Liquid crystal phases of banana-shaped hard-core molecules composed of balls

Piotr Kubala, Michał Cieśla, Wojciech Tomczyk

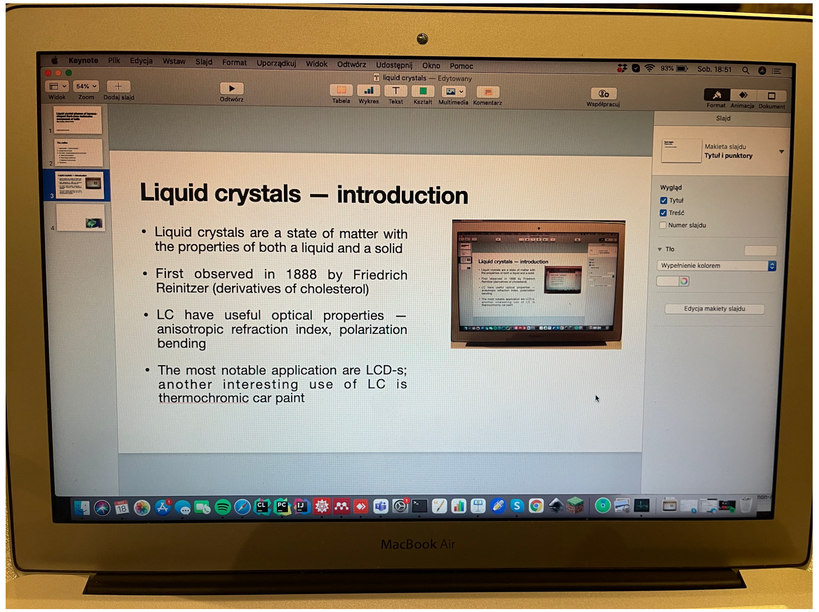
Kraków, September 27th 2021

The outline

1. Liquid crystals — a brief introduction
2. Onsager hard rod (spherocylinder) model
3. Our model — banana shaped particles built of balls:
    A. Monte Carlo simulations
    B. Phase diagram walkthrough
    C. Breaking of chiral symmetry
4. The outlook

Liquid crystals — introduction

- Liquid crystals are a state of matter with the properties of both a liquid and a solid
- First observed in 1888 by Friedrich Reinitzer (derivatives of cholesterol)
- LC have useful optical properties — anisotropic refraction index, polarization bending
- The most notable application are LCD-s; another interesting use of LC is thermo-chromic car paint

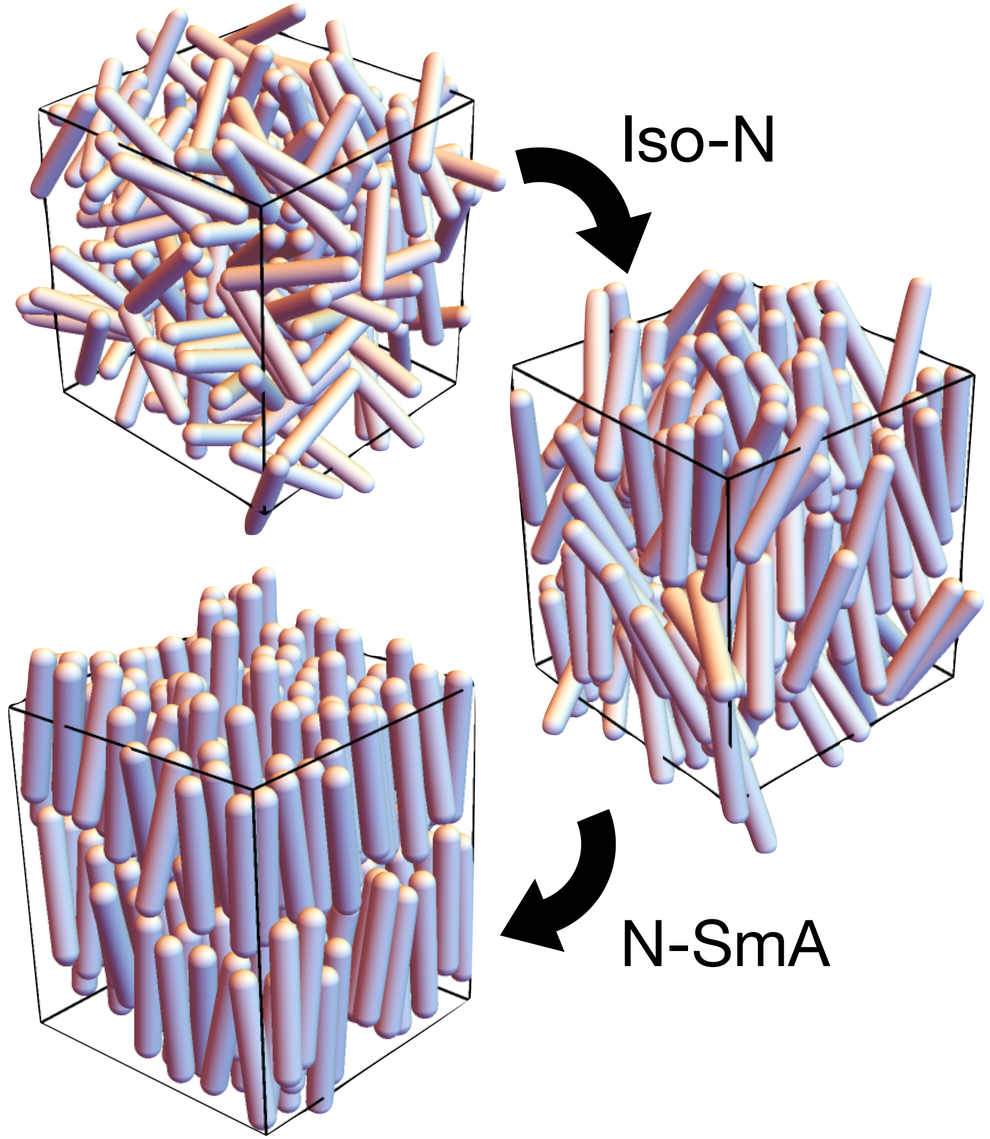


Auto Urban /YouTube

Onsager hard rode (spherocylinder) model

- As demonstrated by Onsager, isotropic-nematic phase transition can be modeled using just hard spherocylinders within second order viral approximation
- Numerical simulations reveal another LC phase transition — nematic-smectic A
- Phase transitions in hard-core models are called entropic phase transitions, as they originate solely from excluded volume effects:

