Phase behavior of liquid-crystal monolayers of rod-like and plate-like particles

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The difference between the phase behaviours of molecularly thick films (Langmuir monolayers) and that of colloidal monolayers confined between two parallel planes is mainly due to the fact that the amphiphilic molecules are allowed to rotate out from the air/liquid interface, while the colloids can rotate only in the plane parallel to the confining walls. The consequence is that the phase behaviour of Langmuir monolayers can be much richer than that of 2D colloidal systems. For example, upon compression, only a few phases (isotropic, nematic, solid) may occur if the confined particles have only 2D orientational freedom [1,2], while several additional, tilted or not tilted, phases can be present in the case of Langmuir monolayers with out-of-plane rotational freedom due to their intermediate quasi-two-dimensional character [3] (i.e. 2D in translations and 3D in orientations).

In the present work the orientational and positional ordering properties of liquid crystal monolayers are examined. Particles forming the monolayer are modeled as hard parallelepipeds of square section and their shapes are controlled by the aspect ratio. The particle centers of mass are restricted to a flat surface and three possible and mutually perpendicular orientations of their axes are allowed. In the case of rod-like shapes, particles align along the layer normal in order to achieve the lowest possible occupied area per particle. This phase is a uniaxial nematic even at very low densities. In contrast, for plate-like particles, the lowest occupied area can be achieved by random in-plane ordering in the monolayer, i.e. planar nematic ordering takes place even at vanishing densities. It is found that the random in-plane ordering is not favorable at higher densities and the system undergoes an in-plane ordering transition forming a biaxial nematic phase or crystallizes. For certain values of the aspect ratio, the uniaxial-biaxial nematic phase transition is observed for both rod-like and plate-like shapes. The stability region of the biaxial nematic phase enhances with decreasing aspect ratios for plate-like particles, while the rod-like particles exhibit a reentrant phenomenon, i.e. a sequence of uniaxial-biaxial-uniaxial nematic ordering with increasing density if the aspect ratio is larger than 21.34. In addition to this, packing fraction inversion is observed with increasing surface pressure due to the alignment along the layers normal. At very high densities the nematic phase destabilizes to a nonuniform phases (columnar, smectic or crystalline phases) for both shapes.

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