Modélisation moléculaire de fluides complexes

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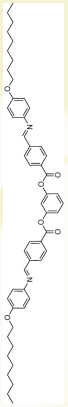
molecular structure



prediction

statistical mechanics

design

macroscopic properties

Methodology

- **Molecular dynamics and Monte Carlo simulation of atomistic** *(chemically realistic)* **and coarse-grained** *(idealized)* **molecular models**
- **Poor man's ab initio molecular dynamics**
  - *Classical interaction potentials for atomistic simulation derived from ab initio quantum chemistry*
- **Mean field theory**
  - *Models single-molecule distribution function*
  - *Condensed phase environment represented by mean field potential*
  - *Facilitates rapid pre-synthesis evaluation of materials and modeling of FTIR and NMR data*
- **Free energy computation**
  - *Thermodynamic integration*
  - *Gibbs-Duhem integration*
  - *Umbrella sampling*
  - *Histogram reweighting*
- **Continuum modeling** *(partial differential equations)*

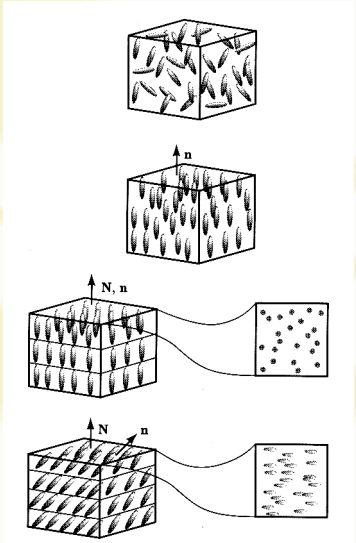
What are liquid crystals?

isotropic

nematic

smectic A

smectic C



Molecular orientational order (MOO)

MOO + 1d positional order

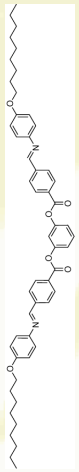
MOO + 1d positional order + tilt order

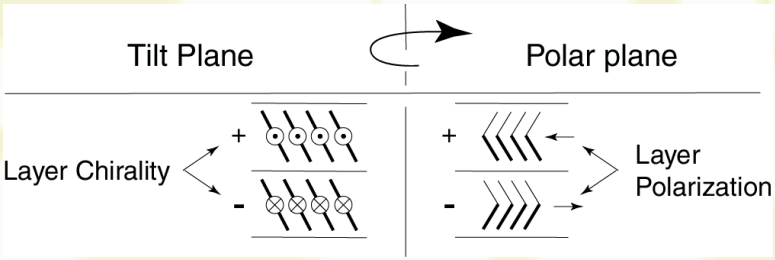
Idealized modeling:

Phase Behavior of bent-core molecules

- *Phase diagram of a simple hard dimer model*

Symmetry breaking with bent-core molecule





Spontaneous chiral symmetry breaking with achiral molecules

Motivation

Achiral banana (bent-core) molecules exhibit spontaneous polar and chiral ordering

- What is the minimal molecular model that captures polar and/or chiral symmetry breaking?
- Are excluded volume interactions sufficient?

Very few materials exhibit both polar smectic and nematic phases

- What is the degree of molecular bending compatible with a nematic ordering?

The overwhelming majority of banana materials have an antiferroelectric ground state

- Is there some fundamental mechanism that favors antipolar ordering in banana phases?

Model

Hard spherocylinder dimers

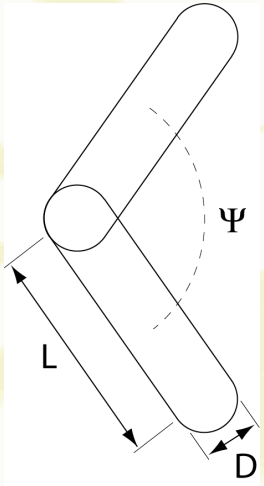
Three-parameter model:

length / breadth ratio: L / D

opening angle: Ψ

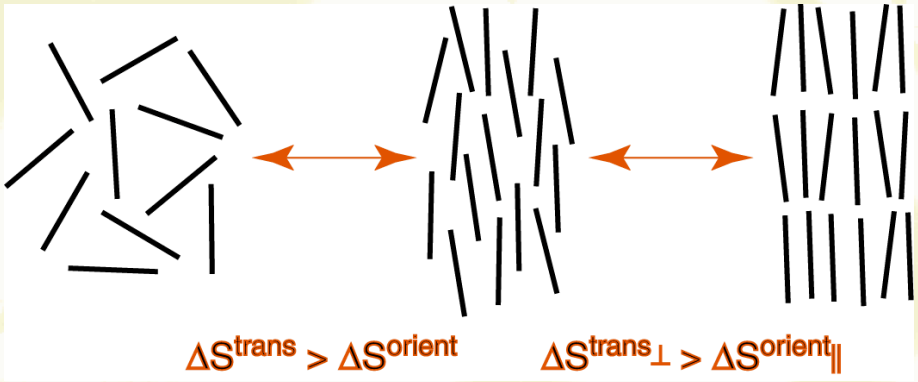
reduced density or pressure: $\rho^* = \rho\, v_0$
or $P^* = \beta\, P\, v_0$

We study the phase diagram as a function of pressure and opening angle for **L / D = 5** by NPT Monte Carlo simulation

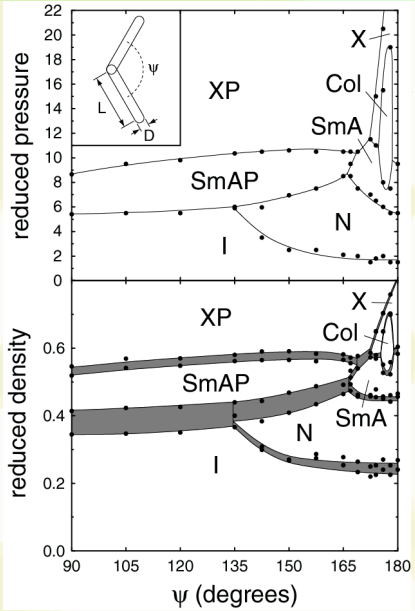


Hard-core spherocylinders

Phase transition driven only by entropic effects, at a given density:



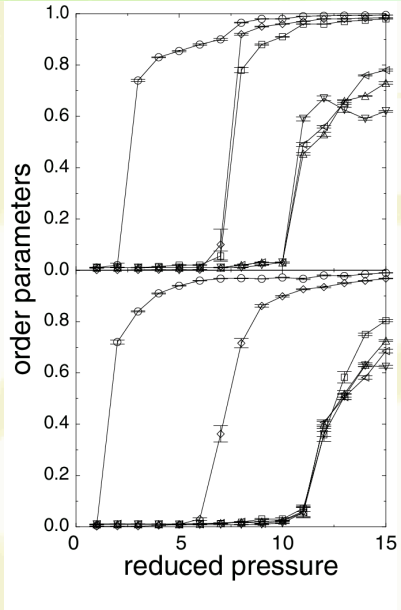
Phase diagram for L / D = 5



Isotropic fluid **(I)**
Nematic **(N)**
Polar smectic A **(SmAP)**
Smectic A **(SmA)**
Columnar **(Col)**
Polar crystal **(XP)**
Crystal **(X)**

No chiral (tilted) smectic phase found.