$$F = U - TS = - TS$$



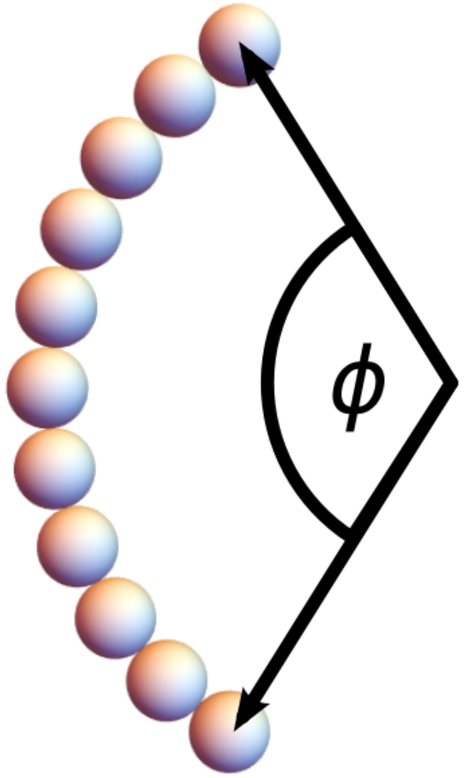
Molecular dynamic Monte Carlo

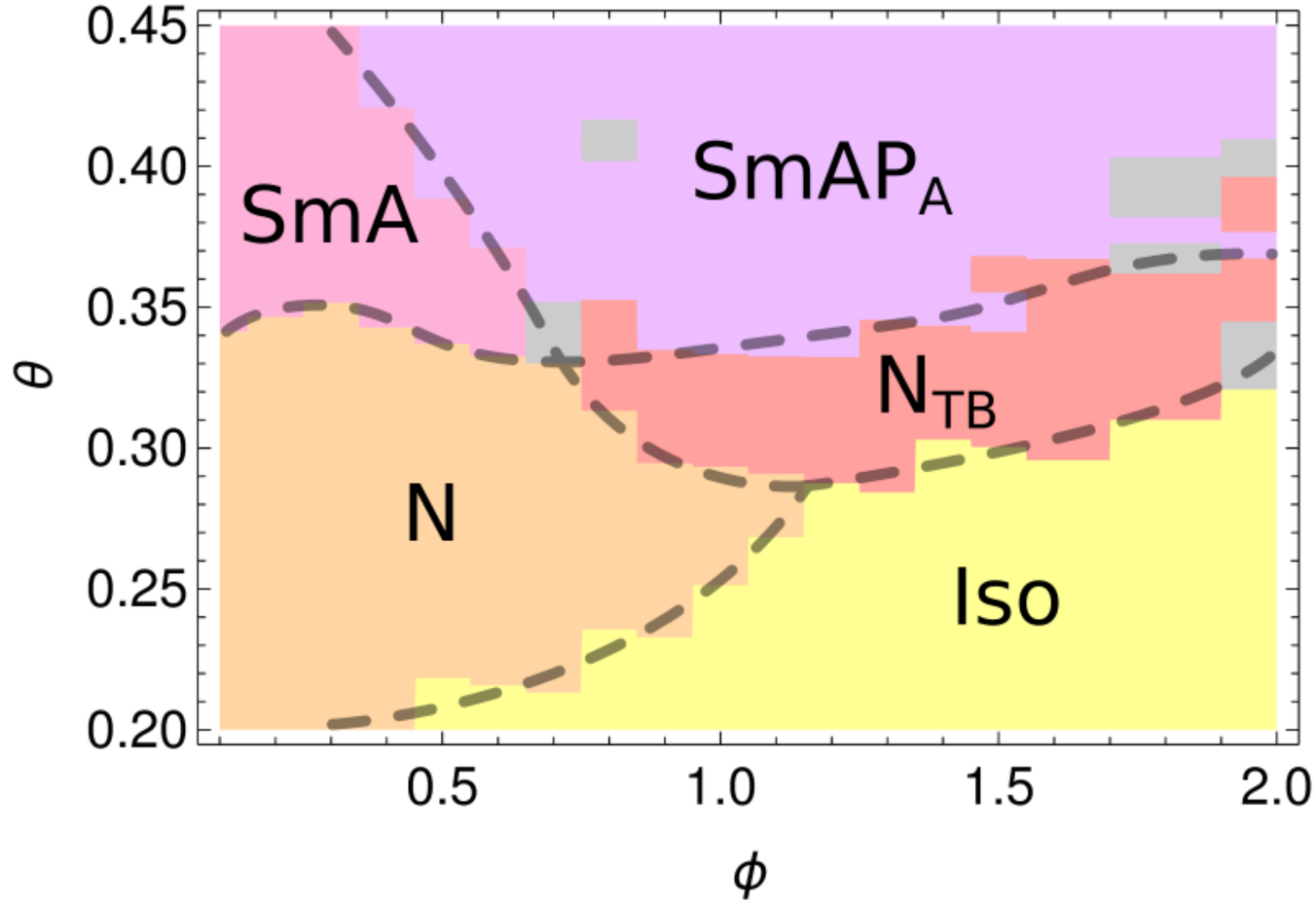
- Our study utilizes molecular dynamic computer simulations
- Hard-core MD can be easily realized by Markov chain Monte Carlo Metropolis-Hasting algorithm (used in general to sample random variables from complicated distributions)
- Simulations were performed within NpT simulation box (with PBC)
- Each of: positions and orientations of molecules and box dimensions are perturbed randomly. All moves introducing overlaps are rejected. Others are accepted with a probability:

$$\min\left\{1, \left(\frac{V'}{V}\right)^{N} e^{\beta p(V-V')}\right\}$$

Banana-shaped particles built of balls

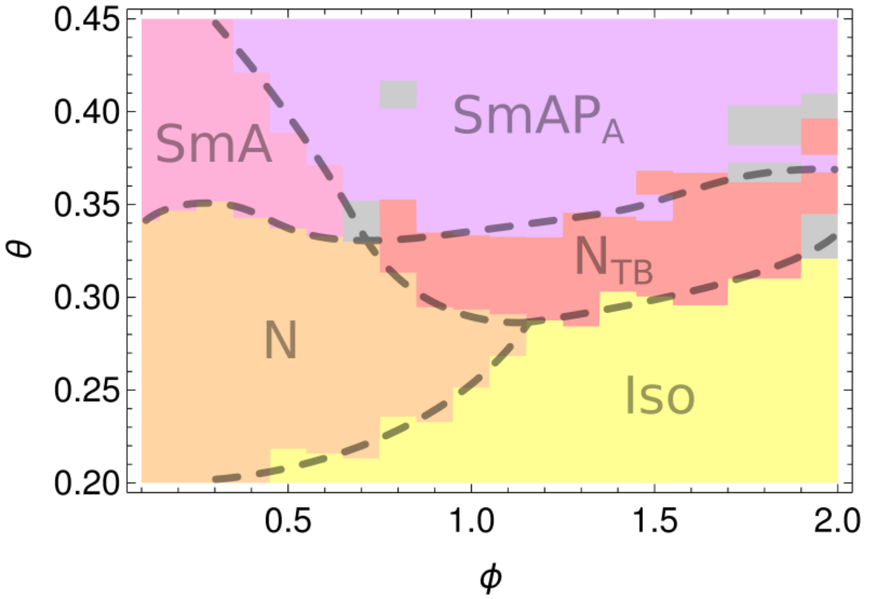
- We have performed MC simulations of hard-core banana-shaped particles built of balls as a function of packing density θ and bend angle ϕ



