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Molecular Simulation Studies of the Isotropic-to-Nematic Transition of Rod-like Polymers in the Bulk and Under Confinement

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OBJECTIVES

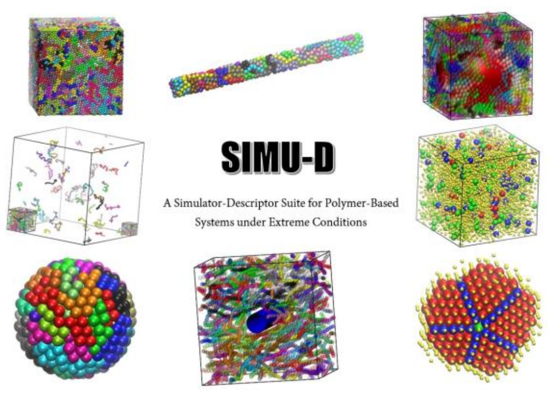
1. Investigate the factors that affect the **isotropic-to-nematic transition** of **hard, colloidal, rod-like polymers**.

- ✓ **Chain length, N**
- ✓ **Packing density, φ**
- ✓ **Plate Confinement in one, two or three dimensions**
- ✓ **Intensity of bending potential, k_θ**

METHOD

Monte Carlo method: *Simu-D* simulator-descriptor [1].

- Simulator part based on Monte Carlo algorithms [2]



MODEL

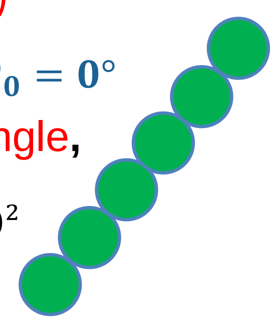
- Polymers are modelled as linear chains of identical tangent hard spheres with a collision diameter σ.
- Systems are composed of N_{at} monomers distributed in N_{ch} chains of average chain length N_{av}.
- Interactions between monomers are described by the **Hard Sphere (HS) potential**.

Hard Sphere (HS) Potential

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

Semiflexible polymers ($k_\theta \gg 0$)

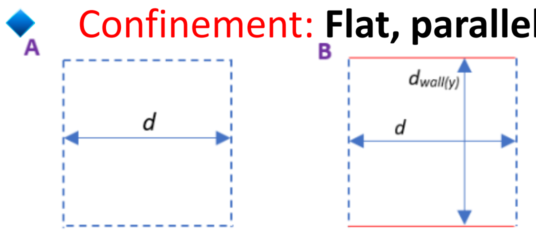
$$\theta_0 = 0°$$



- Tuneable harmonic potential controlling the bending angle, θ, where:
  - k_θ is the bending constant.
  - θ_0 is the equilibrium bending angle.

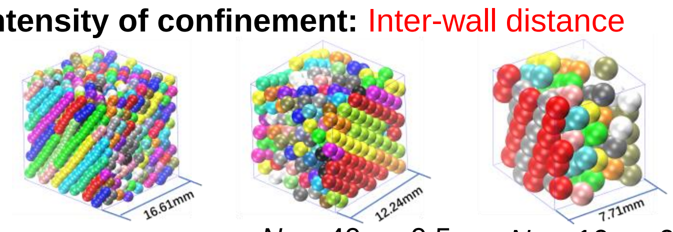
$$U_{bend}(\theta) = k_\theta(\theta - \theta_0)^2$$

- Packing density: $\varphi = \frac{V_{mon}}{V_{cell}} = \frac{\pi}{6}\frac{N_{at}}{V_{cell}}\sigma^3$
- Confinement: **Flat, parallel and impenetrable walls** in at least one dimension.



Bulk case (no confinement)   Confinement in one dimension

Intensity of confinement: Inter-wall distance



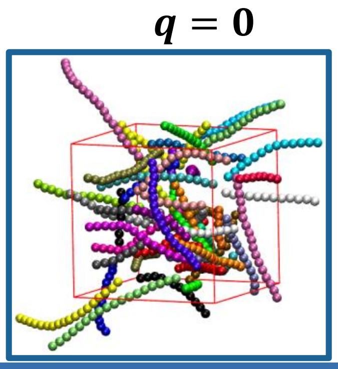
N_{ch} =100 φ =0.5 N_{ch} =40 φ =0.5 N_{ch} =10 φ =0.5

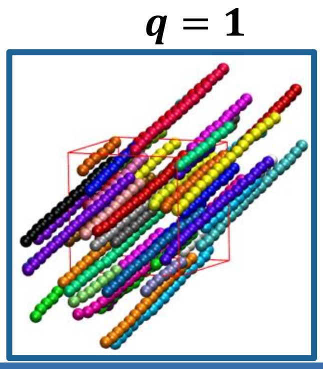
LONG-RANGE ORDER

The **chain orientational order** is defined by the averages of a second-order invariant of all the molecular orientations, the **second-order tensor *Q*** [3,4].