Order parameters



$\Psi = 157.5^{o}$

$\triangle, \nabla, \triangleleft$ *Solid-liquid order*

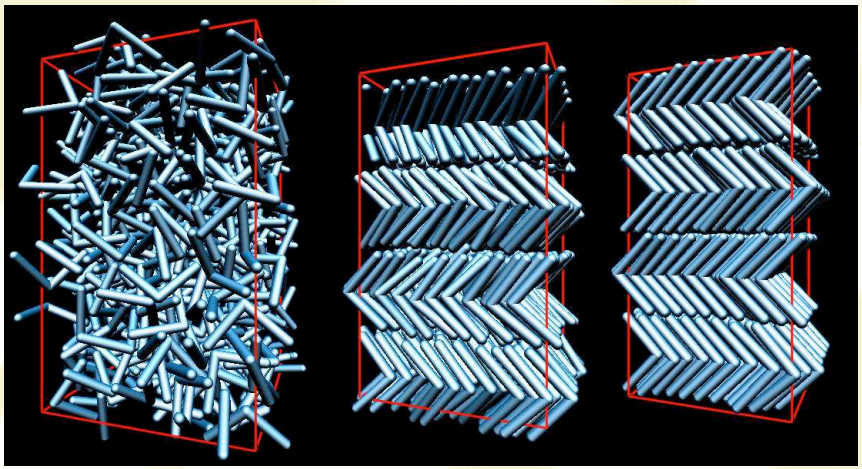
$\square$ *Polar order*

$\diamond$ *Smectic order*

$\bigcirc$ *Nematic order*

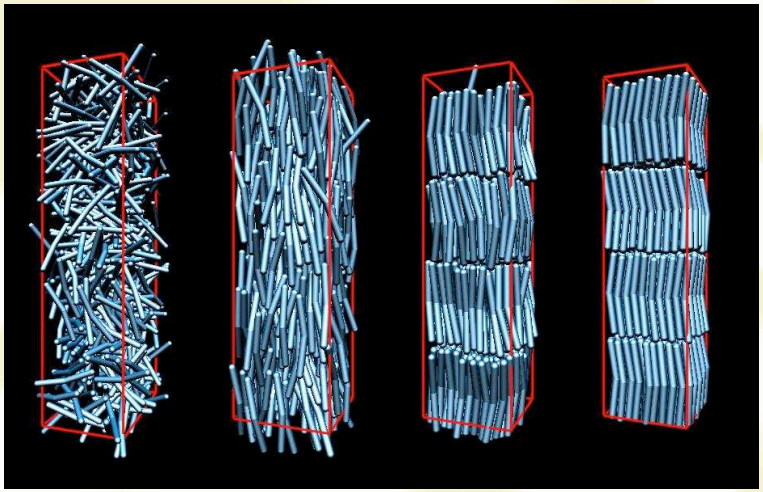
$\Psi = 172.5^{o}$

Final configurations for $\Psi = 90^{o}$



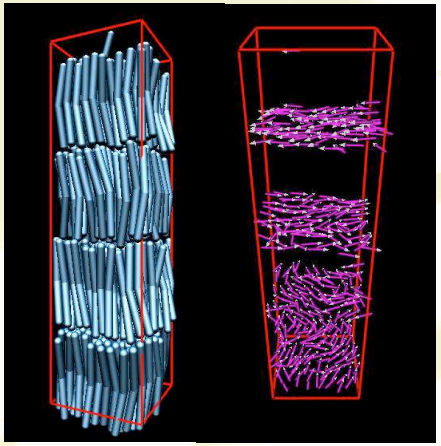
Isotropic	*SmAP*	*Crystal*
P* = 1	P* = 7	P* = 15

Final configurations for $\Psi = 165^{o}$

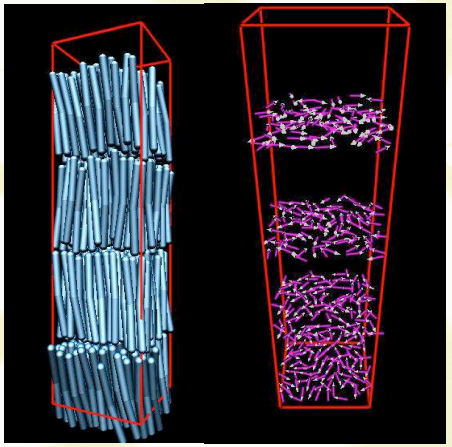


Isotropic	*Nematic*	*SmAP*	*Crystal*
P* = 1	P* = 5	P* = 9	P* = 15

Polar and nonpolar smectic A phases



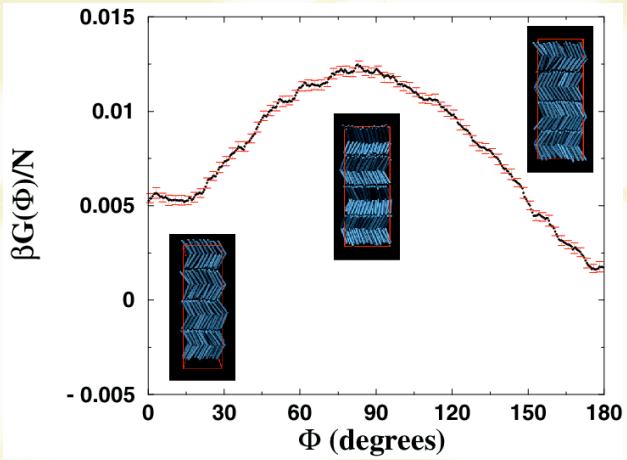
SmAP (in-layer polarity)
$\Psi = 165^{o}$



