Mesophase formation in a system of top-shaped hard molecules

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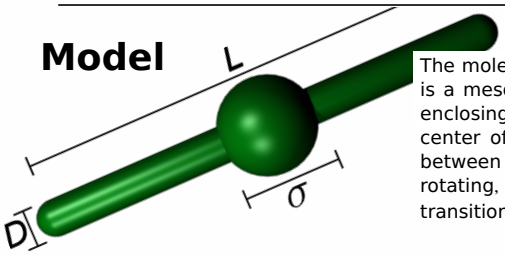
We present the phase diagram of a system of mesogenic top-shaped molecules based on the Parsons-Lee density functional theory and Monte Carlo simulation. The stability of five different phases is studied, namely, isotropic, nematic, smectic A, smectic C, and columnar phases. The positionally ordered phases are investigated only for the case of parallel alignment.

Model



The molecules are modeled as a hard spherocylinder with an embedded hard sphere. The hard spherocylinder, which is a mesogenic unit, consists of a cylindrical core (length L and diameter D) and two hemispheres with diameter D enclosing the ends of the cylinder. The hard sphere (diameter σ), which is a non-mesogenic unit, is placed at the center of the cylinder, which makes the top-shaped molecule symmetric. We assume only hard body interactions between the particles. In the description of the isotropic-nematic phase transition the top-shaped molecules are freely rotating, while for the treatment of the nematic-smectic, nematic-columnar, and smectic A-smectic C phase transitions, the molecules are assumed to be perfectly aligned in the direction of the nematic director.

Density functional theory

We use a Parsons-Lee extension of the second virial density functional theory:

$\beta F_{ex} = \chi \int d(1)\rho(1) \int_{r_{12}\in OR} d(2)\,\rho(2)$ is the excess free energy, where $\chi = (4-3\eta)/(8(1-\eta)^2)$ is the Carnahan-Starling prefactor.

$r_{12}\in OR$ ← the distance between two particles must be in the overlap region.

$(i) = (\vec{r}_i, \vec{\omega}_i)$ position and orientation of particle i.

We parameterize the density distribution for the Sm A and Sm C phases → $\rho(z) = \rho d_0 \frac{\exp[\lambda\cos(2\pi\, z/d_0)]}{\int_0^{d_0} dz' \exp[\lambda\cos(2\pi\, z'/d_0)]}$, and we use a Fourier expansion for the columnar phase → $\rho(\vec{R}) = \rho \sum_{\vec{k}} f_{\vec{k}} \cos[\vec{k}\vec{R}]$

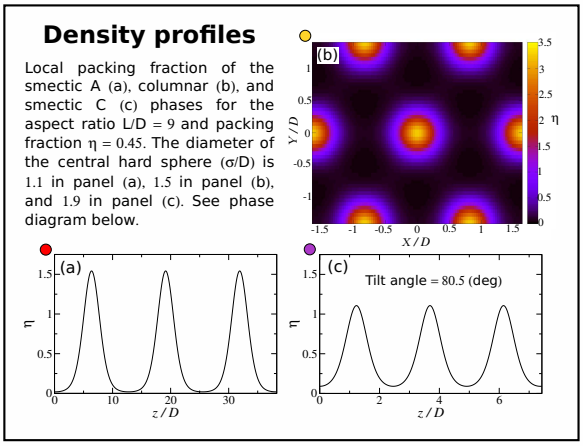
Monte Carlo Simulations

We have tested the theoretical predictions using NpT Monte Carlo simulations in a system of N=256 parallel particles with L/D=9 and different values of σ , the diameter of the central hard-sphere unit. At each pressure 10^6MC cycles are performed. Each cycle consists of N trial particle moves and one attempted volume change.

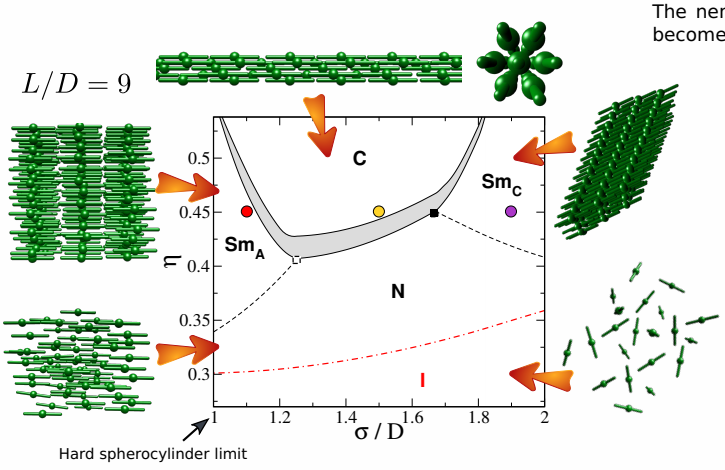
The expected structural phase transitions are diagnosed by means of the dominant Fourier modes of the local particle density since any inhomogeneity in the system will be indicated by enhanced values of structure factors pertaining to certain wave vectors.

