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# Measurement of Smectic-$A$-Phase Order-Parameter Fluctuations in the Nematic Phase of $p$-$n$-Octyloxybenzylidene-$p'$-Toluidine

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A measurement is presented of the anisotropic liquid-structure factor of $p$-$n$-octyloxybenzylidene-$p'$-toluidine in the nematic phase using monochromatic Cu $K\alpha$ radiation. This material has a smectic $A$ phase at lower temperature and exhibits strong pretransition scattering in the nematic phase. The experimental results are used to test the Landau theory of the smectic $A$ phase recently proposed by McMillan and by de Gennes. The experimental peak in the structure factor is approximately Lorentzian in two dimensions and a Lorentzian fit determines the Landau-theory parameters versus temperature. The small deviations from a Lorentzian may be due to higher-order terms in the Landau theory or to thermal fluctuations of the nematic director.

## I. INTRODUCTION

In the nematic phase of liquid crystals the long molecules are aligned preferentially parallel to an axis in space and this phase is described by an orientational order parameter. The smectic $A$ phase is more highly ordered with the molecular centers of mass sitting on parallel equidistant planes (~ 30-Å interplanar distance). The smectic $A$ phase is described by a translational order parameter (the amplitude of a one-dimensional density wave) in addition to the orientational order parameter. A microscopic theory was put forward by the author[1] and by Kobayashi[2] which predicts the temperature dependence of the order parameters and the thermodynamic quantities. The author[3] measured the temperature dependence of the translational order parameter directly in the smectic $A$ phase by measuring the Bragg-scattering intensity from the smectic planes. In this experiment, pretransition scattering was observed in the nematic phase at angles near the smectic-phase Bragg angle and a Landau theory was proposed to describe this effect. de Gennes[4] has independently proposed the same Landau theory. Doane *et al.*[5] have measured the orientational order parameter in the nematic and smectic $A$ phases using NMR.

The purpose of the present experiment is to measure the anisotropic liquid-structure factor with good resolution on an oriented nematic to provide a test of the correctness of the Landau theory and to determine the Landau-theory parameters. The x-ray diffractometer used here is described in Sec. II and the sample preparation in Sec. III. The experimental results are displayed in Sec. IV and in Sec. V the necessary theoretical background is

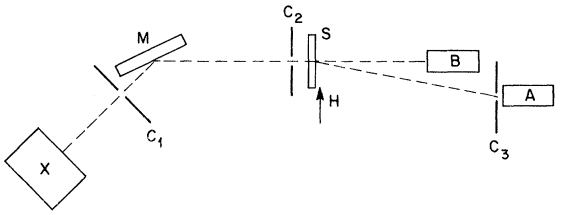



FIG. 1. Sketch of the x-ray apparatus which is described in the text.

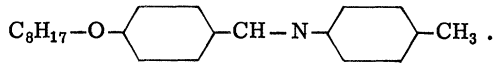
presented. In Sec. VI the Landau theory is fit to the experiment.

## II. APPARATUS

The x-ray diffractometer is pictured in Fig. 1 and consists of a GE C7H copper tube ($X$) powered by a GE XRD-5 regulated power supply. The x-ray beam is limited by a collimator ($C_1$) and falls on a LiF crystal monochromator ($M$). The monochromatic beam (Cu $K\alpha$) passes through a second collimator ($C_2$), through the sample ($S$) in a hot stage and is counted in a scintillation counter ($B$). The space between the sample and the beam counter is filled with helium gas to reduce the background. The scattered radiation which passes through a third collimator ($C_3$) is counted in another scintillation counter ($A$). The photon signals are counted in a frequency counter operated in the ratio mode so that one gets directly the scattered intensity/beam intensity. The hot stage is a two-stage affair which is similar to that described previously[3] except that platinum resistance thermometers are used as temperature sensors instead of thermistors. The temperature regulation is $\pm 0.03\,^{\circ}$C for a period of several hours. The temperature is measured with a third platinum resistance thermometer in contact with the sample holder which utilizes a separate resistance bridge. The sample sits in a 4-mm-diam hole drilled into a 1.6-mm-thick copper block with $\frac{1}{2}$-mil Mylar windows on both sides. The hot stage sits in the 1-in. gap of a 6-in. Varian magnet with a field of 10 G. The magnetic field ($H$) is used to orient the sample in the nematic phase. Scintillation counter $A$ is mounted on a two-dimensional translator mounted perpendicular to the beam. Motion in the field direction is controlled by a micrometer screw and is automated to step and count. Motion perpendicular to the beam and field directions is manual. The collimators $C_2$ and $C_3$ are 1 mm$\times$3 mm, and the sample ($S$)-to-collimator distance $C_3$ is 48.4 cm.

