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Entropy-driven Phase Transition of Semiflexible Hard-Sphere Polymer Packings in Two and Three Dimensions

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Motivation

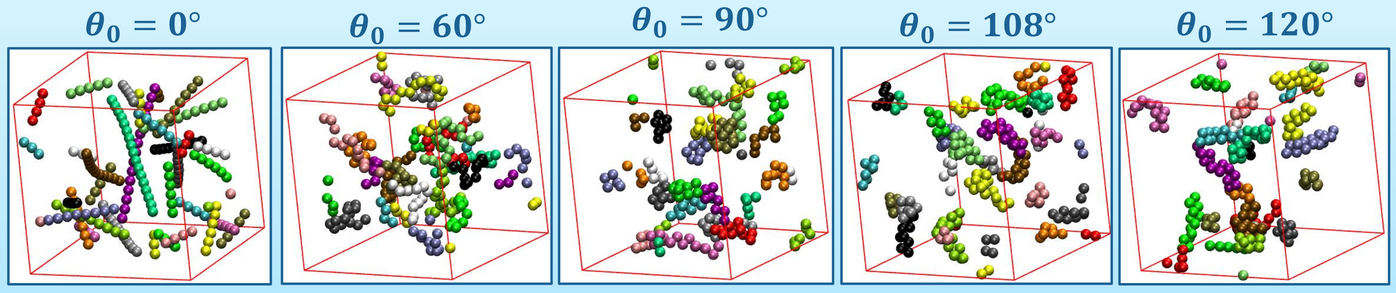
Objective: Study the effect of **chain stiffness** and **concentration** on **crystallization** of **athermal, linear semiflexible polymers** in 3-D **bulk** and 2-D **thin films**.

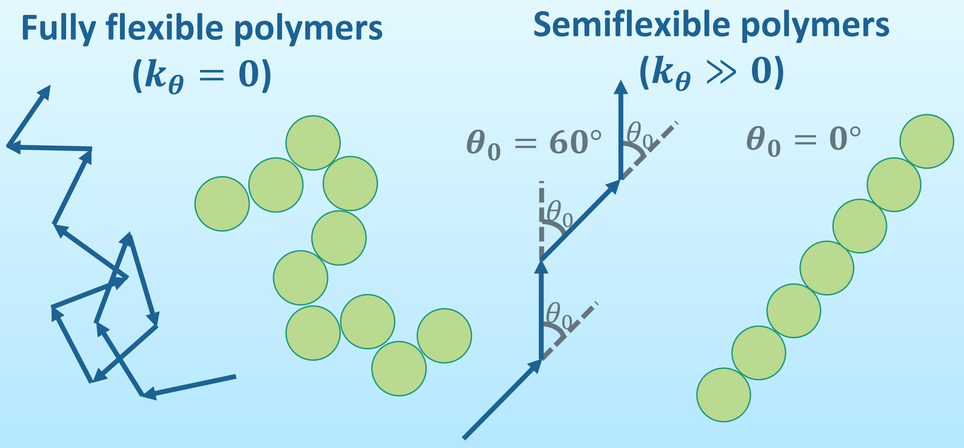
Simulation Tools:
- **Monte Carlo** suite for the simulation of complex, polymer-based systems [1,2].
- **Characteristic Crystallographic Element** (CCE) descriptor to gauge local environment of computer-generated systems [3,4].

Molecular Model

- Linear chains of tangent hard spheres of uniform size.
- **Chain Stiffness** → Bending angle potential: $v^{bend}(\theta) = k_\theta(\theta - \theta_0)^2$

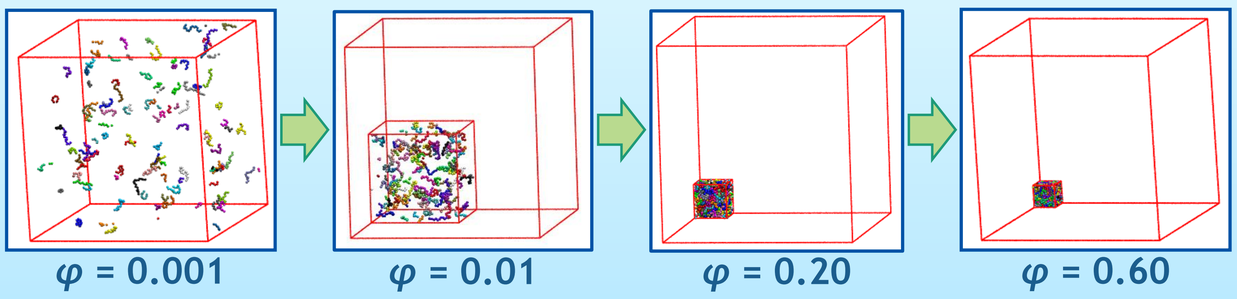
$\theta_0 = 0°$ $\theta_0 = 60°$ $\theta_0 = 90°$ $\theta_0 = 108°$ $\theta_0 = 120°$





