Universidad Politécnica de Madrid
ETSI de Ingenieros Industriales

IOCC 2024 Conference
The 4th International Online Conference on Crystals 18-20 September 2024 | Online

Institute for Optoelectronic Systems and Microtechnology

Phase Behavior of Athermal Colloidal Mixtures of Chains and Monomers

Olia Bouzid, Daniel Martínez-Fernández, Miguel Herranz, and Nikos Ch. Karayiannis (n.karayiannis@upm.es)

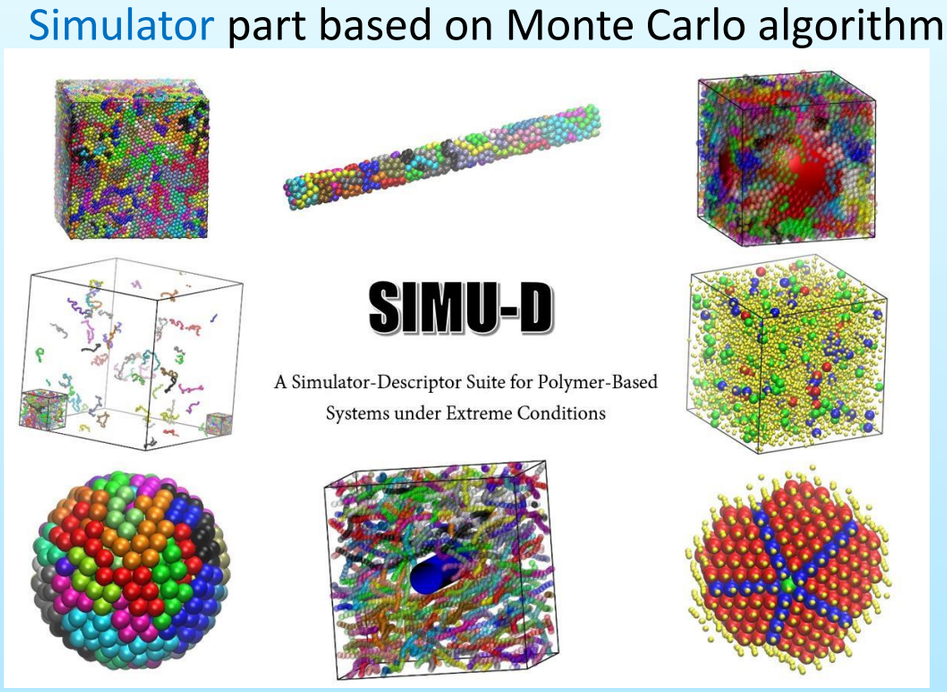
1. Objectives

- Study the **phase behaviour** of **mixtures** of **hard-sphere chains** and **monomers**
- **Hard-sphere chains** and **monomers** have **different melting points** : $\varphi^{M}_{chains} \cong 0.57 > 0.545 = \varphi^{M}_{monomers}$ [1,2,3]
- Explore how **packing density** and **relative molar fraction** affect the ability of the systems to **crystallize.**
- Identify the **entropic origins** of **crystallization** [4] and investigate the possibility of **phase separation** of the **mixture**.

2.A Method: Monte Carlo Simulations

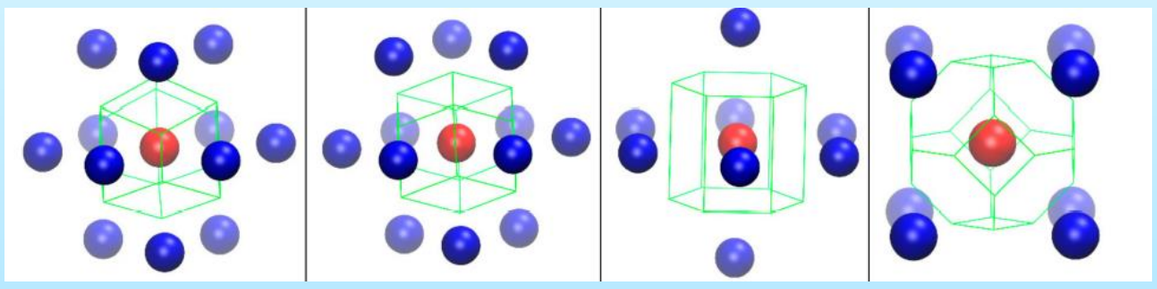
Monte Carlo method: Simu-D simulator-descriptor [5].

- Simulator part based on Monte Carlo algorithms



2.B Method: Characterization

- Structural analysis of computer-generated configurations of general atomic to **gauge local order**.
- **CCE norm: descriptor** to quantify the **orientational** and **radial deviations** from a specific **reference crystal** [6].