## III. MATERIAL

In order to perform this experiment it is necessary to have a material which exhibits nematic and smectic $A$ phases, is sufficiently pure that the liquid-crystal phase transitions are sharp, and is sufficiently stable at the operating temperature that one can perform the experiment without sample deterioration. Since the counting rates are low and the measured intensities vary rapidly with temperature (20% in $0.5\,^{\circ}$C near the phase transition), the stability requirement is severe. It is necessary that the smectic $A$-nematic transition temperature drop less than $0.1\,^{\circ}$C in 8 h at $70\,^{\circ}$C. The material used in this experiment satisfies these requirements: it is a Schiff's base, $p$-$n$ octyloxybenzylidene-$p'$-toluidine (OBT)




The transition temperatures were measured in a polarizing microscope equipped with a Mettler FP5 hot stage and are listed in Table I; the phases were initially identified by their texture. The heats of transition were measured with a Perkin–Elmer DSC-1B differential scanning calorimeter and are also given in Table I.

The material was synthesized from $p$-octyloxybenzaldehyde (Eastman #10755) and $p$-toluidine (Aldrich #T3720-6). Typically, 4 ml of the aldehyde and 1.9 g of toluidine were combined with 10-ml ethanol and heated under reflux for 2 h. The mixture was cooled to precipitate the product and then filtered. The filtrate was then recrystallized twice from ethanol and once from an $n$-hexane/benzene (30-ml/5-ml) mixture. The last recrystallization yielded transparent platelet crystals several millimeters wide. The sample was stored in a vacuum desiccator until use. It was melted into the sample holder and dryed and outgassed by melting and freezing several times in vacuum. This material is very sensitive to water and must be kept dry. The Mylar windows on the sample holder apparently provide adequate protection for the sample during the experiment.

## IV. LANDAU THEORY

The Landau theory has been discussed previously by the author[3] and by de Gennes[4] and will be reviewed briefly here. The smectic $A$ order parameter is a complex scaler $\psi(x)$ and one includes the nematic director $\vec{n}(x)$. The particle density is then

TABLE I. Thermal properties of OBT [$R_0 = 1.986$ cal/(deg mole)].

| Phases | Transition temperature (°C) | Transition entropy |
|---|---|---|
| Crystal-smectic $A$ | 69.8 | $(12.0 \pm 1)R_0$ |
| Smectic $A$-nematic | 70.1 | $(0.80 \pm 0.08)R_0$ |
| Nematic-isotropic | 77.6 | $(0.40 \pm 0.06)R_0$ |

$$\rho(x)=\rho_0[1+\mathrm{Re}(\psi(x))]\,. \tag{1}$$

The free-energy density to second order in $\psi$ is written

$$F=\tfrac{1}{2}\rho_0 kT\,[+(\alpha_{\parallel}/q_0^2)\,|(\vec{n}\cdot\vec{\nabla}-iq_0)\psi|^2 + (\alpha_{\perp}/q_0^2)\,|\vec{n}\times\vec{\nabla}\psi|^2+\beta(T)\psi^2]+\tfrac{1}{2}K|\vec{\nabla}\vec{n}|^2\,, \tag{2}$$

where $q_0=2\pi/d$ and $d$ is the interplanar spacing in the smectic $A$ phase. The nematic elastic energy is included in the isotropic approximation where K is the elastic constant. Here we assume that the nematic is aligned in the $z$ direction by a magnetic field and we neglect the thermal fluctuations of the director. Then writing

$$\psi(x)=\sum_q \psi_q e^{i\vec{q}\cdot\vec{x}}\,, \tag{3}$$

we find the free energy of a density wave of wavelength $2\pi/q$ and amplitude $\psi_q$

$$F(q,\psi_q,T)=\tfrac{1}{2}NkTA_q\psi_q^2\,, \tag{4}$$

where

$$A_q=\beta(T)+\alpha_{\parallel}(|q_{\parallel}|-q_0)^2/q_0^2+\alpha_{\perp}q_{\perp}^2/q_0^2\,. \tag{5}$$

Here $q_{\parallel}(q_{\perp})$ is the wave number parallel (perpendicular) to the external field direction. The quantity $\beta(T)$ is usually assumed to be linear in $T$ (it can be calculated from the microscopic theory),

$$\beta=\beta_0(T-T^*)\,, \tag{6}$$

where $T^*$ is a critical temperature which is lower than the smectic-nematic transition temperature if the transition is first order.

