Smectic ordering of homogeneous semiflexible polymers and rod–coil diblock copolymers

Raúl Cruz Idalgo, Departament de Física de la UdG

A self-consistent-field theory for fluids of wormlike polymers is presented. We have extended the treatment of excluded-volume effects by adding an effective interaction term which describes the excluded volume between wormlike cylindrical segments and terminal or end segments of the polymer molecules. Using this framework, we have investigated the occurrence of smectic-A, nematic, and isotropic phases in the second-virial Onsager approximation. Phase diagrams are calculated for systems characterized by different rigidities i.e., persistence lengths. Systems of semiflexible molecules exhibit mainly a first-order smectic-nematic transition, and their isotropic-nematic-smectic triple points are accessed for different rigidity values. A fluid of rod–coil diblock copolymers, modeled as wormlike chains, is also treated by using this self-consistent field theory. The ‘rod’ and ‘coil’ sections of each molecule are distinguished by their degrees of flexibility (or persistence lengths), but are otherwise identical. The smectic phase is found to have partial bilayer morphology, exhibiting nearly complete interdigitation of the rod-like sections and little interdigitation of the coil sections.