SmA (no polarity)
$\Psi = 172.5^{o}$

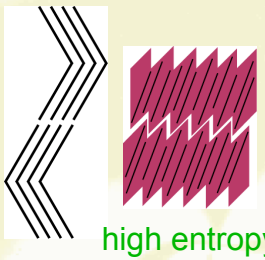
Nature of the SmAP phase

Free energy calculation using umbrella sampling
$\Psi = 120^o$ at P = 7.5 (middle of the SmAP phase)*

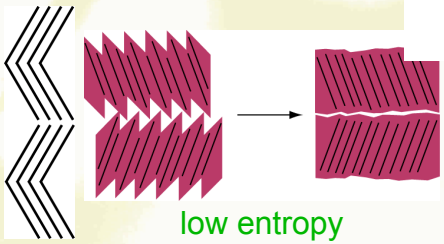


Entropic effects stabilize the antipolar SmAP phase

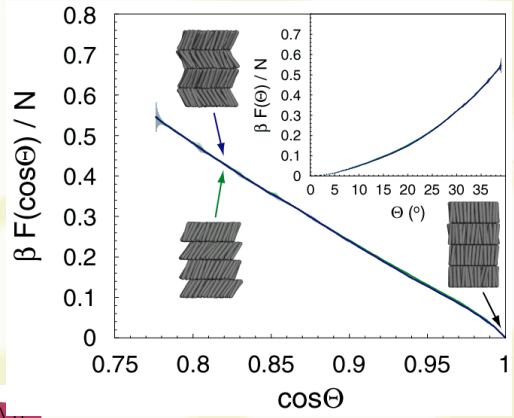
Sawtooth Model



high entropy



low entropy



Atomistic modeling:

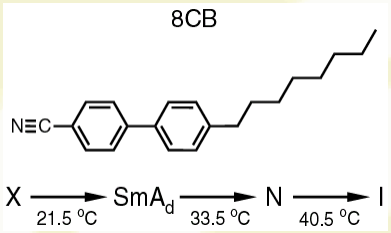
Photo-controlled nanophase segregation in smectic liquid crystal

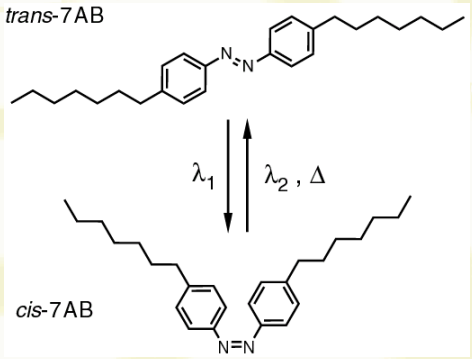
Experiment

A novel photomechanical effect has recently been observed in which a reversible increase in the layer spacing of a SmA solvent (8CB) is found to accompany the *trans-cis* isomerization of a photolabile solute (7AB) under UV illumination.

We have carried large-scale simulation of this system in order to investigate the microscopic origin of this effect.

8CB/7AB mixture





Details of simulations

We carried out NPT molecular dynamics simulations of systems containing 100 8CB molecules and 12 7AB molecules (11% molar concentration) at P = 1 atm and T = 290 K.

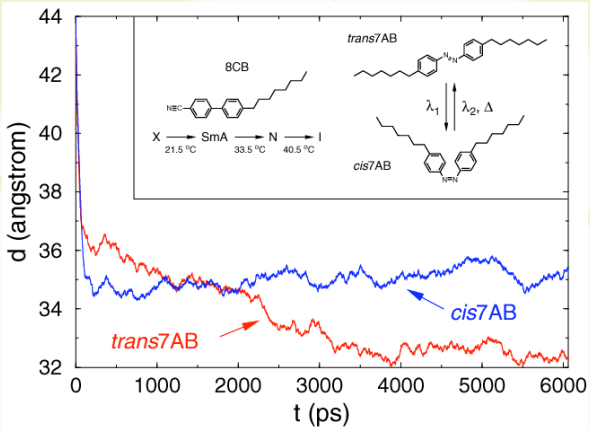
Two simulations were performed: one with all 7AB molecules in the trans configuration (the trans-7AB simulation), and another with all 7AB molecules in the cis configuration (the cis-7AB simulation). The total duration of each simulation was 6.06 ns.