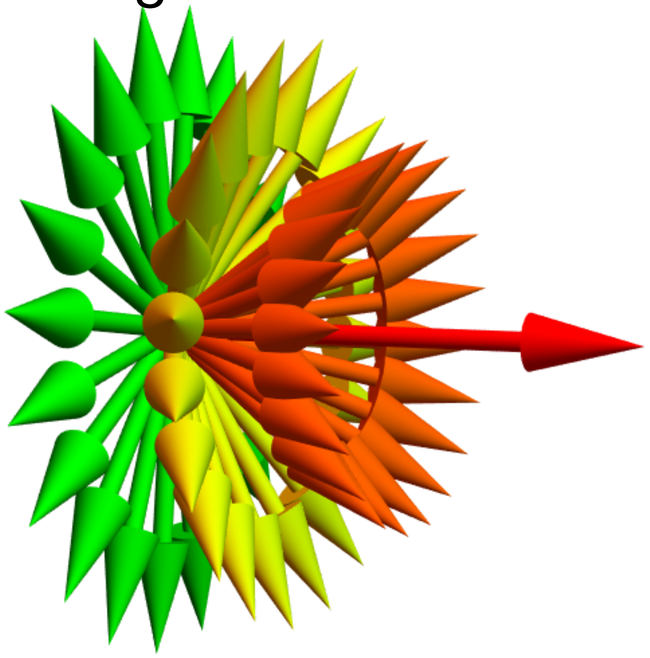


Phase overview — the legend

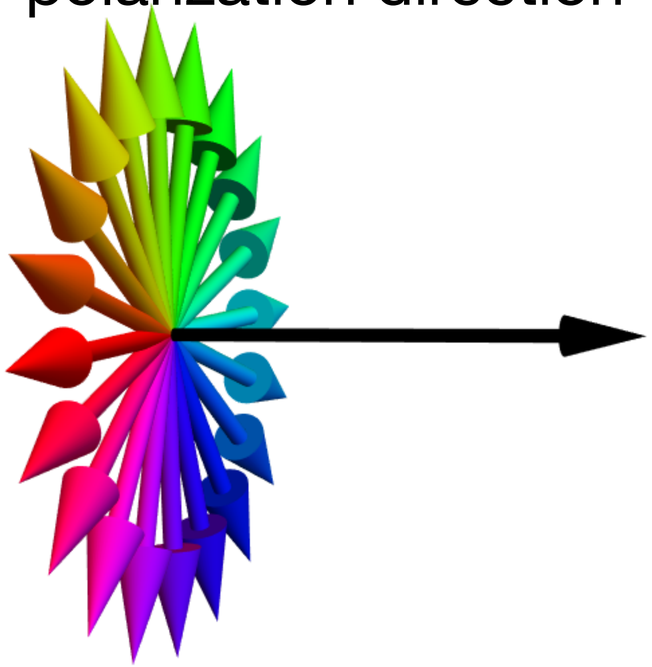
- For each phase, three panels with packings are going to be presented, color-coded as below