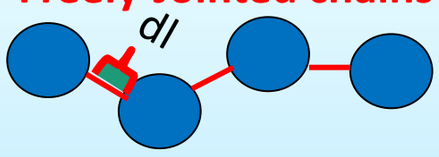


3. Molecular Model and Systems

Hard Sphere model

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

Freely-Jointed chains



N_{at} spheres being part of chains or individual ones N_{at} = 1200

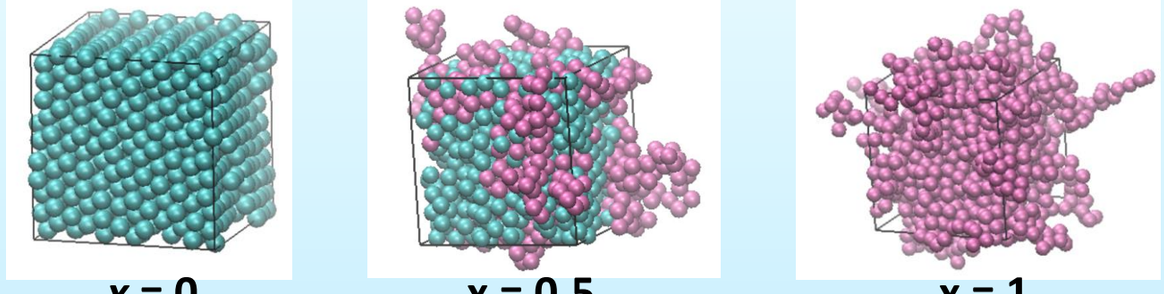
***x*: relative molar fraction** (spheres in chains / total spheres) $x \in [0,1]$

φ : Packing density $\varphi \in [0.55, 0.57]$

Average chain length: N_{av} = 12

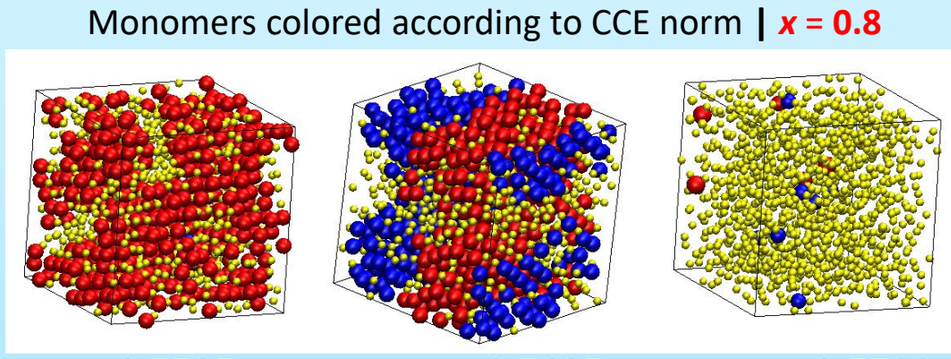
4.A Results: Snapshots

Monomers colored according to their identity | φ = 0.5575



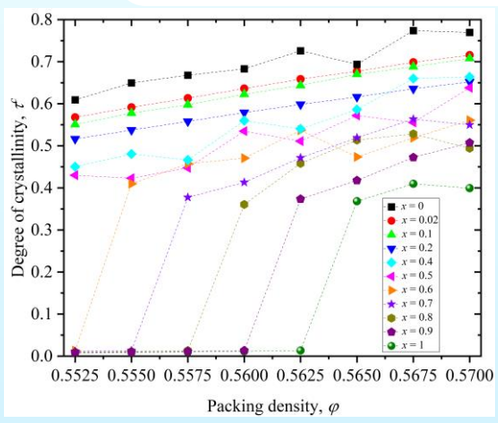
***x* = 0** **x = 0.5** **x = 1**

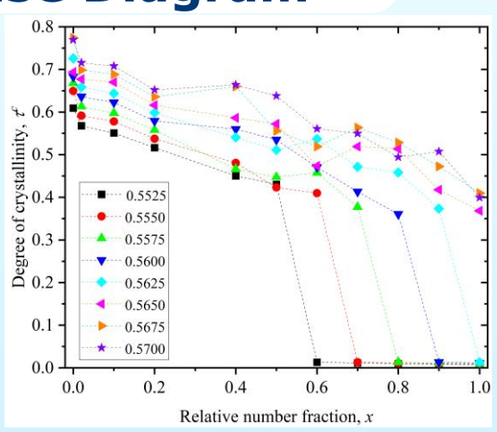
Monomers colored according to CCE norm | *x* = 0.8