The x-ray scattered intensity is proportional to[3]

$$I_q=f_q^2 S_q\,, \tag{7}$$

where $f_q^2$ is the molecular-structure factor and $S_q$ is the liquid-structure factor. Neglecting excluded volume effects the liquid-structure factor is

$$S_q=1+1/A_q\,, \tag{8}$$

where the first term is the contribution for an uncorrelated gas and the second term gives the scattering from the order-parameter fluctuations. The free-energy function $A_q$ is a minimum for $q=2\pi/d$ and in the field direction and scattered intensity is a maximum there; this is just the angle where the Bragg scattering occurs in the smectic $A$ phase. The shape of the scattered intensity is predicted to be Lorentzian with the peak intensity increasing as one approaches the phase transition to the smectic $A$ phase.

## V. EXPERIMENTAL RESULTS

In this section we present the experimental data for the anisotropic liquid-structure factor of OBT in the nematic phase. The Landau theory predicts a Lorentzian peak centered on the position of the smectic-$A$ Bragg peak. In Fig. 2 we show a contour map of the measured liquid-structure factor in the $q_{\parallel}$, $q_{\perp}$ plane. This is also the scattered intensity pattern in the plane of counter A; the x-ray beam is normal to the paper and passes through the origin. From the geometry of the scattering problem

$$q_{\parallel}=(4\pi/\lambda)\sin\theta\cos\varphi\,,\qquad q_{\perp}=(4\pi/\lambda)\sin\theta\sin\varphi\,, \tag{9}$$

where $2\theta$ is the scattering angle [$\tan(2\theta)$ = counter-to-beam distance in the measuring plane/sample to measuring plane distance] and $\varphi$ is the azimuthal angle from the counter-to-field direction. Here $\lambda$ is the wavelength of the Cu $K\alpha$ radiation and equals 1.539 Å. The data were taken along lines in the measuring plane at four fixed temperatures and the peak intensity was measured as a function of temperature. Measured intensities along the longitudinal section $bb'$ are shown in Fig. 3 for four temperatures. Measured intensities along the transverse section $aa'$ are shown in Fig. 4 for the same four temperatures. Measured intensities for the three sections $bb'$, $cc'$, and $dd'$ at the lowest temperature are shown in Fig. 5. The solid lines in these

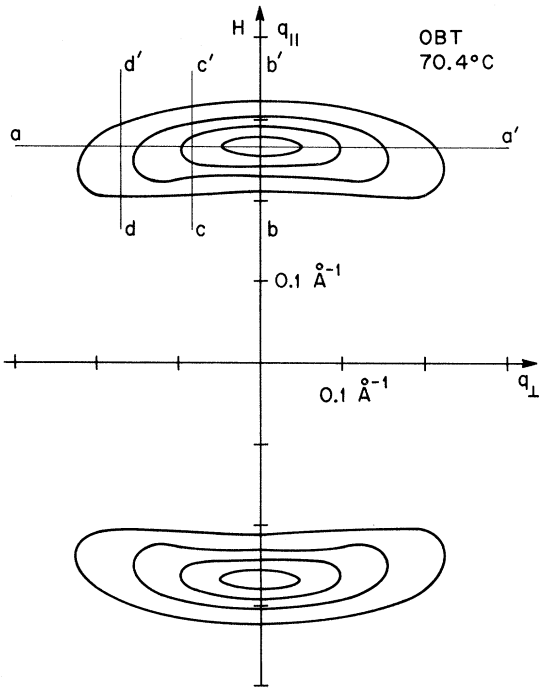



FIG. 2. Contour map of the measured anisotropic liquid-structure factor in the $q_{\parallel}$, $q_{\perp}$ plane at 70.4 °C for OBT. The peak intensity is 3000 and the contours are drawn for intensities of 2000, 1000, 500, and 250. The map is drawn to scale.

