

Measurement of Smectic-Phase Order-Parameter Fluctuations in the Nematic Phase of Heptyloxyazoxybenzene

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A measurement is presented of the liquid-structure factor of *p-n*-heptyloxyazoxybenzene in the nematic phase using monochromatic $\text{Cu } K\alpha$ radiation. This material has a smectic *C* phase at lower temperature and exhibits strong pretransition scattering in the nematic phase. Near the phase transition the liquid-structure factor peaks at a tilt angle of 30° between the plane normal and the nematic director. By using a simple Landau-like theory to describe the phenomenon, one can map out the free energy of a smectic *C* density wave as a function of wavelength, tilt angle, and temperature.

I. INTRODUCTION

Recently, the author¹ reported a measurement of the anisotropic liquid-structure factor in the nematic phase of a material with a smectic *A* phase at lower temperature. A strong peak was observed in the liquid-structure factor near the position of the smectic Bragg peak which was interpreted as being due to small regions of the nematic phase fluctuating into a smectic-*A*-like configuration. These fluctuations can be described by a Landau theory and such a theory had been proposed for the smectic *A* phase by the author² and by de Gennes.³ The measurements were fitted very nicely by the Landau theory and the parameters of the theory determined.

A similar phenomenon has been observed by DeVries⁴ in an x-ray photographic study of *p-n*-heptyloxyazoxybenzene (HAB) which has a smectic *C* phase below the nematic phase. In this paper we report the measurement of the anisotropic liquid-structure factor of HAB in the nematic phase. This material has been the subject of a number of other investigations, and the heat capacity⁵ and elastic constants⁶ have been measured.

In the smectic *A* phase, one has two order parameters, the nematic orientational order parameter and the smectic density wave. In the smectic *C* phase, the molecular long axis tilts away from the plane normal, and de Gennes⁷ has constructed a Landau theory using the tilt angle as an order parameter. The author⁸ has taken a different approach and has written down a microscopic theory of the smectic *C* phase using the intermolecular dipole-dipole interaction. According to that theory, molecular rotation about the long axis freezes out in the smectic *C* phase and one has a second orientational order parameter; the tilt angle passively follows this order parameter. We regard the nature of the smectic *C* phase as unsettled.

HAB transforms directly from the nematic to

the smectic *C* phase, and pretransition phenomena in the nematic phase must involve fluctuations of two order parameters, the density wave and the orientation (or tilt). Under these circumstances, it is surprising that one observes strong pretransition phenomena; however, the entropy of the phase transition is small ($0.5R_0$), which favors pretransition phenomena. There is as yet no proper theory of the fluctuations of both order parameters. In order to analyze the data, which refer only to the density wave, we will use an *ad hoc* modification of the smectic *A* Landau theory which specifies the free energy of a density wave of a given wavelength and tilt angle; using the experimental data, we can then map out this free energy as a function of wavelength, tilt angle, and temperature. For the smectic *A* case the theory predicted the functional form of this free energy, but for the smectic *C* case there is no such prediction.

The apparatus is identical to that used in the previous experiment.¹ A monochromatic beam of $\text{Cu } K\alpha$ x rays falls on a sample oriented by a 10-kG field and the scattered radiation is counted in a scintillation counter. The nematic phase is uniaxial and one measures the scattered intensity as a function of momentum transfer parallel (q_{\parallel}) and perpendicular (q_{\perp}) to the field direction. The experimental data are presented in Sec. II and analyzed in Sec. III.

The sample was custom synthesized by Frinton and recrystallized once from ethanol. The transition temperatures were measured on a polarizing microscope with a Mettler FP5 hot stage and the heats of transition were measured on a Perkin-Elmer DSC-1B differential scanning calorimeter; these data are recorded in Table I.

II. EXPERIMENTAL RESULTS

A contour map of the measured intensity corrected for resolution in the q_{\parallel} - q_{\perp} plane is shown in

TABLE I. Transition temperatures and transition entropies [$R_0=1.986$ cal/(deg mole)] for HAB.

Transition	Temperature (°C)	Entropy (R_0)
crystal-smectic C	74.6	13.1 ± 1.3
smectic C-nematic	95.0	0.52 ± 0.06
nematic-isotropic	124.3	0.38 ± 0.06

Fig. 1 for $T=96^\circ\text{C}$. Measurements were made along one transverse section aa' and four longitudinal sections $bb'-ee'$ at six temperatures in the nematic phase. The measured intensities along the transverse section aa' are shown in Fig. 2 and along the longitudinal sections bb' and cc' in Figs. 3 and 4. Measurements along the four longitudinal sections at $T=96^\circ\text{C}$ are shown in Fig. 5. The intensities are given as counts per 4-min counting period; part of the data is an average of several runs. The over-all reliability of the data is $\pm 5\%$ except in the wings, where the counting statistics are poor.