Density profiles

Local packing fraction of the smectic A (a), columnar (b), and smectic C (c) phases for the aspect ratio L/D = 9 and packing fraction η = 0.45. The diameter of the central hard sphere (σ/D) is 1.1 in panel (a), 1.5 in panel (b), and 1.9 in panel (c). See phase diagram below.



Phase diagram: packing fraction vs HS diameter



The nematic phase is destabilized with respect to the isotropic one with σ (the molecule becomes more spherical and the packing entropy gain by orientational ordering is smaller).

The Sm A phase is also destabilized by increasing σ because the packing of the mesogenic units is less efficient (the spheres give rise to extra unoccupied regions in the layers). As a result, the formation of the smectic A phase is shifted in the direction of higher density, and its stability range shrinks due to the formation of a columnar structure.

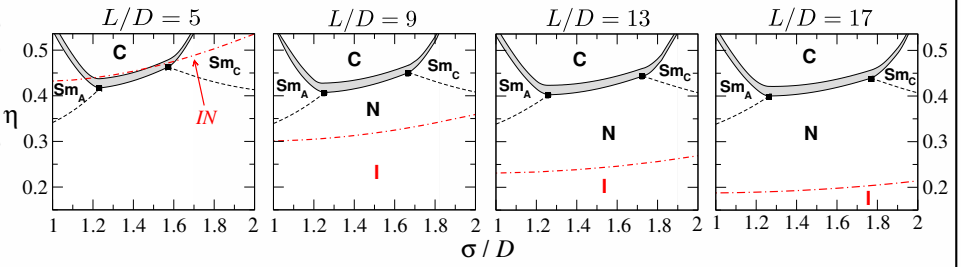
The tendency of decreasing in-plane fluidity favors the formation of a two dimensional solid structure in the layers (a columnar phase). In addition, by increasing σ there is more room between the adjacent mesogenic units, which favors the fluidization of the system in the direction perpendicular to the solid layers. For σ/D > 1.2, the smectic A phase disappears and a direct nematic-columnar phase transition takes place. However, further increase of σ is not favorable for the columnar phase, because the distance between the neighboring columns is of the order of σ, giving rise to large unoccupied regions in the space,

A new structure, the smectic C phase, appears, where the mesogenic units are tilted such that they almost lie inside the layer. With this arrangement the system becomes more packed as the mesogenic units get closer to each other and, in addition, it becomes a two-dimensional fluid again.

Role of the aspect ratio (L/D) in the phase diagram

The aspect ratio has to exceed five in order to stabilize the smectic and columnar phases. Increasing the aspect ratio stabilizes the nematic phase with respect to the isotropic one, as the particle becomes more anisotropic.

Interestingly, the aspect ratio has a small effect on the stability regions of the observed smectic A, smectic C, and columnar phases. It moves the regions of smectic A and smectic C phases in opposite directions by enhancing the stability region of the columnar ordering.



Comparison between Density Functional Theory and Monte Carlo Simulations

(1)

	MC		DFT	
σ/D	η	d_0 /D	η	d_0 /D
1.00	0.44–0.66	11.5–9.9	0.34–0.56	13.52–12.13
1.02	0.45–0.60	11.2–10.2	0.34–0.54	13.50–12.24
1.04	0.46–0.57	11.0–10.3	0.35–0.51	13.47–12.33
1.06	0.47–0.53	10.9 –10.5	0.35–0.50	13.44–12.42

(2)

	MC			DFT		
σ/D	η	Ψ(deg)	d_0 /D	η	Ψ(deg)	d_0 /D
1.80	0.44	80.6	1.9	0.43	80.14	2.51
1.85	0.43	81.3	1.8	0.42	80.12	2.53
1.90	0.43	80.6	1.9	0.42	80.09	2.55

(1) Stability range of the smectic A phase (packing fraction and period) for different sizes of the central hard-sphere in a system of particles with L/D=9.

(2) Packing fraction, tilt angle and period for the smectic C phase that coexists with a nematic phase in a system of particles with L/D=9

See also:

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