# Static and dynamic behavior near a second-order smectic $A$ – nematic phase transition by light scattering*

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Measurements are presented of the intensity and lifetime of Rayleigh light scattered from thermally excited twist and splay modes of *p*-cyanobenzylidine-*p*-*n*-octyloxyaniline (CBOOA) in the nematic phase near the smectic $A$–nematic phase transition. The temperature dependence of the twist and splay elastic constants and viscosities are deduced. The phase transition is continuous ($T_c - T^* < 3\,^\circ$mK); this contradicts the prediction of Halperin, Lubensky, and Ma that this phase transition would be weakly first order. The critical behavior of the twist elastic constant $K_{22}$ and the twist viscosity $\gamma_1$ is consistent with mean-field predictions from 3 °mK to 7 °K above the transition; these data are inconsistent with the critical behavior predicted by the helium analogy. The splay mode is not renormalized, as expected.

## I. INTRODUCTION

We present a measurement of the intensity and relaxation time of Rayleigh light scattered from thermally excited twist and splay modes of *p*-cyanobenzylidine-*p*-*n*-octyloxyaniline (CBOOA) in the nematic phase near the smectic $A$–nematic phase transition. From these measurements we can deduce the temperature dependence of the twist and splay elastic constants and viscosity coefficients.

One motivation for this experiment is to test the various theories of the critical behavior of the second-order or nearly second-order smectic $A$–nematic phase transition. The microscopic theory[1] first indicated that this phase transition could be second order although only first-order materials were known at the time. Several candidates for the second-order transition were found[2] and have been studied intensively. de Gennes and McMillan[3] proposed Landau theories to describe the phase transition. The smectic order parameter is a complex scalar which couples to the nematic director in the same way that the superconducting order parameter couples to the vector potential in the Ginzberg-Landau theory.[4] de Gennes recognized that if the smectic order parameter exhibited critical fluctuations as expected, there should be a close analogy to liquid He which also has a complex order parameter. He proposed that the correlation length vary as

$$\xi(T)=\xi_0(T/T_c-1)^{-\nu}, \tag{1}$$

with $\nu=\frac{2}{3}$ in the critical region. McMillan's version of the Landau theory was worked out within mean-field theory ($\nu=\frac{1}{2}$). de Gennes calculated the contribution of smectic order-parameter fluctuations to the elastic constants and found that the bend and twist elastic constants were renormalized:

$$K_{22}=K_{22}^0+\text{const}\times\xi(T)\quad\text{(twist)}, \tag{2}$$

$$K_{33}=K_{33}^0+\text{const}\times\xi(T)\quad\text{(bend)}, \tag{3}$$

while the splay elastic constant is not renormalized.

$$K_{11}=K_{11}^0\quad\text{(splay)}. \tag{4}$$

The bend and splay elastic constants of CBOOA were measured from the Freedericks transition by Cheung, Meyer, and Gruler[5] and found to agree with Eq. (3) with $\nu=\frac{2}{3}$. Cladis,[6] however, finds $\nu=\frac{1}{2}$ for the bend mode of CBOOA using the same method. Durand and coworkers[7] have used light scattering to measure the enhancement of $K_{22}$ for CBOOA and find $\nu=\frac{2}{3}$. The Rayleigh scattering intensity is given by

$$I_t\propto(\Delta n)^2/K_{22}\quad\text{(twist)}, \tag{5}$$

$$I_s\propto(\Delta n)^2/K_{11}\quad\text{(splay)}, \tag{6}$$

where $\Delta n$ is the anisotropy of the index of refraction.

Using an extended dynamical scaling argument and the helium analogy, Brochard[8] proposed a similar renormalization of $\gamma_1$, the rotational viscosity in the Leslie-Erickson hydrodynamics.[9] Brochard and Janig[10] found the same result in a more detailed calculation using essentially a mode-mode coupling approach with restricted dynamic scaling. Independently of this work Meiboom[11] observed a pretransition increase in $\gamma_1$ for a compound similar to CBOOA, and McMillan[12] proposed a dynamical Landau theory to explain Meiboom's observations. The theoretical result for $\gamma_1$ is

$$\gamma_1=\gamma_1+\text{const}\times\gamma_3\xi, \tag{7}$$

where $\gamma_3$ is a new viscosity which describes the

flow of molecules normal to the smectic planes. There is a similar renormalization of $\gamma_2$ and one of the fluid viscosities. Using dynamical scaling $\gamma_3 \sim \xi^{-1/2}$ so that

$$\gamma_1 = \gamma_1^0 + \text{const} \times (T/T_c - 1)^{-1/3}, \tag{8}$$

which is the result of Brochard and Janig. Within the mean-field approximation $\gamma_3 \sim$ const. so that

$$\gamma_1 = \gamma_1^0 + \text{const} \times (T/T_c - 1)^{-1/2}, \tag{9}$$

which is McMillan's result. The lifetime of the twist mode as measured in the Rayleigh scattering experiment is

$$\tau_t = \gamma_1 / K_{22} q^2, \tag{10}$$

where $q$ is the wave number of the mode. According to the helium analogy, this lifetime is asymptotically proportional to $(T/T_c - 1)^{1/3}$ near the phase transition so that the twist mode speeds up. According to mean-field theory the lifetime approaches a constant near the phase transition. Neither the elastic constant nor the viscosity of the splay mode is renormalized and we have

$$\tau_s = \gamma_s / K_{11} q^2 \approx \text{const}. \tag{11}$$

$\gamma_1$ has been measured by Ho and coworkers[14] for CBOOA who find an exponent of $0.37 \pm 0.07$ from a dynamical Freedericks transition experiment. A simple physical model of these pretransition effects was given in Ref. 13.