The principal difference between these data (smectic C) and the previous case (smectic A) is that the liquid-structure factor peaks at a finite value of q_\perp , that is, at a finite tilt angle. This tilt angle decreases as one increases the temperature. At zero tilt angle ($q_\perp=0$) the structure factor peaks at $q_\parallel=0.207 \text{ \AA}^{-1}$, which corresponds to a molecular length of $30.4 \pm 0.2 \text{ \AA}$. The length of a space filling model of HAB in the transconfiguration is 30.4 \AA . At finite tilt angle (finite q_\perp) the structure factor peaks at a somewhat smaller value

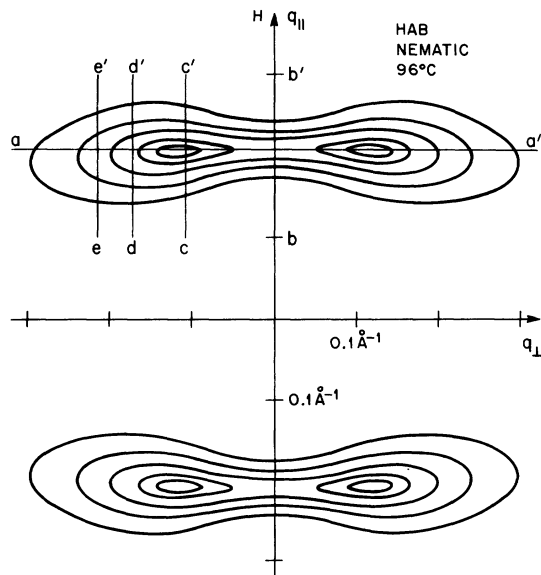


FIG. 1. Contour map of the liquid-structure factor of HAB at 96°C , corrected for instrumental resolution. The contours are drawn for intensities of 3000, 2000, 1000, 500, and 250.

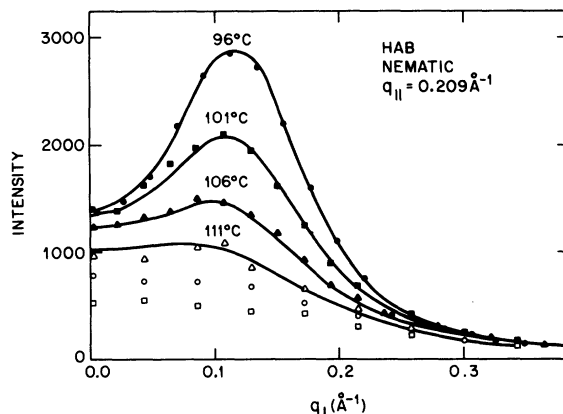


FIG. 2. Measured intensities along transverse section aa' for six temperatures (in $^\circ\text{C}$): 96 (closed circles), 101 (closed squares), 106 (closed triangles), 111 (open triangles), 116 (open circles), 121 (open squares). The lines are the fit to Eqs. (7)-(10), convoluted with the instrumental resolution function.

of q_\parallel . For a model of elliptical molecules with length l , and width w the interplanar spacing versus tilt angle is given by

$$d = (l^2 \cos^2 \theta + w^2 \sin^2 \theta)^{1/2}, \quad (1)$$

which gives rise to a peak in the liquid structure for q_\parallel equal to

$$q_\theta = q_0 (1 - w^2 q_\perp^2 / 2l^2 q_0^2), \quad (2)$$

where $q_0 = 2\pi/l$. From the observed shift of q_θ with q_\perp we find $w^2/2l^2 = 0.04$ for HAB and 0.08 for the previous sample¹ (OBT). These values are about a factor of 2 larger than expected but are in the right order of magnitude; thus, we have a reasonable physical explanation for the shift of q_θ with q_\perp . The measured d spacing in the smectic C phase of HAB is 24.5 \AA at 94°C , which from (1) gives a tilt angle of 38° ; the d spacing at 76°C is 23.4 \AA , giving a tilt angle of 42° .

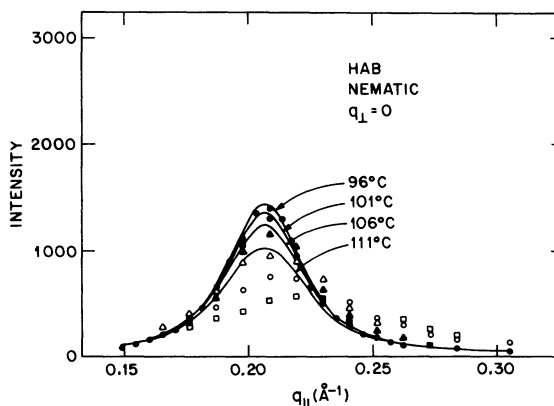


FIG. 3. Measured intensities along longitudinal section bb' for six temperatures labeled as in Fig. 2.