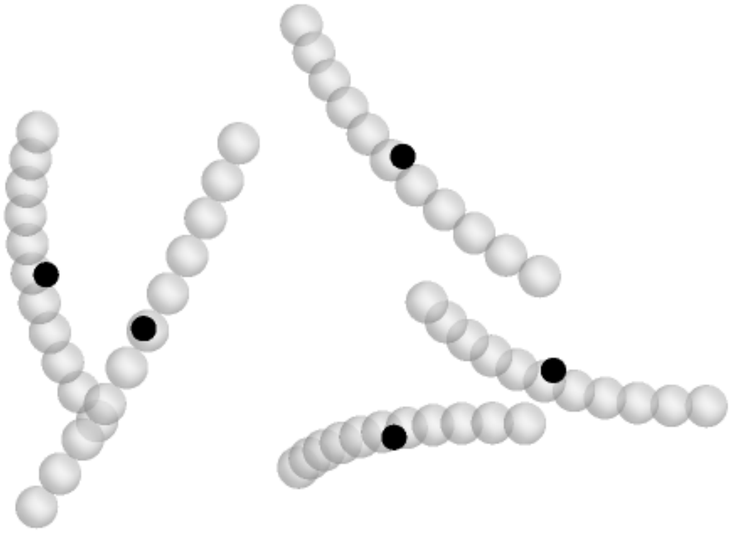
angle w.r.t. director



polarization direction

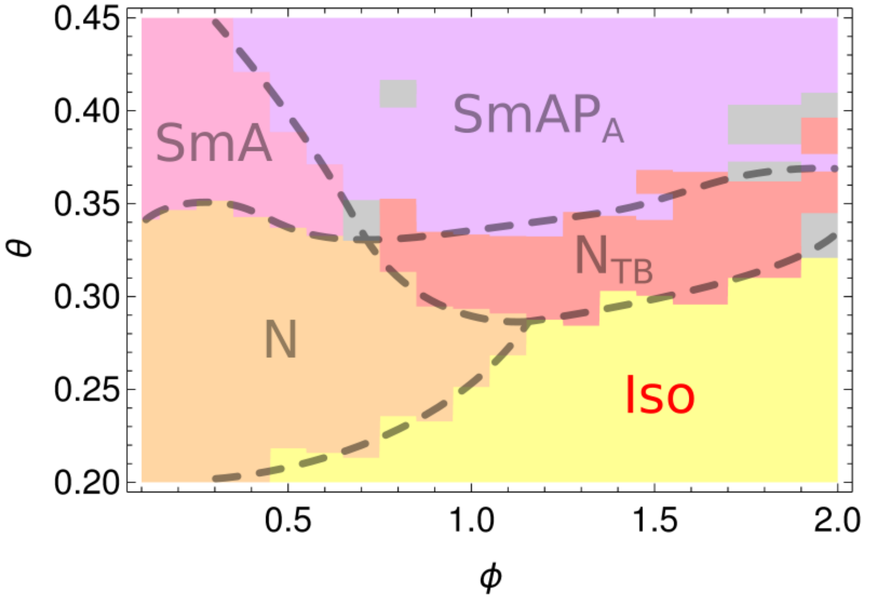


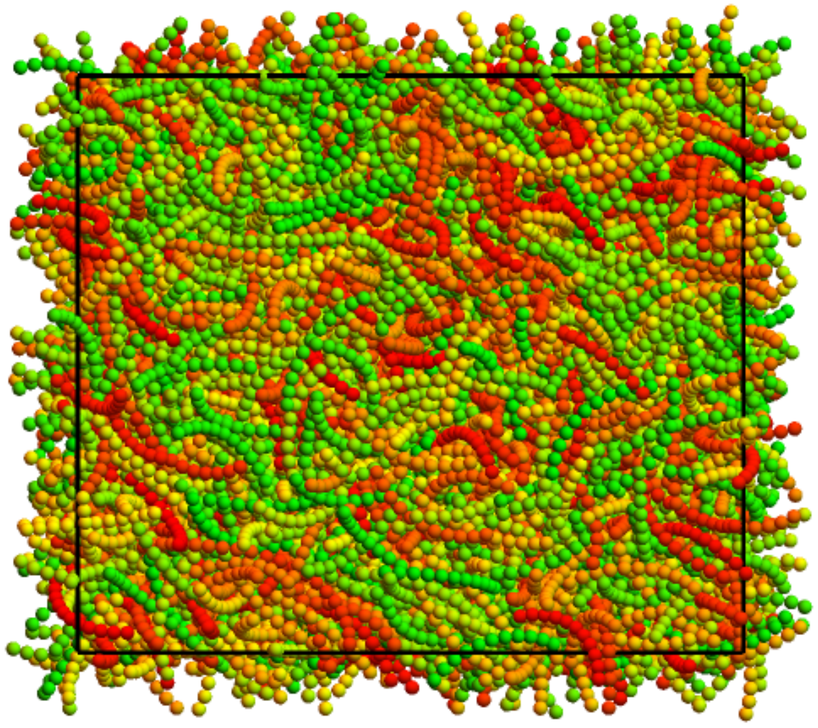
mass centres

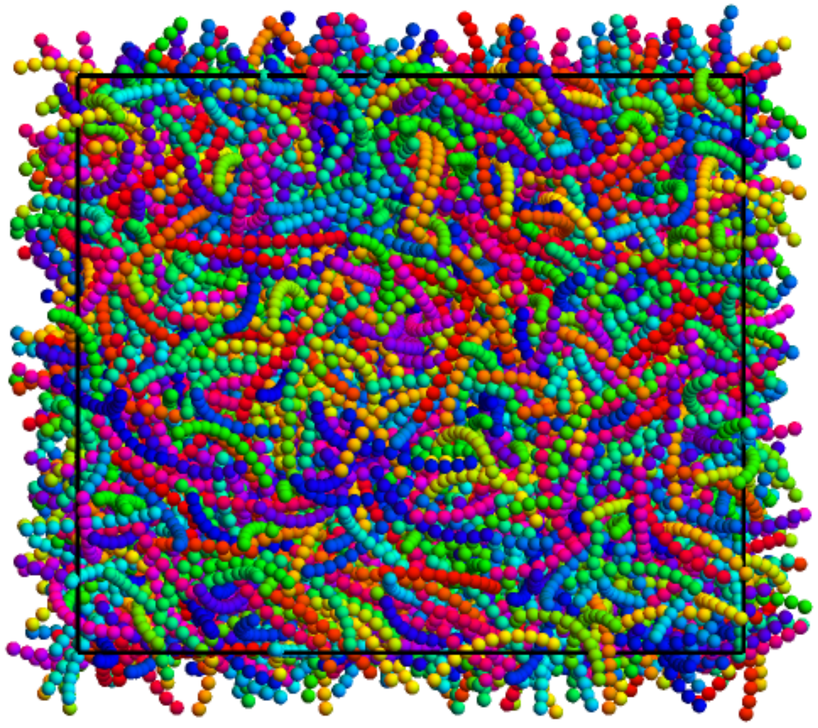


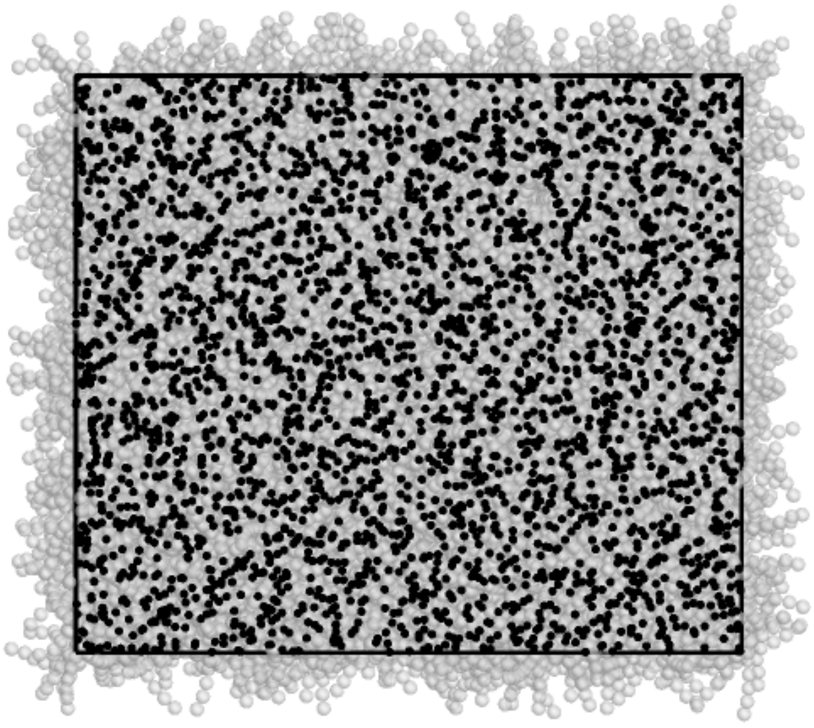
Isotropic phase

- A standard liquid-like phase with a high compressibility factor, but neither translational nor orientational long-range order



