystals.

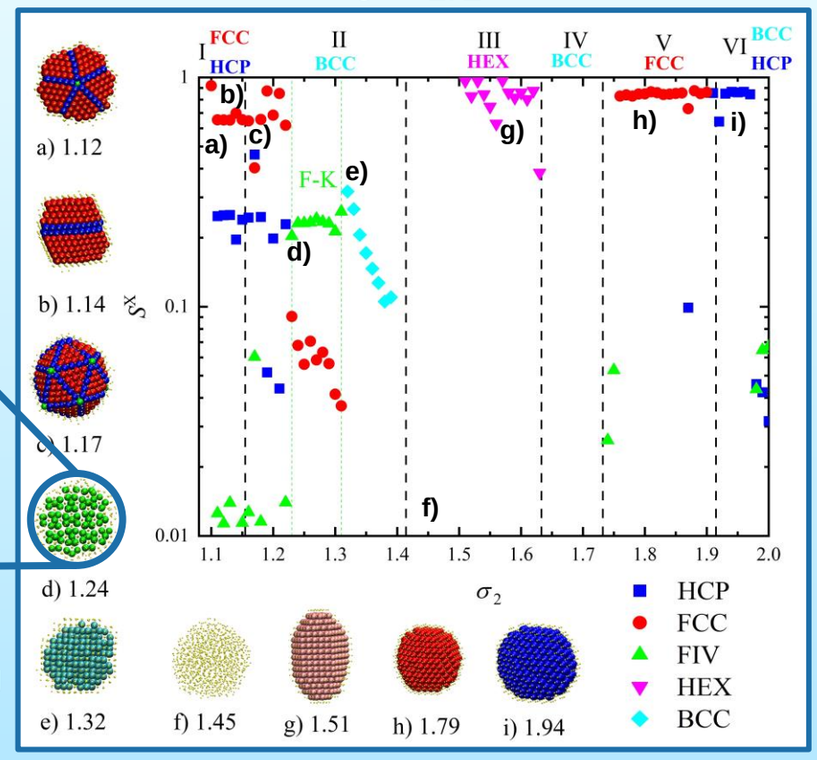
6. Freely-jointed Chains

Freely-jointed polymers ($k_\theta = 0$)



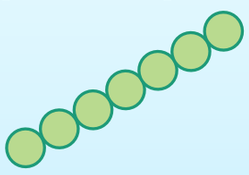


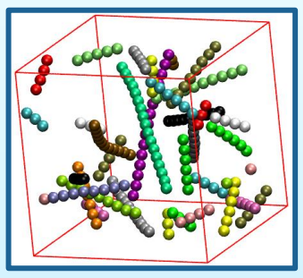
Frank-Kasper (F-K) phase, *σ* variant
Triangle and square tiling pattern: **$3^2.4.3.4$** [8]

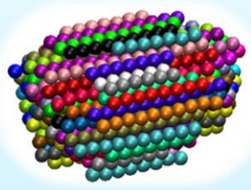


7. Results of Rod-like Chains

Rod-like polymers ($k_\theta \gg 0, \theta_0 = 0°$)

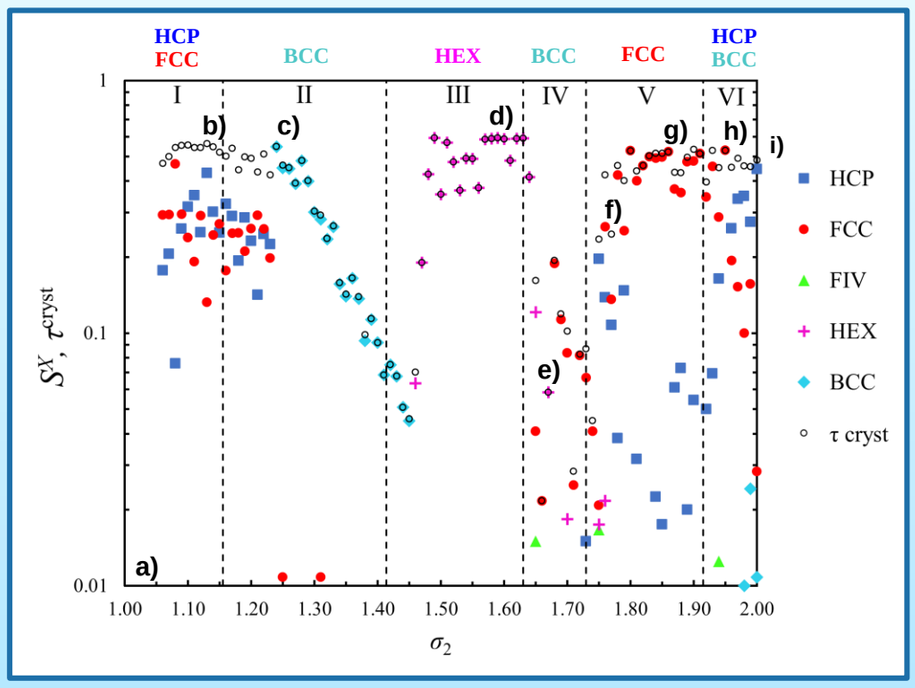


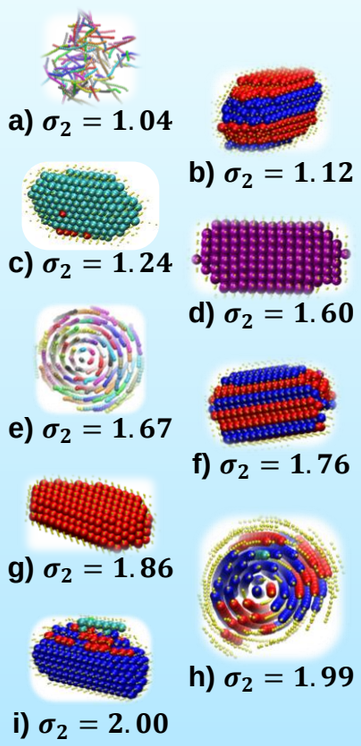




Comparing with is counterpart of **Freely-jointed Polymers**.

- **Rod-like polymers agree better** with the **GN model** than fully flexible polymers.
- No **Frank-Kasper phases**.
- Most rod-like systems present almost **perfect nematic phases**.
- In specific **regions of low crystallinity**, rod-like clusters form **spiral morphologies**.





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[2] M. Herranz *et al.*, *Polymers* **12** (5), 1111 (2020).
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[7] J. Serrano-Illán, G. Navascués and E. Velasco, *Phys. Rev. E* **73**, 011110 (2006).
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