Shrinkage Simulations

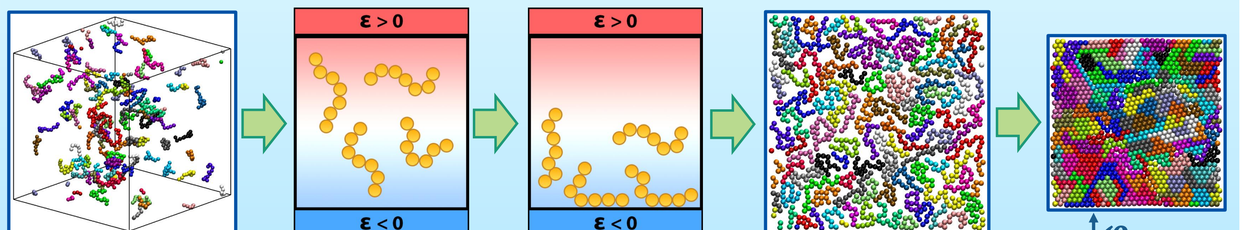
- **Shrinkage simulations** generate configurations from dilute conditions up to the maximally random jammed (MRJ) state [5,6].



φ : Packing density

Creation of 2-D Thin Films

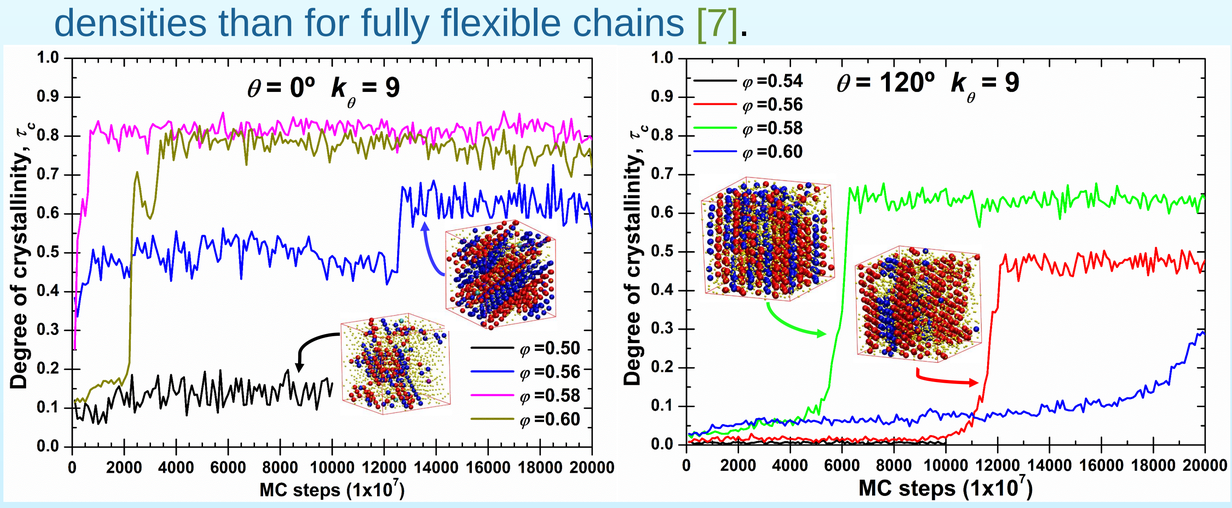
- Starting from bulk configurations, we insert flat walls and repulsive/attractive potential for polymers to be adsorbed on one surface, forming a **thin film of one-layer thickness**.