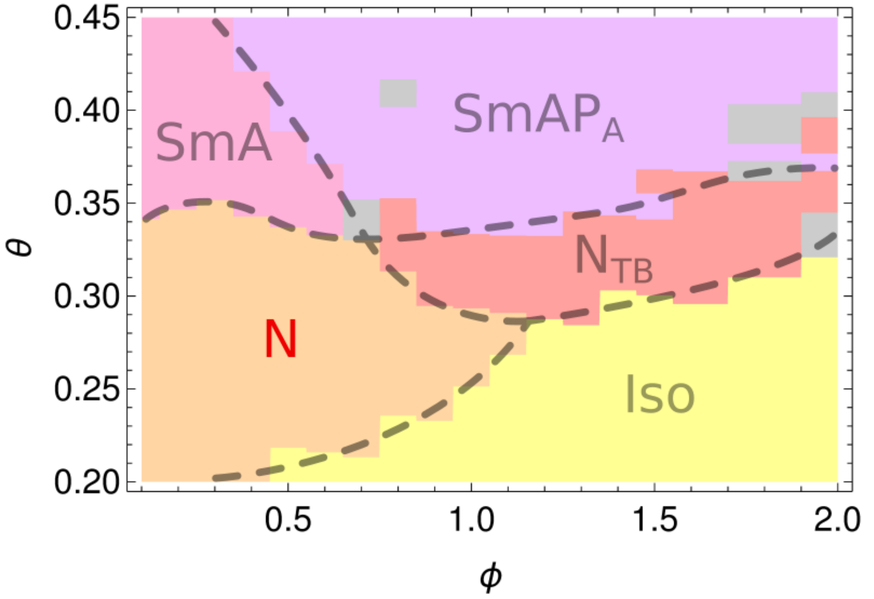


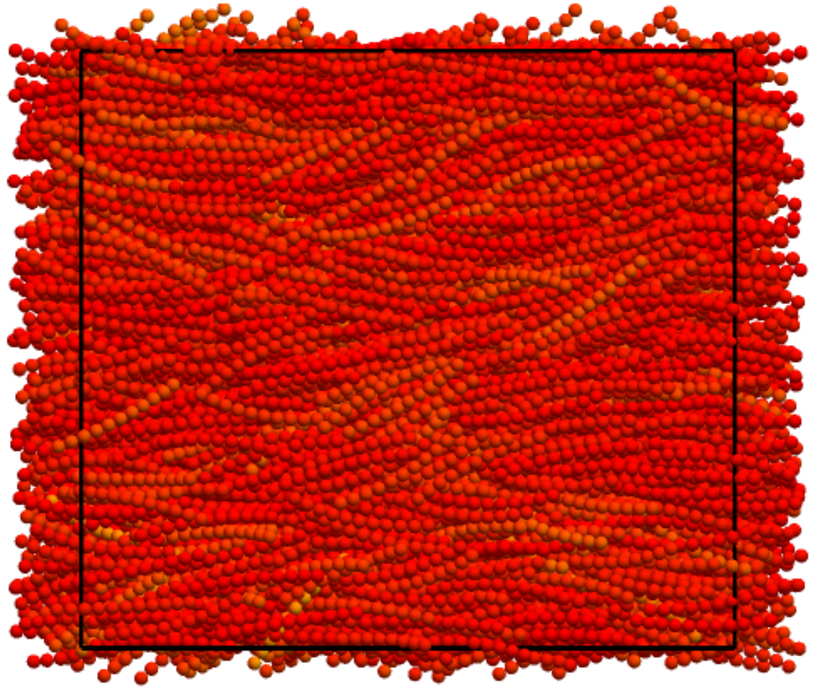


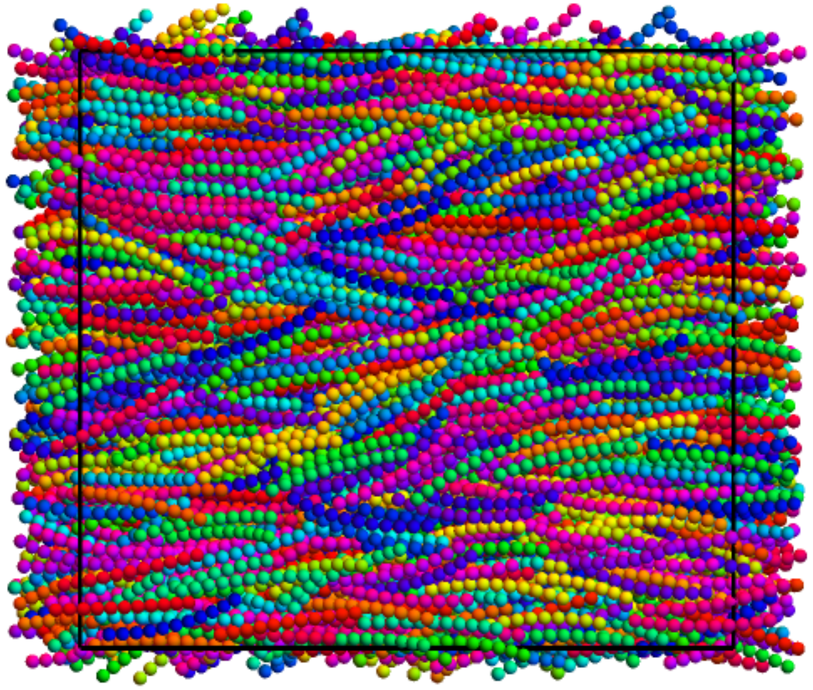


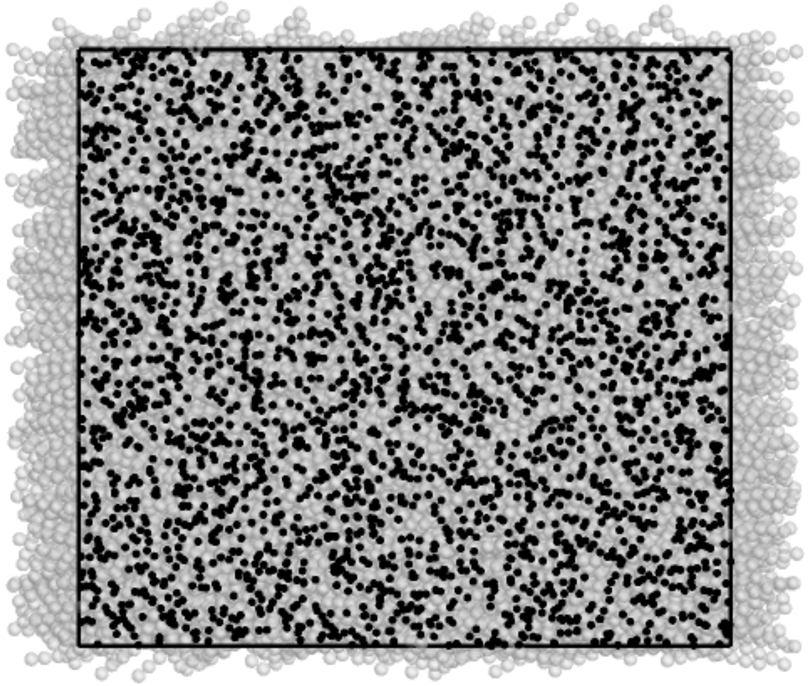
Nematic phase

- A phase with liquid-like mass centers, but the particles orient in one, preferred direction



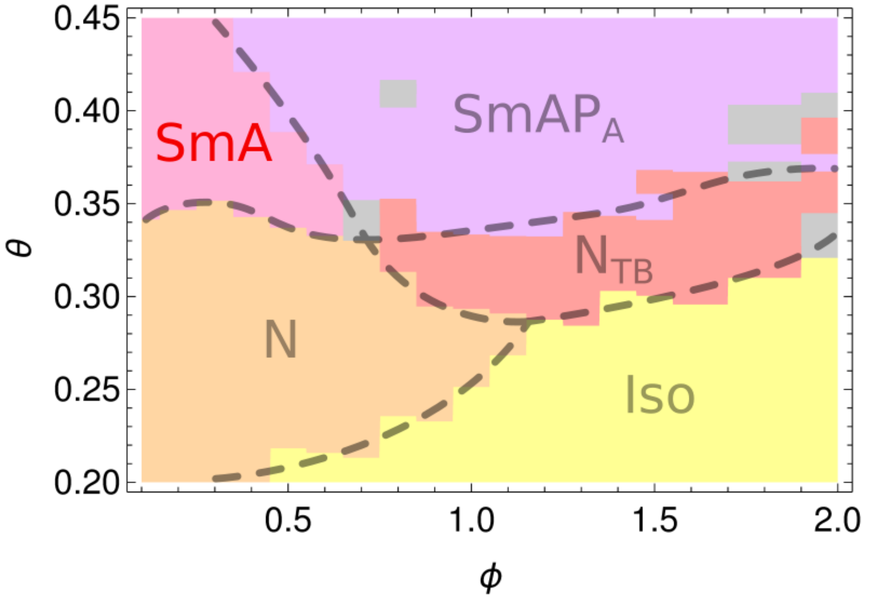


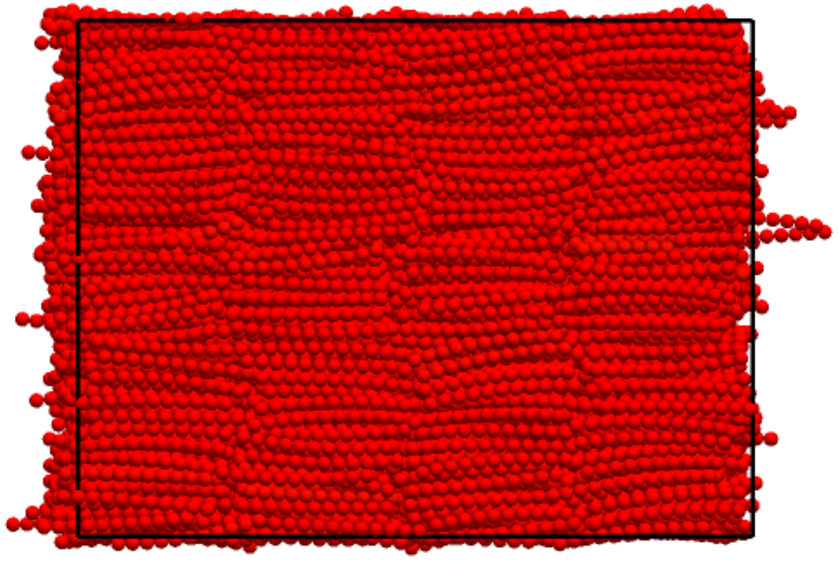


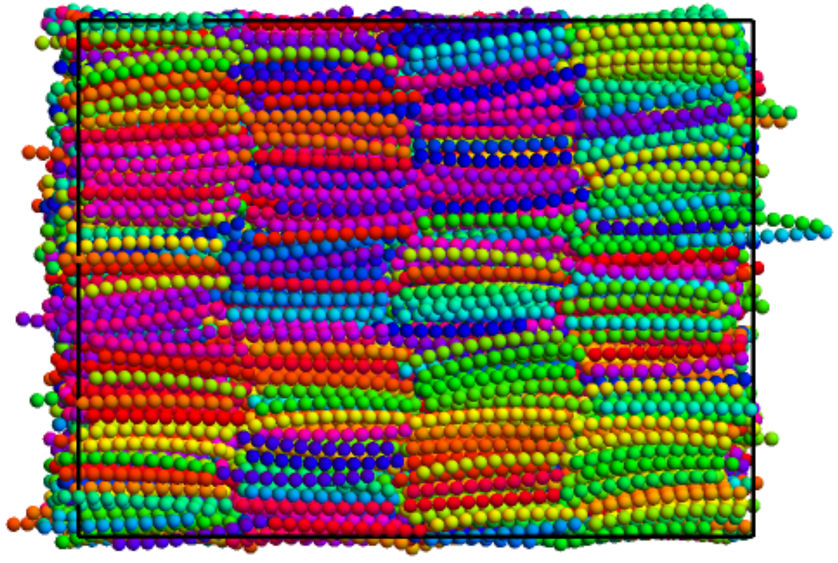


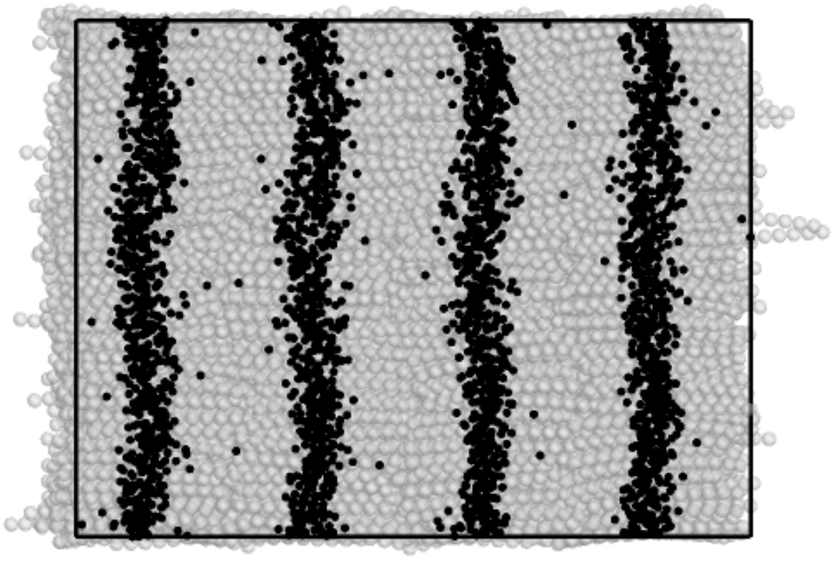
Smectic A phase

- Orientational order, long translational order in one direction (visible layers), no translational order or polarization within the layer