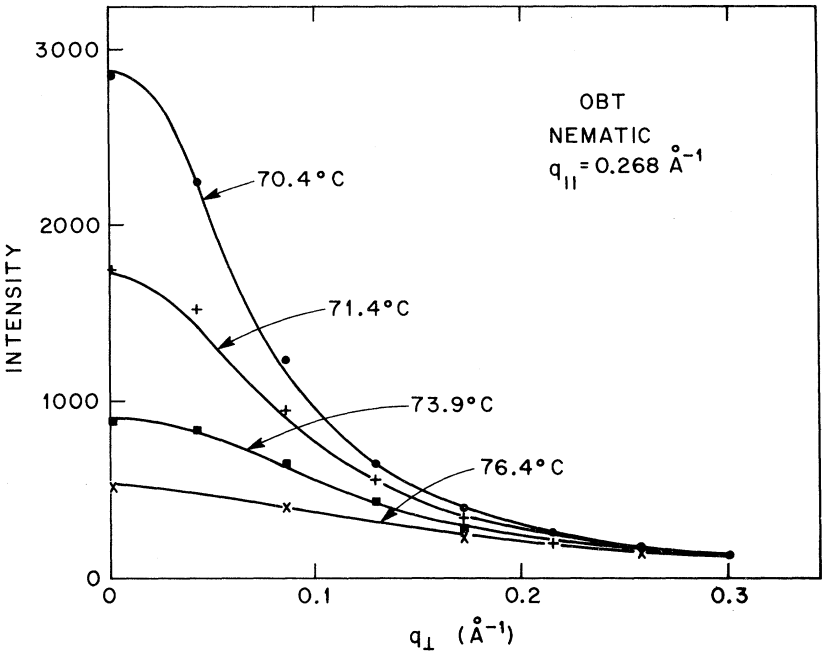



FIG. 3. Scattered intensity vs $q_{\parallel}$ along section $bb'$ for OBT in the nematic phase. The data points are 70.4 °C (filled circles); 71.4 °C (crosses); 73.9 °C (filled squares); 76.4 °C (×'s). The lines are the fit to the theory described in the text.

figures are the Lorentzian fit described in Sec. VI. Finally, the peak intensity versus temperature is shown in Fig. 6. The counting time is about 4/min and the vertical scale in these figures is counts per unit counting time. The plotted points are based on two or three counts which provide ~6000 counts in the peak at low temperature and correspondingly few counts in the wings of the curves. The overall reliability of the data appears to be about ±3% although it is poorer in the wings because of poor counting statistics. The background is about 20 counts and has been subtracted. These results are independent of magnetic field strength; the peak intensity at the lowest temperature changes less than 3% on going from 1 to 10 kG. The resolution of the apparatus is good; the half-width at half-height of the beam profile is 0.008 Å$^{-1}$ (0.022 Å$^{-1}$) in the longitudinal (transverse) direction. The interplanar

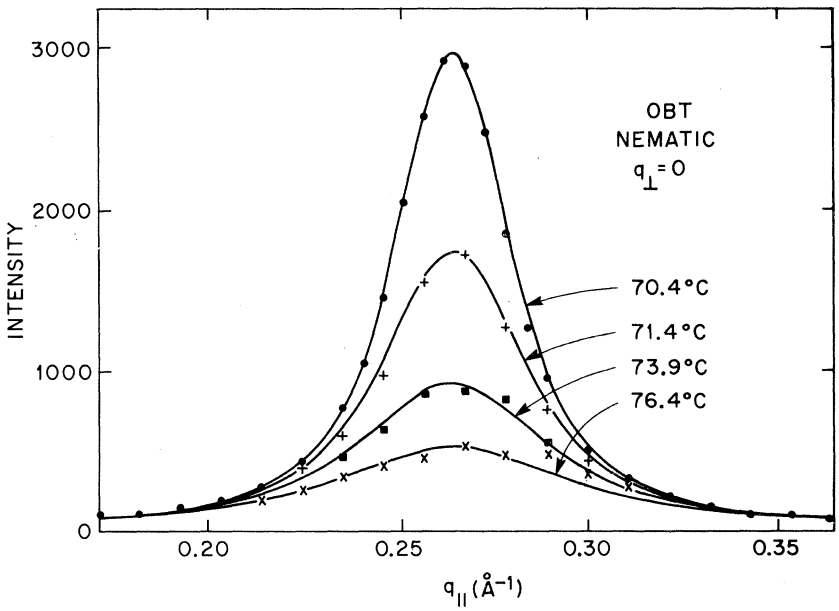



FIG. 4. Scattered intensity vs $q_{\perp}$ along section $aa'$ for OBT in the nematic phase. The labeling follows Fig. 3.