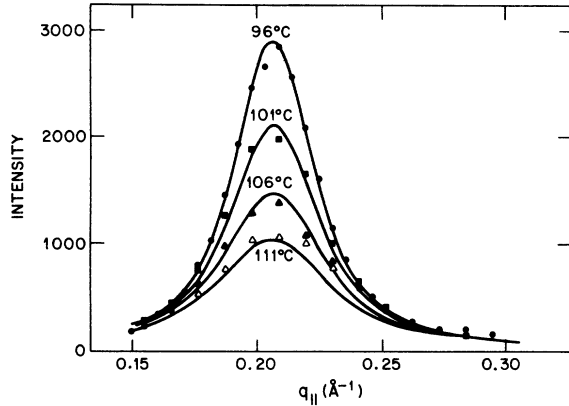


FIG. 4. Measured intensities along longitudinal section cc' for four temperatures labeled as in Fig. 2.

III. DATA ANALYSIS

We will analyze the data in terms of a modification of the smectic A Landau theory. The smectic planar structure can be described by a complex order parameter $\psi(x)$ where the particle density is

$$\rho(x) = \rho_0 [1 + \text{Re}\psi(x)]. \quad (3)$$

We write

$$\psi(x) = \sum_q \psi_q e^{i\alpha \cdot x} \quad (4)$$

and assume that the free energy of a density wave of wavelength $2\pi/q$ and amplitude ψ_q can be written

$$F(q, \psi_q, T) = \frac{1}{2} NkT A_q \psi_q^2. \quad (5)$$

The short-ranged correlation between the dipole moments is not included explicitly and we assume that this motion has been averaged over in obtaining (5). As before,¹ the liquid-structure factor is

$$S_q = 1 + 1/A_q. \quad (6)$$

The data along the longitudinal sections are accurately Lorentzian and we fit the intensity with the following expression:

$$I_q = \frac{\gamma}{\alpha + \beta (q_{||} - q_\theta)^2 / q_0^2}. \quad (7)$$

It is necessary to assume that β and q_θ are functions of q_\perp and that α is a function of both q_\perp and temperature. We have chosen the following functional forms, of which the first two have no theoretical significance:

$$\alpha(q_\perp, T) = \alpha_0 + \alpha_1 (q_\perp / q_0)^2 + \alpha_2 \exp[-\alpha_3 (q_\perp / q_0)^2], \quad (8)$$

$$\beta(q_\perp) = \beta_0 + \beta_1 \exp[-\beta_2 (q_\perp / q_0)^2], \quad (9)$$

$$q_\theta(q_\perp) = q_0 [1 - \delta_0 (q_\perp / q_0)^2]. \quad (10)$$

The finite resolution of the apparatus is taken into account by smearing (7) with a Gaussian beam pro-

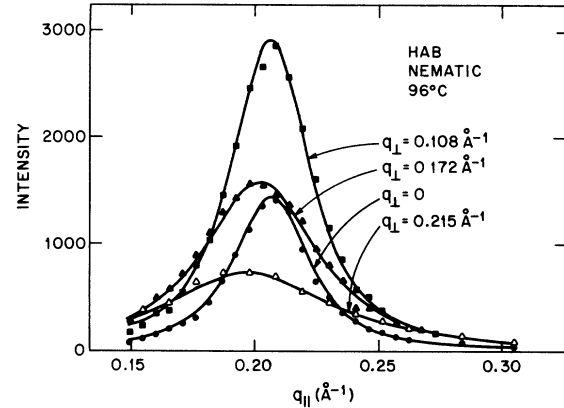


FIG. 5. Measured intensities along four longitudinal sections at 96°C: bb' , $q_\perp = 0$ (closed circles); cc' , $q_\perp = 0.108 \text{ \AA}^{-1}$ (closed squares); dd' , $q_\perp = 0.172 \text{ \AA}^{-1}$ (closed triangles); ee' , $q_\perp = 0.215 \text{ \AA}^{-1}$ (open triangles). The lines are the fit to Eqs. (7)–(10).

file. The half-width at half-height of the beam profile is 0.008 \AA^{-1} (0.022 \AA^{-1}) in the parallel (perpendicular) directions. The smearing is not serious; the peak intensity at the lowest temperature is reduced 20% by the finite resolution.