A **scalar order parameter, *q*,** is obtained by comparing the ***Q*** tensor of the system with the Q^{PRO} tensor of a perfect prolate nematic system.

Isotropic (ISO) $q = 0$ **Prolate Nematic (PRO)** $q = 1$





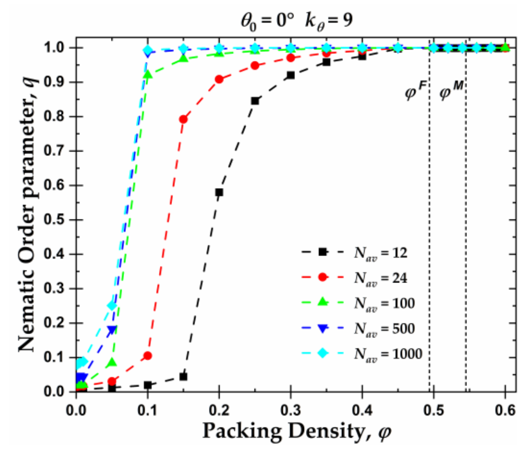
Tensor *Q*

$$Q = \frac{1}{N_{ch}}\sum_{i=1}^{N_{ch}} u_i u_i - \frac{1}{3}\delta$$

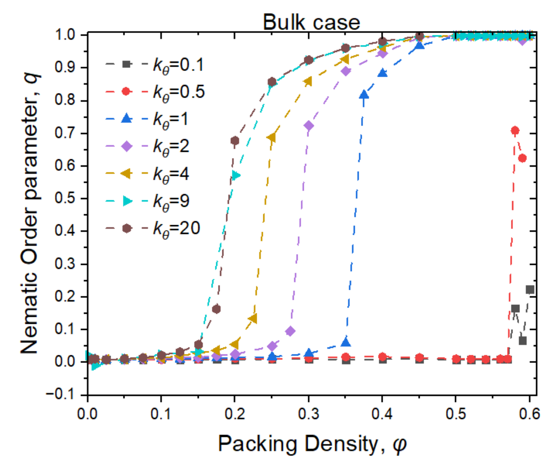
u_i : Unit vector of chain i

RESULTS & DISCUSSION

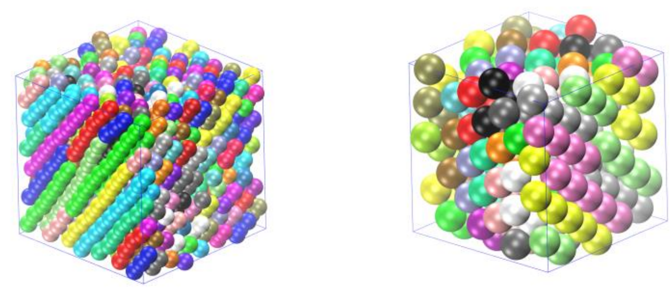
- In **bulk** case, the effect of different N_{av}



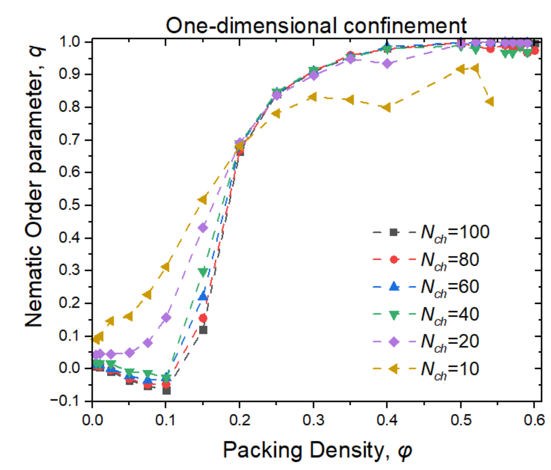
- In **bulk** case, the effect of different k_θ