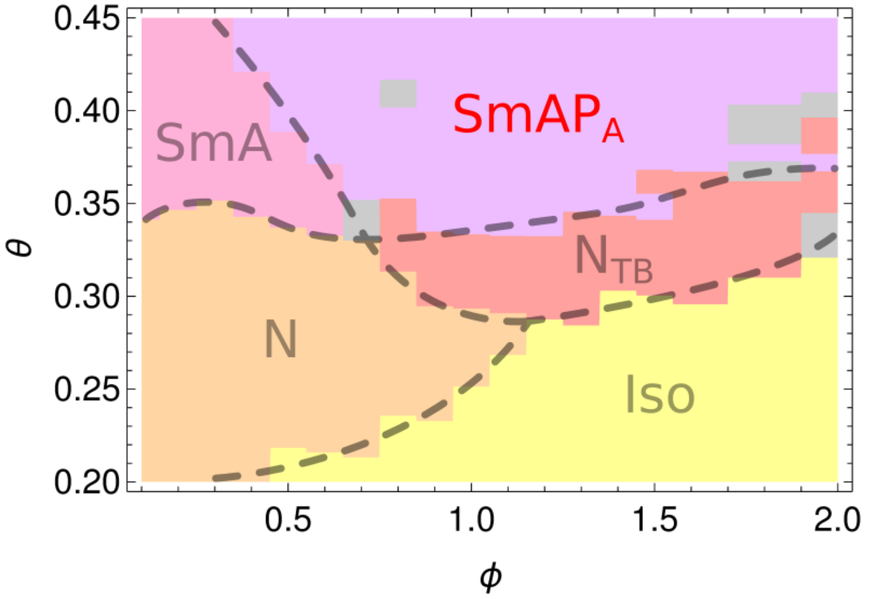


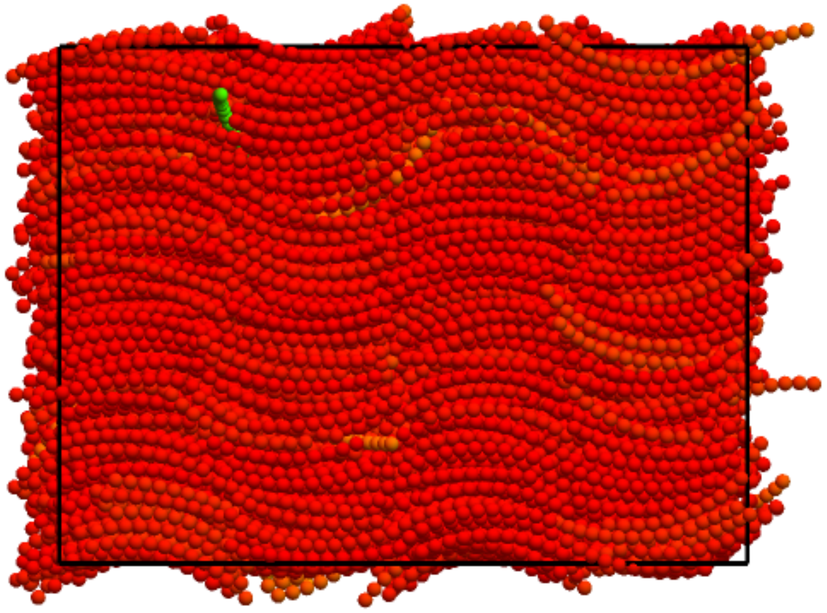


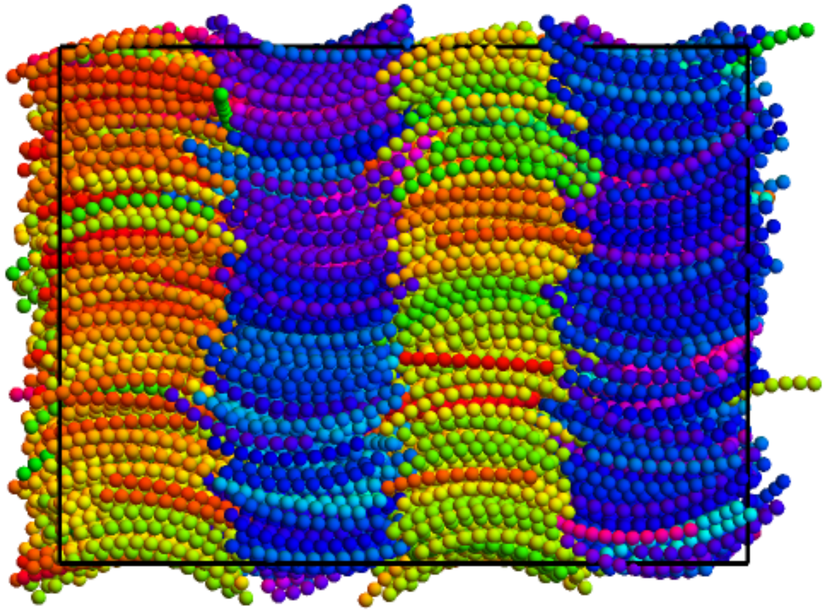


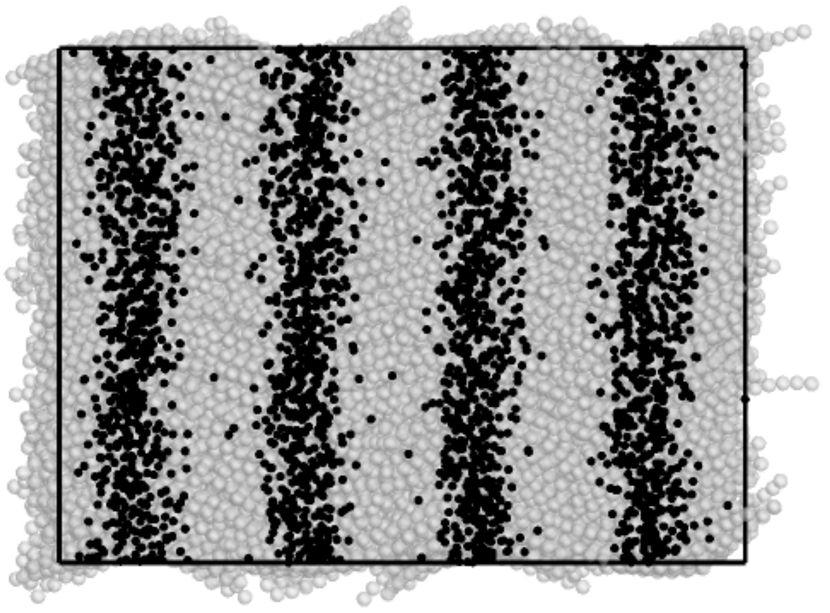
Antipolar smectic A phase

- Smectic A with a well defined polarization within one layer, adjacent layers have an opposite polarization