φ_{sup} : Surface coverage

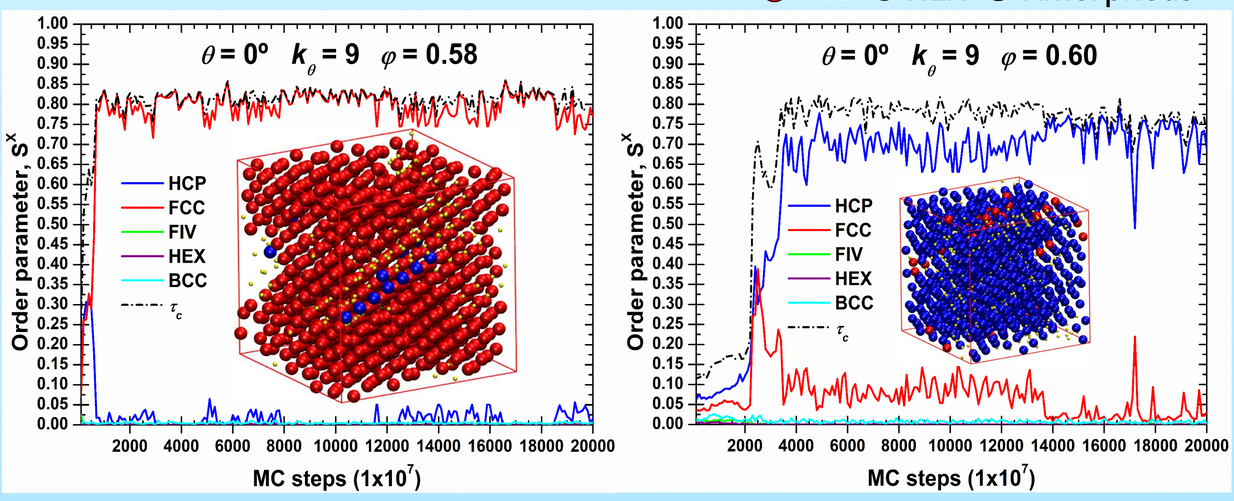
Bulk (3-D) systems

- For **semiflexible polymers**, crystallization occurs at lower packing densities than for fully flexible chains [7].



- Almost **perfect HCP or FCC crystals** are observed for the rod-like polymer chains ($\theta_0 = 0°$).

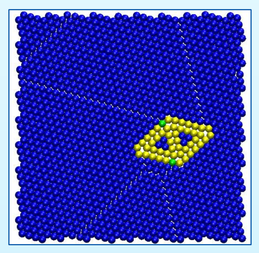
HCP BCC Fivefold
FCC HEX Amorphous



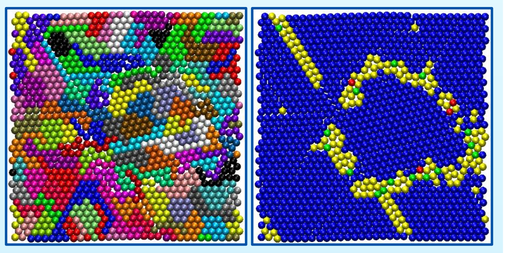
Thin-Film (2-D) systems

- **2-D films of fully flexible polymers** form almost perfect triangular crystals (within 3% of the maximum possible ($\mathbf{0.907}$)).

Single spheres $\varphi_{sup} = 0.8961$



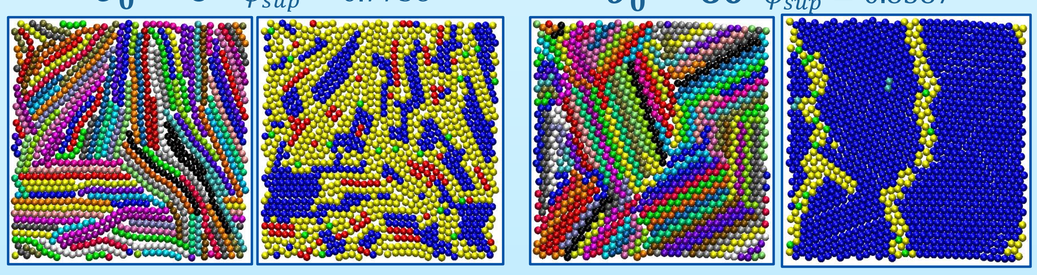
Fully flexible chains $\varphi_{sup} = 0.8748$



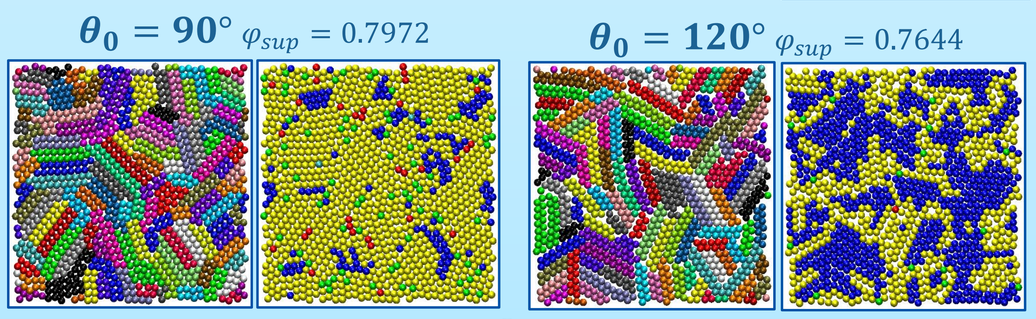
- **Chain Stiffness** has an appreciable effect on packing ability.

$k_\theta = 9$

$\theta_0 = 0°$ $\varphi_{sup} = 0.7736$ $\theta_0 = 60°$ $\varphi_{sup} = 0.8387$



$\theta_0 = 90°$ $\varphi_{sup} = 0.7972$ $\theta_0 = 120°$ $\varphi_{sup} = 0.7644$



Triangular Square Pentagonal Amorphous

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