## Entropy strikes again: computer simulations of a fully entropy-driven cholesteric phase

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## Entropy & Colloids

#### **Hard Spheres**



## Entropy & Colloids

#### **Hard Spheres**



In a solvent (Brownian motion)





Phase behaviour of concentrated suspensions of nearly hard colloidal spheres P. N. Pusey & W. van Megen\*

#### Nature (1985)

## **Entropy & Colloids**

#### Hard Spheres

#### Hard Spheres in Spherical Confinement



#### *B. De Nijs\*, S. Dussi\* et al.* Nature Materials 14, 56 (2015)

#### **Hard Rods**





Local Nematic Order

T. Besseling, S. Dussi et al. to be submitted

#### Hard Rods & Hard Spheres



H. Bakker, S. Dussi et al. to be submitted

## **Colloidal nematics**





nematic director

## CHOLESTERIC

Silica rods (also TMV, gibbsite, boehmite ...)



*Courtesy of Henriëtte Bakker SCM group, Utrecht*  Filamentous viruses (fd, M13, but also DNA, helical flagella...)



Tombolato, Ferrarini, Grelet Phys. Rev. Lett. (2006)



**Pitch** 

Dogic, Fraden *Langmuir* (2000)



Phys. Rev. Lett. (2003)

Can entropy alone stabilize cholesterics?

## Theory says yes



Frezza, Ferrarini et al.





Harris, Kamien, Lubensky Phys. Rev. Lett. (1997) Rev. Mod. Phys. (1999)





Our work: Phys. Rev. E (R) (2014) J. Chem. Phys. (2015)

## Theory says yes



Frezza, Ferrarini et al.

Straley (1976)



Harris, Kamien, Lubensky Phys. Rev. Lett. (1997) Rev. Mod. Phys. (1999)





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#### Any evidence from simulations?









## "In printero" synthesis...



## First (?) simulation of entropy-driven isotropic-cholesteric transition



NPT-MC simulations under P.B.C.

# First (?) simulation of entropy-driven isotropic-cholesteric transition

NPT-MC simulations under P.B.C.



Particles colored according to orientation

#### How to determine the equilibrium pitch?

### **Periodic Boundary Conditions**

Nematic director -> remove drift -> fit  $|\cos(\vartheta(z))|$  to extract pitch



#### Hard walls (NVT ensemble)

#### **Promising method**



Effect of hard walls (that usually introduce biaxial order) seems negligible



#### Racemic mixtures do not phase separate

#### 50:50 Right/Left mixture

Colored according orientation



**Red**=right-handed **Green**=left-handed



## **Conclusions & Outlook**

- A simple model of hard chiral particles, namely twisted prisms, allowed the first computer simulations of a fully entropic cholesteric phase. The equilibrium cholesteric pitch, obtained by using two hard walls, is in a good agreement with our theory.
- Such a simple model can be used in future studies on
  - nucleation of a cholesteric phase
  - wetting/interfacial behaviour
  - particle dynamics
  - chiral colloidal membranes



Dogic Lab (Brandeis) Nature 2012,2014

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## Thank you for your attention!