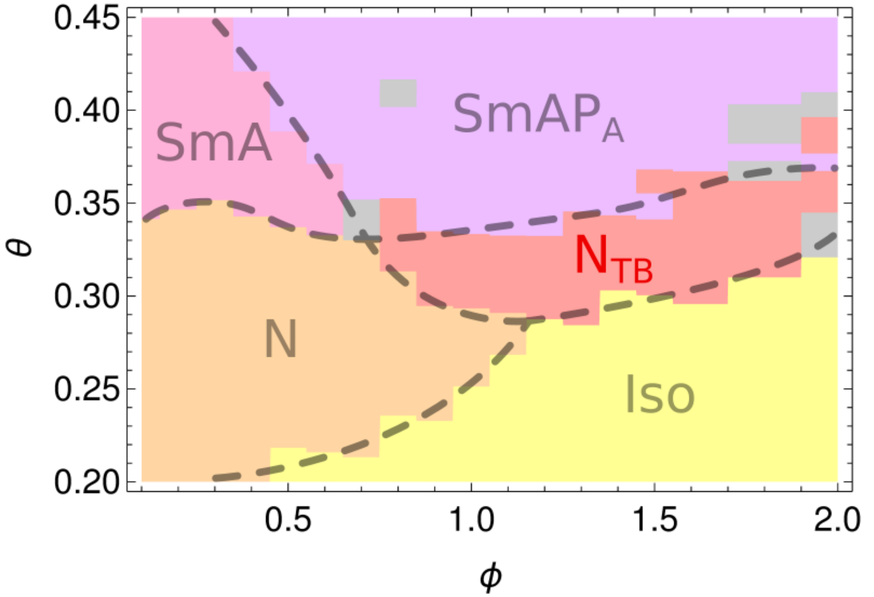


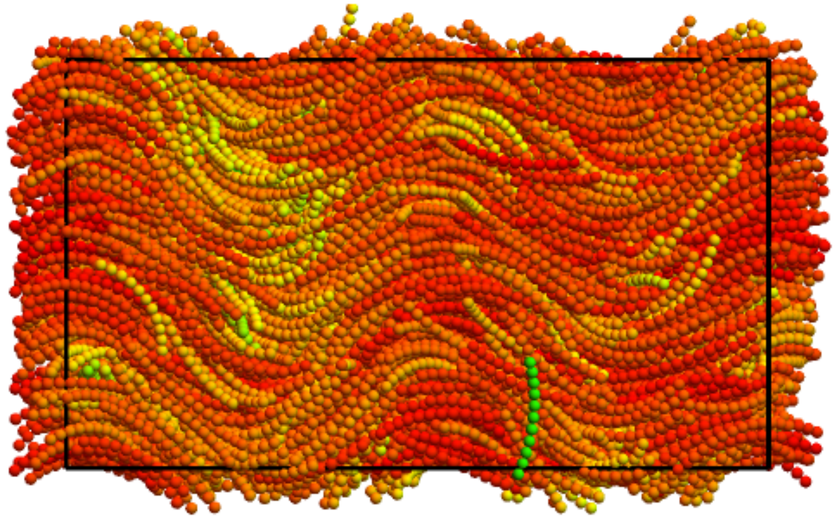


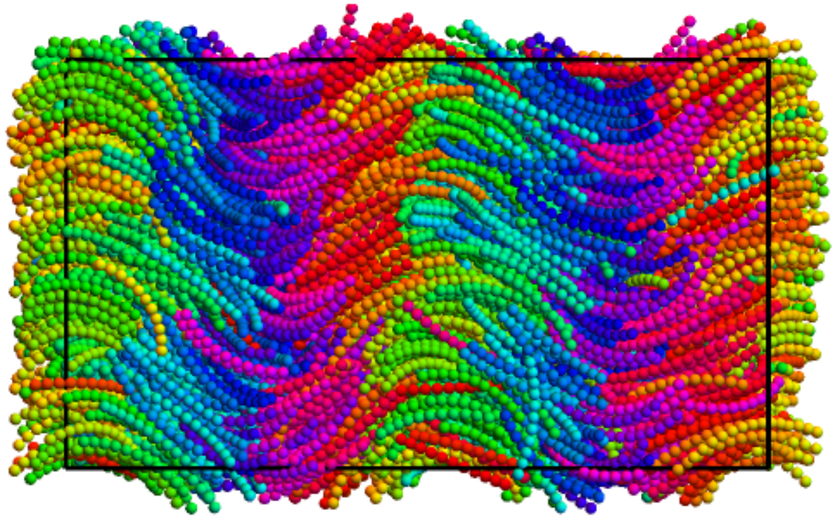


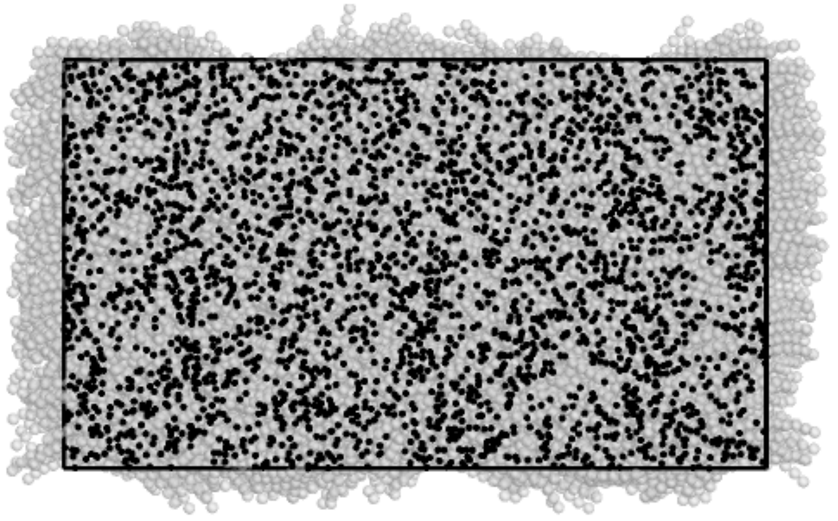
Twist-bend nematic phase

- A nematic phase with essentially uniform density profile, where the director field is constant in a plane, but revolves around a conus in a normal direction (polarization vector as well)







