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X-RAY SCATTERING BY COLUMNAR LIQUID CRYSTALS

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SEVERAL disc-shaped molecules are known to form thermotropic liquid crystals[1]. The mesophases so far discovered fall into two distinct categories, the columnar and the nematic. In the columnar type, the discs are stacked one on top of the other in columns, the different columns forming a 2D lattice. A number of variants of this structure have been identified—hexagonal, rectangular, etc. In the nematic type, the discs are preferentially aligned more or less parallel to a plane without any long range positional order.

The columnar phases represent a new class of thermotropic liquid crystal, which in its simplest form may be looked upon as a system with translational periodicity in two dimensions but not in the third. In this note we discuss the fundamental question of fluctuations in such a system and their influence on X-ray scattering—a question of great importance in view of the fact that the 2D lattice is, strictly speaking, unstable[2]. However, as we shall see presently the curvature elasticity of the liquid-like columns stabilizes the columnar structure. It emerges that the mean square amplitude of the fluctuations is rather more sensitively dependent on the sample size than in the case of a 3D lattice, and the Debye-Waller factor is significantly different from that for the 2D or 3D lattice or the smectic A liquid crystal.

We shall suppose that the liquid-like columns are along the z-axis and that the 2D lattice (taken to be hexagonal) is confined to the xy plane. We shall consider only the vibrations of the lattice in its own plane. The free energy density may be written as[3]

$$F = \frac{B}{2}\left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y}\right)^2 + \frac{D}{2}\left\{\left(\frac{\partial u_x}{\partial x} - \frac{\partial u_y}{\partial y}\right)^2 + \left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right)^2\right\} + \frac{k_{33}}{2}\left\{\left(\frac{\partial^2 u_x}{\partial z^2}\right)^2 + \left(\frac{\partial^2 u_y}{\partial z^2}\right)^2\right\}, \tag{1}$$

where B and D are the elastic constants for the deformation of the 2D lattice in its own plane, u_x and u_y are the displacements along x and y at any lattice point, and k_{33} is the elastic constant associated with the curvature deformation (bending) of the columns. It may be emphasized that k_{33} will be extremely small as compared with the constants B and D.

Writing the displacement $\mathbf{u}$ in terms of its Fourier components, *i.e.*,

$$\mathbf{u} = \sum_{\mathbf{q}} \mathbf{u}(\mathbf{q}) \exp[i\,\mathbf{q}\cdot\mathbf{r}], \tag{2}$$

substituting in (1) in the harmonic approximation we get

$$F = \frac{1}{2}\sum_q (B_o q_\perp^2 + k_o q_z^4) \langle u_q^2 \rangle, \tag{3}$$

and from the equipartition theorem

$$\langle u_q^2 \rangle = \frac{k_B T}{B_o q_\perp^2 + k_o q_z^4}, \tag{4}$$

where $B_o = B + 2D$, $k_o = 2k_{33}$, $q_\perp = (q_x^2 + q_y^2)^{\frac{1}{2}}$ and k_B is the Boltzmann constant.

An analysis of the stability requires an evaluation of the mean square displacement at any lattice point. The mean square displacement is given by

$$\langle u^2 \rangle = \sum_q \langle u_q^2 \rangle \sim \int \langle u_q^2 \rangle \, d\mathbf{q}, \tag{5}$$

which may be simplified to

$$\langle u^2 \rangle \sim \frac{T}{B_o(\lambda d)^{\frac{1}{2}}}\left[1 - (d/L)^{\frac{1}{2}}\right], \tag{6}$$

where $\lambda = (k_0/B_0)^{1/2}$ is a characteristic length, d is the periodicity of the 2D lattice and L its linear dimension. We have assumed here that the length of the columns is very much greater than L.

For the 3D lattice

$$\langle u^2 \rangle \sim \frac{T}{B_o d}(1 - d/L). \tag{7}$$

Thus the columnar structure, like the 3D lattice, is stable as $L \to \infty$, but the dependence of $\langle u^2 \rangle$ on L is different in the two cases. On the other hand, for smectic A as well as the 2D lattice $\langle u^2 \rangle$ diverges as $\ln L$.