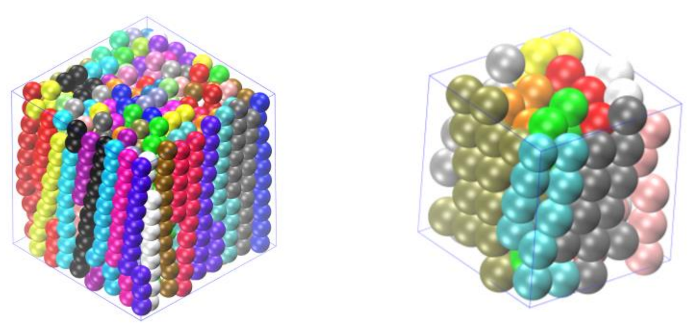
- **One-dimensional confinement**



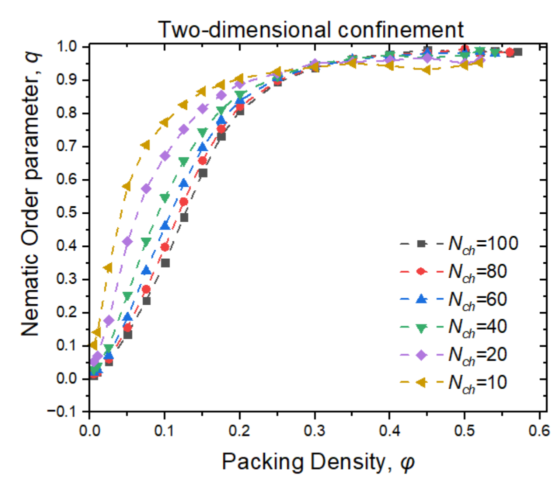
N_{ch} =100 φ =0.5 N_{ch} =20 φ =0.5



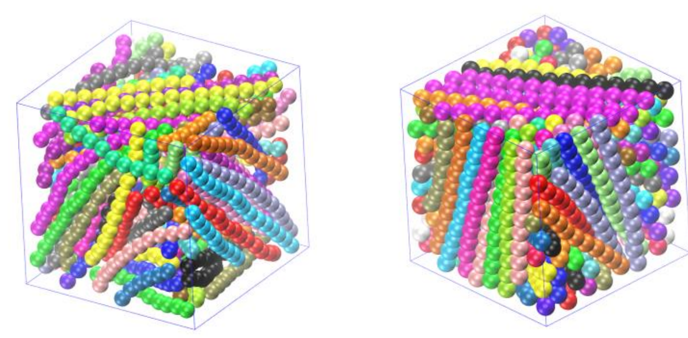
- **Two-dimensional confinement**



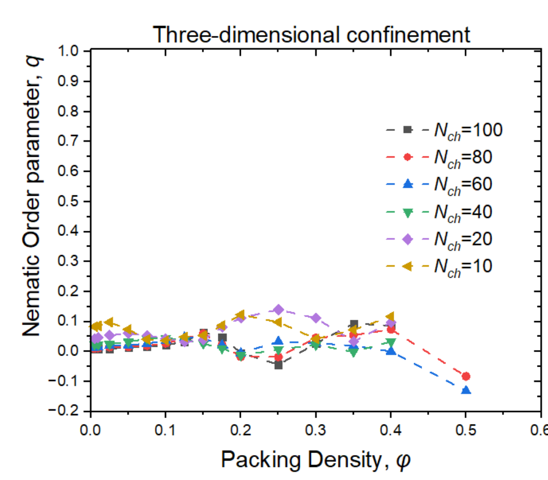
N_{ch} =80 φ =0.5 N_{ch} =10 φ =0.5



- **Three-dimensional confinement**



N_{ch} =100 φ =0.25 N_{ch} =100 φ =0.4



CONCLUSION

- ➢ The longer the chain the lower the critical packing density required for the nematic-to-isotropic transition.
- ➢ Bending stiffness affects profoundly the isotropic-to-nematic transition. The transition occurs at very high packing densities for low values of k_θ.
- ➢ Intensity of confinement accelerates the transition but also reduces the level of long-range order.
- ➢ Full confinement inhibits the long-range ordering transition.

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