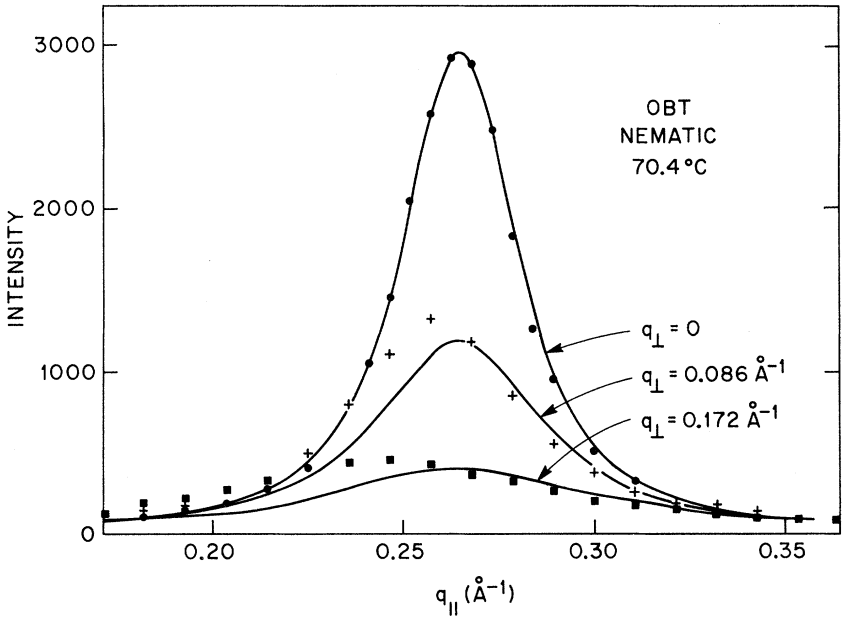



FIG. 5. Scattered intensity vs $q_\parallel$ for OBT in the nematic phase at 70.4 °C. The filled circles are along section $bb'$ ($q_\perp = 0$); the crosses are along section $cc'$ ($q_\perp = 0.086$ Å$^{-1}$); and the filled squares are along section $dd'$ ($q_\perp = 0.172$ Å$^{-1}$). The solid lines are calculated from Eq. (10) using parameters fitted to the data of Figs. 3 and 4.

spacing in the smectic $A$ phase in 24.1 Å and the length of a space-filling model of the molecule in the all transconfiguration is 23.9 Å. The peak in the pretransition scattering occurs at an equivalent $d$ spacing of $2\pi/q_0 = 23.8$ Å.

## VI. DATA ANALYSIS

The Landau theory predicts that the scattered intensity in the measuring plane is a two-dimensional Lorentzian and we take the following expression to fit the data, [the random-gas term in (8) is too small to be observed, and we have neglected the variation of the molecular-structure factor over this region of $q$ space]:

$$I(q_\parallel, q_\perp, T) = \frac{C}{B(T) + (A_\parallel/q_0^2)(q_\parallel - q_0)^2 + A_\perp q_\perp^2/q_0^2} \quad . \tag{10}$$

This expression is then numerically smeared by the beam profile to correct for the finite resolution of the apparatus. The peak height at the lowest temperature is reduced 20% by finite resolution. We first choose $B(70.3\,°\text{C})$, $A_\parallel$ and $q_0$ in order to fit the data along section $bb'$ at 70.3 °C (the constant $C$ is arbitrary). The higher-temperature $B$'s were then chosen to fit the other three curves of Fig. 3. We then chose $A_\perp$ to fit the data of Fig. 4. The data of both these figures are fitted quite closely by Eq. (10). With the parameters fixed

