Two microscopic mechanisms of smectic ordering in conventional and unconventional liquid crystals

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Phenomenological theory of smectic ordering has been proposed long ago by de Gennes, and a molecular-statistical theory of smectic phases has been developed after the papers of McMillan and Wulf. However, the existing theory is based on a simple interpretation of the smectic ordering which is mathematically very similar to the one-dimensional crystallization determined by attraction and repulsion between the molecules as a whole. At the same time there exists a different mechanism of smectic ordering found, for example in lyotropic lamellar phases where smectic layers are formed as a result of a nano-scale segregation. It has been recognized long ago that an element of nano-scale segregation (between molecular cores and tails) may be important even in conventional smectics. The tendency for a segregation of different molecular fragments is strongly enhanced in novel smectic materials including de Vries type mesogens which possess fluorinated or siloxane chains, ionic smectics with strong chrge separation and thermotropic flexible mesogens with a strongly polar head.

We present a general molecular theory of smectic ordering in which the coefficients in the expansion of the mean field potential are calculated numerically directly from a model pair potential including the Gay-Berne potential and the potentials modelling attraction and repulsion between molecular fragments. The theory enables one to calculate all order parameters and the interlayer spacing by minimization of the free energy, and to distinguish between two types of transitions into the smectic phase. In conventional materials the smectic A phase is primarily stabilized by the high orienttaional order while the smectic order parameter is not very high. In materials with the segregation of molecular fragments the transition is governed by the orienttaional-density wave and the smec tic A phase is characterized by very high smectic order and abnormally low nematic one. The theory explains many properties of unconventional smecitc materials.