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 $\sigma$), 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:

$$\beta F = \int \rho(x) v(\rho(x)) \rho(x) \, dx = \int \rho(x) u(\rho(x)) \rho(x) \, dx + \int \rho(x) \rho(y) \delta(x-y) \, dx \, dy$$

where $\rho(x)$ is the density of particles at position $x$, $v(\rho(x))$ is the free energy per particle, $u(\rho(x))$ is the excess free energy per particle, and $\delta(x-y)$ is the Dirac delta function.

We characterize the density distribution for the Sm A and Sm C phases using 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.

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 $\sigma$, the diameter of the central hard-sphere unit. At each pressure $10^3$ MC 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.

Phase diagram: packing fraction vs HS diameter

The nematic phase is destabilized with respect to the isotropic one with $\sigma$ (the molecule becomes more spherical and the packing entropy gain by orientational ordering is smaller). The Sm A phase is also destabilized by increasing $\sigma$ 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 $\sigma$ 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 $\sigma/\sigma_0 > 1.2$, the smectic A phase disappears and a direct nematic-columnar phase transition takes place. However, further increase of $\sigma$ is not favorable for the columnar phase, because the distance between the neighboring columns is of the order of $\sigma$, giving rise to large unoccupied regions in the space.

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

See also:

Mesophase formation in a system of top shaped hard molecules. Density functional theory and Monte Carlo simulation.

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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 $L/D=9$.

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 $L/D=9$.

Packaging fraction, tilt angle and period for the smectic C phase that coexists with a nematic phase in a system of particles with $L/D=9$.

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 $L/D=9$.

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 $L/D=9$. 

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 $\sigma/\sigma_0 = 0.43$. The diameter of the central hard sphere ($\sigma/\sigma_0$) is 1.1 in panel (a), 1.5 in panel (b), and 1.9 in panel (c). See phase diagram below.