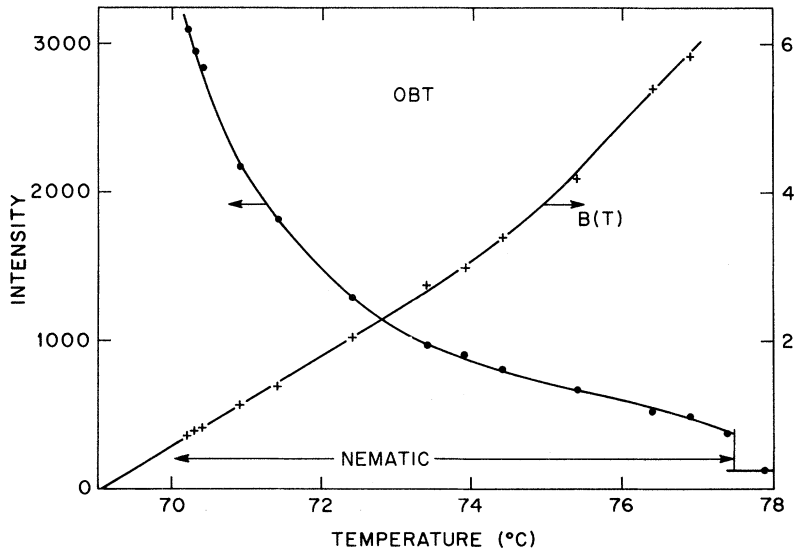



FIG. 6. Peak intensity (filled circles) and the parameter $B(T)$ (crosses) vs temperature for OBT in the nematic phase. $B(T)$ extrapolates linearly to zero at 69.1 °C. The lines are drawn as a guide to the eye.

TABLE II. Parameters determined by fitting the experimental data using Eq. (10).

| $T$(°C) | $B(T)$ | $\xi_{\parallel}(T)$ (Å) | $\xi_{\perp}(T)$ (Å) | $C$ | $A_{\parallel}$ | $A_{\perp}$ | $q_0$ (Å)$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 70.4 | 0.80 | 72.0 | 16.9 | 3000.0 | 288.0 | 15.9 | 0.264 |
| 71.4 | 1.48 | 53.0 | 12.4 | | | | |
| 73.9 | 3.0 | 37.0 | 8.7 | | | | |
| 76.4 | 5.5 | 27.0 | 6.4 | | | | |

we then plotted Eq. (10) for the sections $bb'$, $cc'$, and $dd'$ at 70.3 °C (Fig. 5). The deviations here are not large but they are well outside experimental error. For larger values of $q_{\perp}$ the peak occurs at smaller $q_{\parallel}$. This is responsible for the contours in Fig. 2 being sausage shaped rather than concentric ellipses as predicted by (10). There are at least two possible explanations for these deviations. The first is that we have expanded the free energy in a power series about $q_0$ and since the deviations occur far from $q_0$, we could include higher-order terms in the expansion. By adding to the denominator of (10) the term

$$D(q_{\parallel} - q_0)q_{\perp}^2/q_0^3 , \tag{11}$$

with $D = 46$ we find a reasonable fit for the data. The second explanation, which is important in any case, is that thermal fluctuations of the director lead to a smearing of the peak in the $\varphi$ direction and therefore to a broadening of the peak in the transverse direction and to the sausage shape. One can calculate this effect quantitatively from the Landau theory once the nematic elastic constants have been measured. One will find a larger value for $A_{\perp}$ once these corrections have been made. From the peak intensity versus temperature we can find $B(T)$ and this function is plotted in Fig. 6. It is linear near the nematic-smectic $A$ transition and extrapolates to zero at a critical temperature $T^*$ which is 1.0 °C below the transition temperature.

We do not have an absolute normalization of the data and we cannot determine absolute magnitudes for the Landau-theory parameters $\beta(T)$, $\alpha_{\parallel}$, $\alpha_{\perp}$. However the coherence lengths are accurately determined and are given in Table II along with the fitting parameters:

$$\begin{aligned} q_0\xi_{\parallel}(T) &\equiv [\alpha_{\parallel}/\beta(T)]^{1/2} = [A_{\parallel}/B(T)]^{1/2} , \\ q_0\xi_{\perp}(T) &\equiv [\alpha_{\perp}/\beta(T)]^{1/2} = [A_{\perp}/B(T)]^{1/2} . \end{aligned} \tag{12}$$

The ratio of coherence lengths is constant $\xi_{\parallel}/\xi_{\perp} = 4.2$ which is approximately the length-to-width ratio for the molecule. At 70.3 °C the longitudinal coherence length is 72 Å which is three molecular lengths. The transverse coherence length is 16.9 Å which is approximately three molecular widths.

## VII. CONCLUSIONS

We have measured the anisotropic liquid-structure factor in the nematic phase of octyloxybenzylidene toluidine. This measurement enables one to map out the $q$ dependence of the free energy of the density-wave order parameter. The measurements have been fitted by the Landau-theory expression and confirm both the temperature and momentum dependence of the Landau free energy. Observed deviations may be owing to thermal fluctuations of the director, which can be included in the theory, or to higher-order terms in the theory. The smectic-$A$-nematic phase transition in this material is first order; it would be particularly interesting to have similar measurements on a material in which this transition is second order. A measurement of the elastic constants of OBT is necessary in order to correct the data for thermal fluctuations of the director.

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