φ = 0.5525 **φ = 0.5625** **φ = 0.5700**

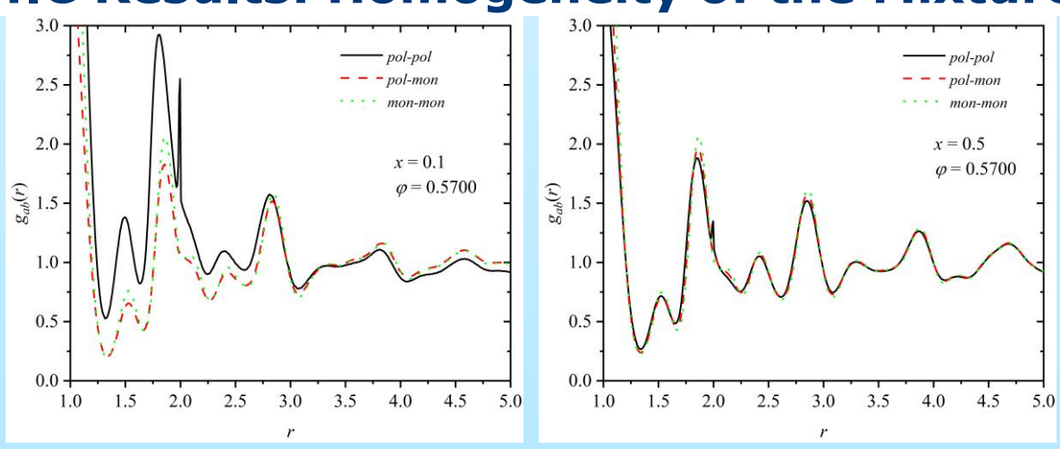
4.B Results: Phase Diagram





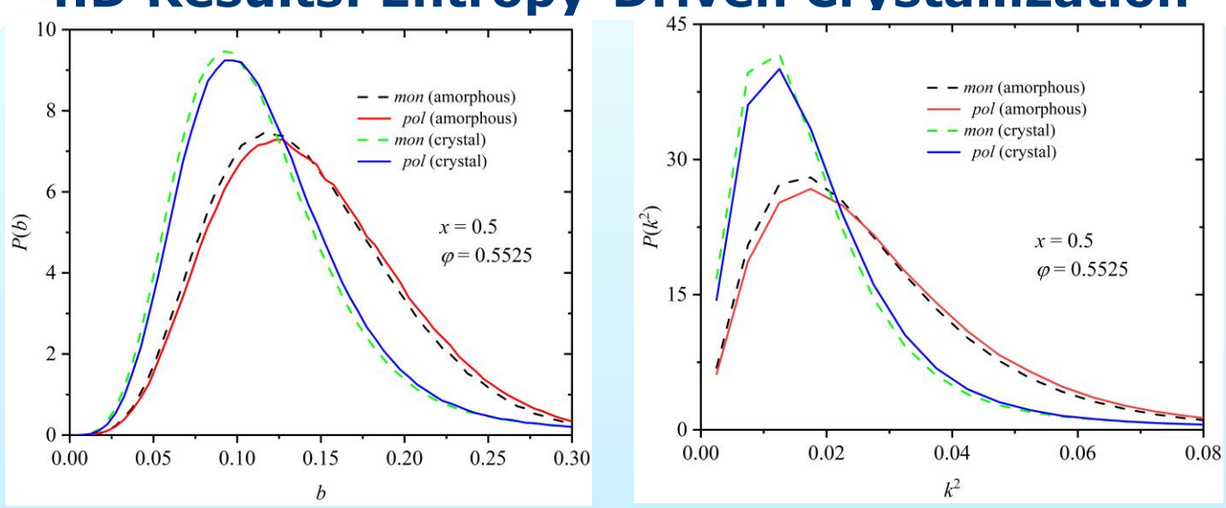
- Crystallinity drops with increasing *x*
- Crystallinity increases with increasing φ
- Under specific conditions the melting point shifts to higher φ

4.C Results: Homogeneity of the Mixture



Perfect mixing ⇒ no phase separation [7]

4.D Results: Entropy-Driven Crystallization



Asphericity, *b* and relative shape anisotropy, k^2 of the Voronoi polyhedra

- The local environment becomes more spherical and isotropic in the crystal phase ⇒ increase in translational entropy
- The local environment around individual spheres is systematically more spherical and symmetric compared to the one of spheres belonging to chains.

[1] N. C. Karayiannis, K. Foteinopoulou and M. Laso, *Phys. Rev. Lett.* **103**, 045703 (2009).
[2] D. Martinez_Fernandez *et al*., Polymers **15**, 551 (2023).
[3] N. C. Karayiannis, K. Foteinopoulou and M. Laso, *Soft Matter* **11**, 1688 (2015).
[4] W. G. Hoover and F. H. Ree, *J. Chem. Phys.* **49**, 3609 (1968).
[5] M. Herranz *et al*., *Int. J. Mol. Sci.* **22**, 12464 (2021).
[6] P. Ramos *et al*., *Crystals* **10**, 1008 (2020).
[7] O. Bouzid *et al*., *Polymers* **16**, 2311 (2024).

Acknowledgements

Financial Support through:
- Project "PID2021-127533NB-I00" of MICIU/DEFER (Spain)
- "Programa Propio" UPM-Santander Bank

Computational Support through:
- CeSViMa (UPM, Spain)