The most extensive data were taken at the lowest temperature; the constants were chosen to fit the data at this temperature and then α_0 and α_2 were permitted to vary with temperature to fit the higher-temperature curves. The fitted parameters are given in Table II and the solid lines in Figs. 2–5 were calculated using these numbers. Since the longitudinal sections are Lorentzian, one can compute a longitudinal coherence length for each section. This length is 67 \AA at 96°C and is constant from $q_\perp = 0$ out to about $q_\perp = 0.13 \text{ \AA}^{-1}$ even though the peak intensity varies by a factor of 2. The free energy at $q_{||} = q_\theta$ is proportional to $\alpha(q_\perp, T)$ and this function is plotted in Fig. 6 versus tilt angle. The free-energy minimum occurs at $\theta = 30^\circ$ at 96°C and moves to smaller angles at higher tempera-

TABLE II. Parameters found from fitting Eqs. (7)–(10) to the data at four temperatures. Only α_0 and α_2 were permitted to vary with temperature.

	Temperature (°C)			
	96	101	106	111
α_0	-4.1	-3.65	-2.94	-2.1
α_2	5.1	4.7	4.1	3.5
α_1	4.97			
α_3	1.72			
β_0	58			
β_1	133			
β_2	5.22			
δ_0	0.04			
γ	1608			
q_0	0.206 \AA^{-1}			

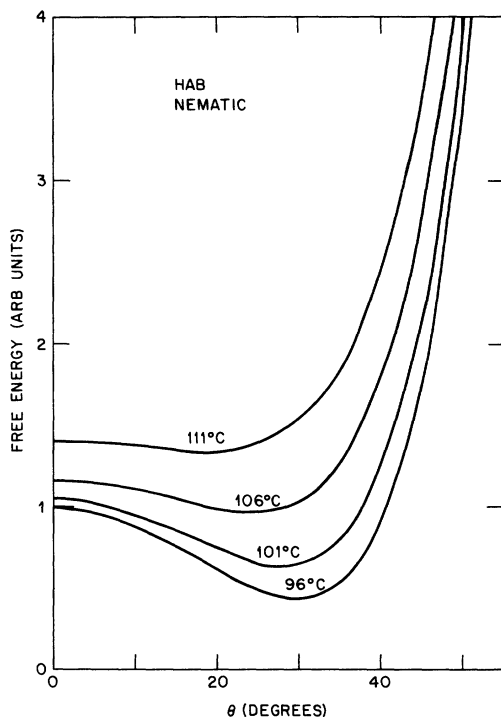


FIG. 6. Free-energy function $\alpha(q_L, T)$ vs tilt angle θ at four temperatures derived by fitting Eqs. (7)–(10) to the measured intensities.

tures. At 111°C the minimum has nearly moved into zero.

IV. CONCLUSIONS

We have carefully mapped out the liquid-structure factor of HAB in the nematic phase. We ob-

serve pretransition phenomena for the smectic *C* phase, which is qualitatively different from the smectic *A* case. We observe a peak in the liquid structure for $q_{||} \approx 2\pi/l$ which grows stronger as one approaches the transition to the smectic *C* phase. At high temperature ($111 < T < 124^\circ\text{C}$), the peak lies in the field direction (no tilt), while at lower temperature ($95 < T < 111^\circ\text{C}$), the liquid structure peaks at a finite tilt angle which reaches 30° at the phase transition.

In the smectic *A* case, a relationship was derived between the liquid-structure factor and free energy of a smectic density wave. We have assumed that that relationship holds here and have plotted the free energy versus tilt angle and temperature. The present theories of the smectic *C* phase are insufficiently sophisticated to permit a prediction of the tilt angle and temperature dependence of the free energy. It would be interesting to have such predictions to compare with the present experiment.

One can argue from the microscopic theory that if the molecules rotated freely about their long axes—that is, if there were no short-ranged correlation between the directions of the molecular dipole moments—there would be no tendency for the molecules to tilt over. The terms in the free energy driving the tilt must be proportional in some sense to the amount of short-ranged correlation between the dipoles. Since this force becomes stronger at lower temperature, we conclude that the short-ranged correlation between the dipoles becomes stronger as one approaches the phase transition.

¹W. L. McMillan, Phys. Rev. (to be published).

²W. L. McMillan, Phys. Rev. A **6**, 936 (1972).

³P. G. deGennes, Solid State Commun. **10**, 753 (1972).

⁴A. DeVries, Acta Crystallogr. A **25**, S135 (1969).

⁵H. Arnold, Z. Phys. Chem. (Leipz.) **226**, 146 (1964).

⁶H. Gruler (unpublished).

⁷P. G. deGennes (unpublished).

⁸W. L. McMillan (unpublished).