

## Liquid crystals

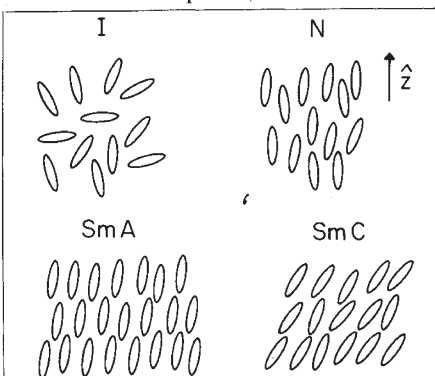
## Numerical models of mesophases

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SMECTIC (from the Greek for soap) is the name chosen for certain liquid phases with physical properties reminiscent of soap. Iridescent soap films, which show beautiful diffraction colours under a white light, do so mainly because the soap molecules form layered structures. Consequently, the characteristic feature of all smectic phases is their layered structure. It is generally believed that an attractive interaction between the molecules is essential for the formation of smectic phases. Using molecular-dynamic and constant-pressure 'Monte Carlo' simulations on a system of hard spherocylinders (cylinders capped at each end by a hemisphere of the same radius) however, D. Frenkel, H. N. W. Lekkerkerker and A. Stroobants on page 822 of this issue<sup>1</sup>, challenge this idea. They observe a smectic phase with distinguished layers and without long-range positional order of rods within the layers, without there being any attractive interaction between the rods. The only interaction in this system is one in which the cylinders cannot interpenetrate each other — the 'steric' or 'excluded-volume' interaction.

Liquid crystals consist of anisotropic organic molecules, which have one or more mesophases (intermediate phases) between the crystalline and the isotropic-liquid states. Transitions to these mesophases can be brought about by purely thermal processes (thermotropic) or by varying the concentration of solvents (lyotropic)<sup>2</sup>. The most extensive characterization of the physical properties of various smectic phases has been carried out in thermotropic liquid crystals which were originally classified by G. Friedel in 1922 into three categories<sup>3</sup>: nematic, cholesteric and smectic.

In the nematic phase, the molecules are



**Fig. 1** Schematic molecular arrangement for isotropic (I), nematic (N), smectic-A (SmA) and smectic-C (SmC) phases in liquid crystals;  $\hat{z}$ , average of molecular directors.

spontaneously oriented with their long axes (molecular directors) pointing to some specific direction which distinguishes itself from the isotropic phase (Fig. 1). The nematic material has a viscosity about the same as that of light machine oil at room temperature and the molecules fill a container with no positional ordering, as in a liquid. The cholesteric mesophase is similar to the nematic phase except that it is composed of optically active molecules. As a consequence a helical structure shows up with the molecular director precessing around the normal of the molecular director. The typical size of the pitch is about 1  $\mu\text{m}$  which is much larger than the width of the molecules (about 7  $\text{\AA}$ ).

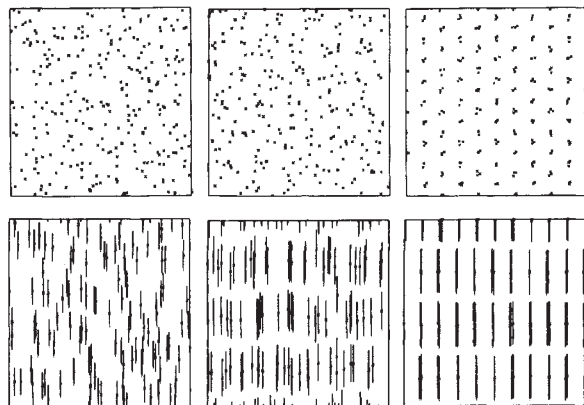
During the past 10 years, extensive high-resolution X-ray investigations of various smectic liquid crystals have revealed the molecular arrangements within each layer. Two different categories have been identified<sup>4</sup>: one with long-range positional order within the layers and one without. In fact, 20 different mesophases have now been identified within the old smectic phase, and 'smectic' is now reserved for those without long-range positional order. The phase discussed<sup>1</sup> by Frenkel *et al.* is the smectic-A phase in the field of thermotropic liquid-crystals. On average, the molecular directors are normal to the layer and there is no long-range positional order within the layers (Fig. 1).

L. Onsager did early model calculations on the isotropic-nematic phase transition, caused by increased density, by considering a fluid of long thin rods with no force between them except the steric interaction<sup>5</sup>. The first attempts to address the formation of the smectic-A phase<sup>6,7</sup> used an attractive pair potential between elongated molecules, as have all subsequent models.

In a previous computer study<sup>8</sup> using hard spherocylinders without attraction with length-to-width ratios of 0.25 (disk-like) to 5 (rod-like), Frenkel and co-workers found that as the density increases, the molecules first align from the isotropic phase to form the smectic phase, and then crystallize onto a lattice. But between the nematic and crystalline phases of all except the most disk-like molecules, periodic oscillations arise along the mole-

cular director, strongly indicative of the formation of the smectic-A phase (Fig. 2). Although it is understandable that the repulsive steric interactions should cause the spherocylinders to align, it is not clear how they are drawn into the layered structure of the smectic-A phase without any attractive interaction.

In this issue<sup>1</sup>, Frenkel *et al.* confirm the smectic-A phase of rod-like molecules and show that it is thermodynamically stable with respect to the isotropic, nematic phases and crystalline phases. The pre-translational smectic-layer fluctuations



**Fig. 2** The nematic (left), smectic (middle) and solid (right) phases of a system of rod-like spherocylinders without attraction. The views along the molecular directors (top) show that long-range positional ordering within the planes occurs only in the solid phase. The views from the side (bottom) show the molecules being drawn into planes as the density increases from left to right. (From ref. 8.)

seen near the nematic-smectic-A transition suggests that this transition could be continuous or weakly first-order. The present study, however, uses too small a sample to distinguish these alternatives.

One obvious extension of the present study is the smectic-C phase in which the molecular directors tilt away from the layer normal (Fig. 1). The molecular tilt angle can continuously decrease to zero as the temperature increases toward the smectic-C-smectic-A transition. This phase transition can be well characterized by a mean-field theory<sup>9</sup>. It remains to be seen, however, whether the steric interaction is sufficient to account for the formation of the smectic-C or whether dipolar interactions are essential. In this respect a computer simulation on a realistic object, similar to a liquid crystal molecule, should be extremely useful.  $\square$

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