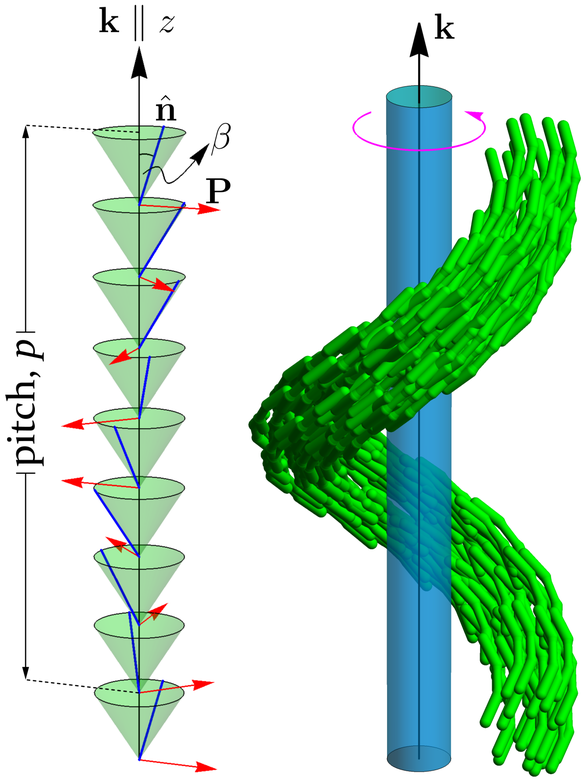


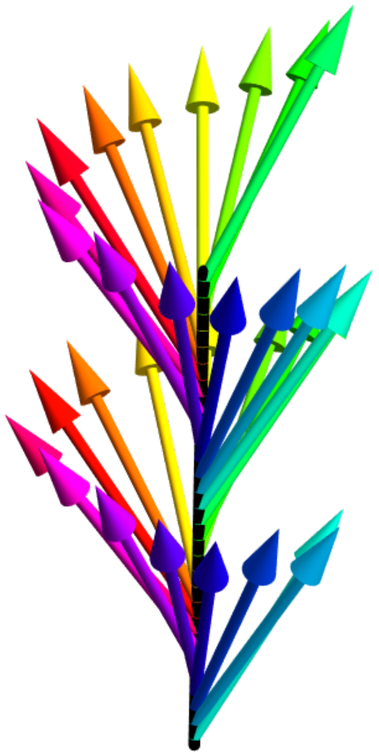
Twist-bend nematic phase

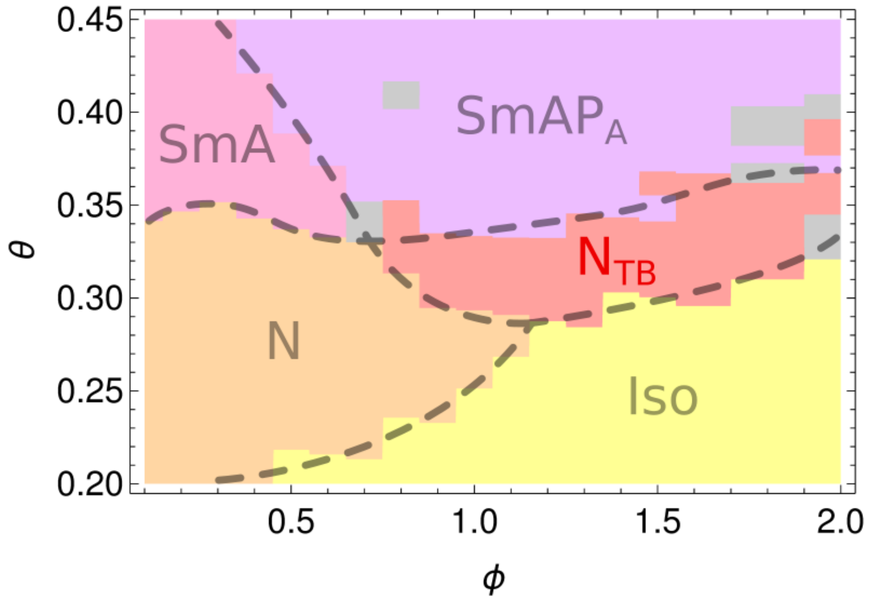
- A director field can be modeled via:

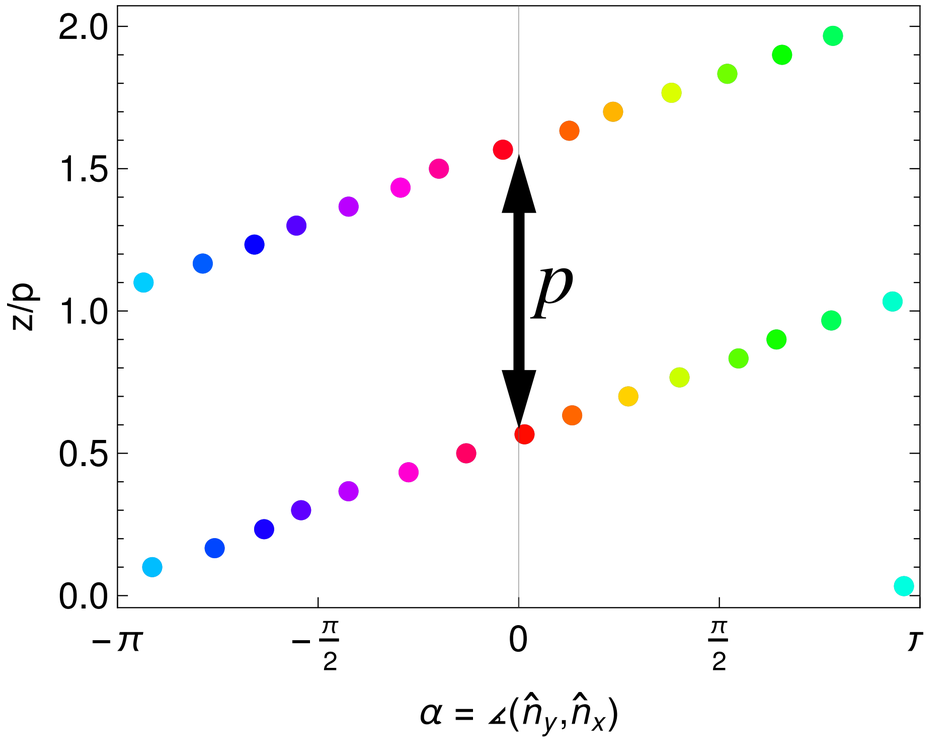
$$\hat{n}(x,y,z) = \sin(\beta)\cos(kz)\,\hat{x} + \sin(\beta)\sin(kz)\,\hat{y} + \cos(\beta)\,\hat{z}$$

β – conical angle; $p = 2\pi/k$ – pitch (period)







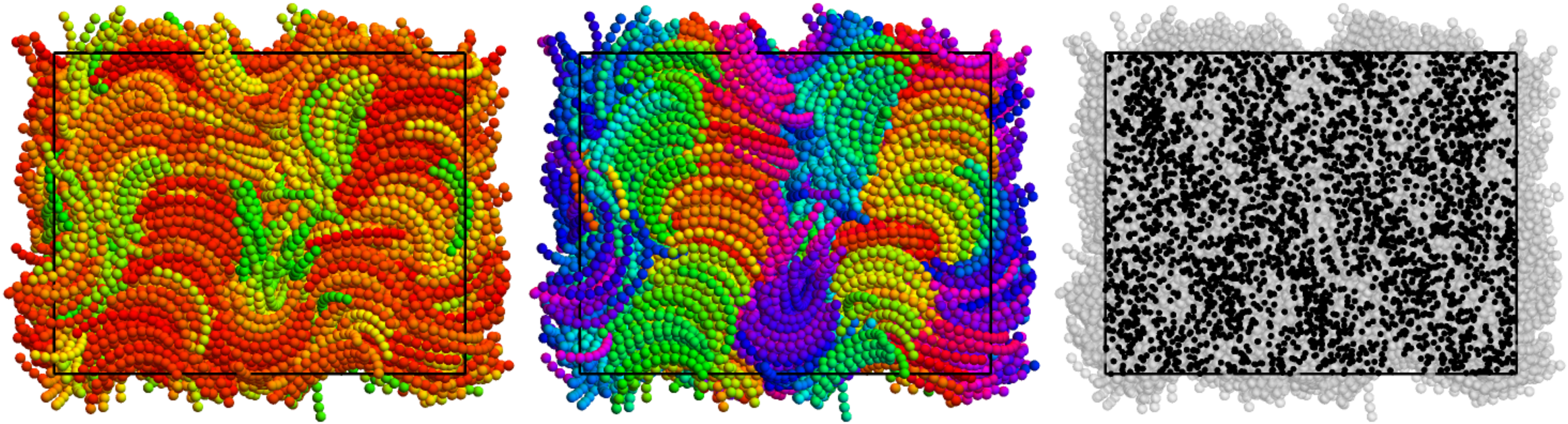


Summary

- We have indicated how liquid crystal phase transitions can be modeled via hard-core particle models
- We have generated the phase diagram for achiral banana-like hard particles via Monte Carlo simulations
- We have analyzed all liquid phases in the model with a special care about twist-bend nematic phase which breaks chiral symmetry of particles
- We have presented some arguments why we can observe such phases and justified their extent in the parameters space

The outlook

- Solid phases in the model present an interesting direction of study
- We have already observed several crystalline phases, some of which can be attributed to maximal packings of spheres (hcp lattice), as well as disordered glassy phases



Thank you for your attention!

Bibliography:

1. Onsager, L. (1949). „The effects of shape on the interaction of colloidal particles”. *Annals of the New York Academy of Sciences*. **51**(4), 627.
2. Greco, C., & Ferrarini, A. (2015). „Entropy-Driven Chiral Order in a System of Achiral Bent Particles”. *Physical Review Letters*, **115**(14), 147801.
3. Lansac, Y., Maiti, P. K., Clark, N. A., & Glaser, M. A. (2003). „Phase behavior of bent-core molecules”. *Physical Review E*, **67**(1), 011703.