A SmA2-like initial condition was used, with 7AB molecules placed within smectic layers and oriented along the layer normal.

Both systems were simulated using periodic boundary conditions, with long-range electrostatics interactions explicitly included using the particle-mesh Ewald (PME) method.

Simulations of 8CB/7AB mixtures

Smectic layer spacing vs. time

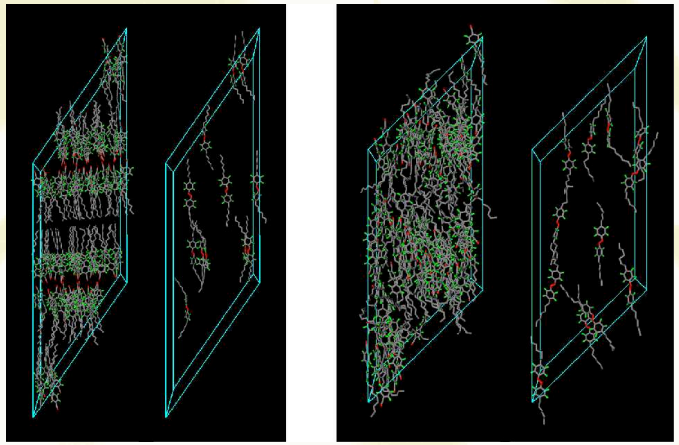


The equilibrium layer spacing of the cis-7AB system is significantly (2.7 angstrom) larger than that of the trans-7AB system.

Snapshots from trans7AB simulation

initial

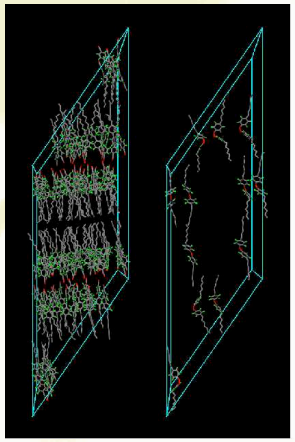
final



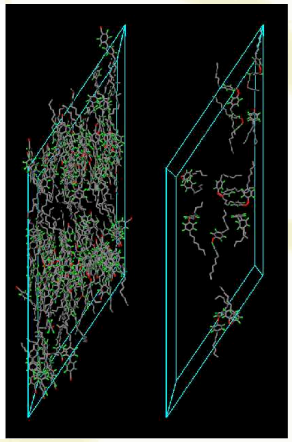
trans7AB exhibits intralamellar segregation

Snapshots from cis7AB simulation

initial



final

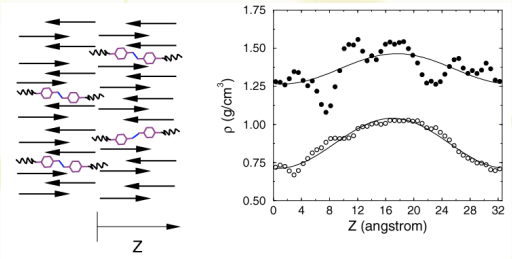


cis7AB exhibits interlamellar segregation

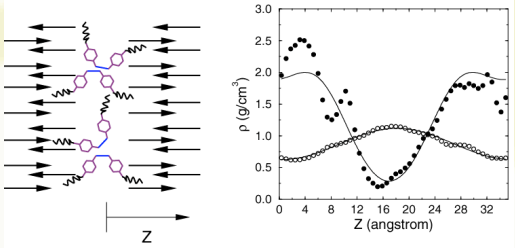
Density Profiles for 8CB/7AB Mixtures

- *Partial mass density profiles for 8CB and 7AB clearly show that 7AB molecules are driven from within smectic layers to between smectic layers upon photoisomerization*
- *The observed photomechanic effect results from this light-driven transition from intra- to interlamellar segregation*
- *What thermodynamic driving force is responsible for this transition?*

trans7AB



cis7AB



Projets

- Matériaux magnétiques / supraconducteurs
  - Simulations atomistiques (ab initio, MD, MC, réseaux)
  - Modèles idéalisés (MD systèmes dissipatifs forcés)
- Fusion solide-liquide à 2D (modèles élastiques)
- Colloides (MD/MC équilibre et forcé)
- Polyelectrolytes en géométries confinées (MD/coarse-grained)