These thermal fluctuations will naturally affect the nature of the X-ray reflections from the columnar phase. In the presence of such vibrations, the structure factor is

$$S(\mathbf{K}) = \int dz \sum_m \sum_n \exp\left[i \left\{ \mathbf{K}\cdot(\mathbf{R}_m - \mathbf{R}_n) \right\} \right]$$

$$\exp\left[-\frac{1}{2} K_\perp^2 \left\langle | u_n - u_m |^2 \right\rangle \right]. \quad (8)$$

The second exponential term on the right side is the familiar Debye-Waller factor $\exp(-W)$. From (2)

$$\left\langle (u_n - u_m)^2 \right\rangle \sim \left\langle [u(r) - u(0)]^2 \right\rangle$$

$$\sim \int \left\langle u_q^2 \right\rangle \; [1 - \exp(i\mathbf{q}\cdot\mathbf{r})] d\mathbf{q} \quad (9)$$

The first term in the integral (9) leads to (6), while the second term simplifies to

$$\sim \frac{T}{B_o(\rho\lambda)^{\frac{1}{2}}} \times$$

$$\left[\exp\left\{ -\frac{z^2}{4\rho\lambda} \right\} \left[U\left(\frac{1}{4}, \frac{1}{2}, \frac{z^2}{4\rho\lambda}\right) \right]^2 \right] \quad (10)$$

where $\rho = (x^2 + y^2)^{\frac{1}{2}}$ and U is the confluent hypergeometric Kummer function[4]. For $z \gg (\rho\lambda)^{\frac{1}{2}}$ this simplifies further to

$$\sim \frac{T}{B_o z} \exp\left(-\frac{z^2}{4\rho\lambda}\right) \quad (11)$$

These results are quite different from those for smectic A and the 2D lattice. For smectic A[5] with its liquid-like layers parallel to xy, we have instead of (11)

$$\sim \frac{T}{B_o\lambda} \ln \frac{1}{z} \qquad \text{for } \lambda z \gg \rho^2$$

$$\sim \frac{T}{B_o} \ln \frac{1}{\rho} \qquad \text{for } \lambda z \ll \rho^2 \quad (12)$$

and for the 2D lattice[5]

$$\sim \frac{T}{B_o} \ln \frac{1}{r}. \quad (13)$$

It is this logarithmic form of the displacement—displacement correlation in smectic A and the 2D lattice that washes out the Bragg reflections (or the δ-function singularities in $S(\mathbf{K})$) and results in much weaker singularities. On the other hand the columnar liquid crystal does give Bragg reflections. To evaluate the thermal diffuse part of $S(\mathbf{K})$ arising from fluctuations, one has to make use of the full expression (10).

So far it has been assumed that the length (L') of the liquid columns is much larger than L. One may similarly consider the opposite extreme situation $L' \ll L$. In this case, it turns out that for the bounded sample

$$\langle u^2 \rangle \sim \text{const} \qquad \text{for very small } L'$$

$$\sim \frac{1}{L'} \ln L' \qquad \text{for larger } L' \quad (14)$$

If one of the surfaces is free there are additional terms that are peculiar to the 2D lattice.

Note added in proof

We have just received a preprint of a paper by Kammensky and Kats of the Landau Institute of Theoretical Physics, Moscow, discussing the same problem in considerable detail—in fact more thoroughly than has been done by us. The general conclusions of this paper are essentially identical to ours, but the treatment includes the vibrations of the columns parallel to themselves, a complete analysis of the effects of a free surface, long and short columns, etc.

One of us (SC) would like to take this opportunity of thanking Dr. E. I. Kats and Dr. V. G. Kammensky for the discussions he had with them in Moscow in November 1981 on this and other related topics.

1. For up-to-date reviews, see Chandrasekhar, S., *Mol. Cryst. Liq. Cryst.*, 1981, **63**, 171; Destrade, C., Tinh, N. H., Gasparoux, H., Malthete, J. and Levelut, A. M., *Mol. Cryst. Liq. Cryst.*, 1981, **71**, 111; Chandrasekhar, S., in *Advances in liquid crystals*, Vol. 5, (In press).
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