Recently Halperin, Lubensky, and Ma[15] (HLM) have predicted that the smectic $A$–nematic phase transition will be weakly first order. The physical argument is as follows. A bend or twist distortion lowers the transition temperature; it follows that thermal fluctuations of the bend and twist modes in the nematic phase lower the effective transition temperature. These modes also carry considerable entropy. In the smectic $A$ phase the bend and twist modes are frozen out and the transition temperature is not renormalized. The entropy of the fluctuation modes forces the transition to the nematic phase below the unrenormalized transition temperature and the phase transition is first order. Torza and Cladis[16] have measured the liquid density of CBOOA through the phase transition and concluded that the transition is weakly first order. Djurek *et al.*[17] have reported observing a small heat of transition for CBOOA. The present experiment is ideal for studying this effect because one observes thermal fluctuations of the modes which drive the first-order transition.

In the present experiment we measure the Rayleigh intensity and lifetime of the twist and splay modes of CBOOA from 2 °mK to 20 °K above the smectic $A$–nematic transition. (Durand and coworkers[18] at Orsay are performing a very similar experiment and reported lifetime measurements on the twist mode at the Stockholm meeting.) We find that the splay mode exhibits no pretransition anomaly as expected. From the twist-mode data we find a pretransition increase of a factor of 6 for $K_{22}$ and a factor of 15 for $\gamma_1$. A quantitative analysis of the data shows that it is consistent with the mean-field model but not consistent with the helium analog. In fact from 3 °mK to 7 °K above the transition we find no significant deviations from the mean-field predictions. We do not find any hint of a first-order phase transition. The rounding of the phase transition is 2 °mK and we can place an experimental upper limit of 3 °mK on $T_c - T^*$ where $T_c$ is the first-order transition temperature and $T^*$ is the extrapolated critical temperature. This result is inconsistent with the theory of Halperin *et al.*[15]

The plan of the paper is as follows: We have already discussed the theories of this phase transition. In Sec. II we discuss the "hot stage" and the light-scattering apparatus. In Sec. III we present the experimental data, and we perform the data analysis in Sec. IV. In Sec. V we discuss theoretical estimates of the magnitude of the pretransition effects and in Sec. VI we discuss our results.

## II. APPARATUS

### A. Hot stage

The outer hot stage is a massive brass box with the temperature regulated electronically to ±0.1 °K. The inner hot stage is a massive brass block insulated by $\frac{1}{2}$ in. teflon from the outer stage. The temperature of the inner stage is measured with a $L+N$ calibrated platinum resistance thermometer, calibrated to ±3 °mK and traceable to the NBS standard. The resistance is measured in an Anderson four-terminal bridge[19] using a Guerst ratio standard ratio transformer. A PAR HR-8 lock-in amplifier with a type-C preamplifier impedance matched to the bridge with a Triad G-10 transformer is used to detect bridge off-balance. Both proportional and integral feedback are used to provide the voltage for the heater. The noise on the temperature measurement is ±0.1 °mK with a 1-sec time constant and this is the apparent stability of the inner stage. Repeated measurements of intensities at the phase transition indicate that the actual stability is 0.1 or 0.2 °mK over times of $\frac{1}{2}$ h. The platinum resistance and ratio transformer bridge should provide good long-term stability. The thermometer was not recalibrated *in situ* and our temperature scale is probably within 10 °mK of absolute; this is unimportant in the present experiment. Glass windows permit entry and exit of the light. The sample cell is placed inside the inner hot stage in good thermal contact with it.

### B. Light-scattering apparatus

The optical experiment is performed with a conventional self-beating Rayleigh scattering apparatus with polarizer and analyzer and using pinhole optics as shown in Fig. 1. A Spectra-Physics 120 HeNe laser ($TEM_{00}$, multiple longitudinal modes) provides a stable source of 6238 Å light. The light beam is attenuated, polarized and passes through a 300 $\mu$m pinhole near the sample. After scattering from the liquid crystal the light passes through a second pinhole 700 $\mu$m in diameter, 1.2 m from the sample, is analyzed and detected by an ITT FW-130 photomultiplier in cooled housing. An SSR photon counting preamplifier discriminator is used to detect the photons. The laser beam is attenuated to 20 $\mu$W to reduce the heating of the sample to <1 °mK. This heating effect is readily measured by observing the apparent transition temperature vs laser power. The laser power passing through the liquid crystal is monitored with a Hewlett-Packard radiance meter and is constant within 1% after warmup. The pinhole optics were used in order to have a well-defined geometry; the detection area is much less than one coherence area. The incident light beam is normal to the glass surface (parallel to the director); the scattered light is detected 5.9° from the normal.

The full autocorrelation function was found by digital processing, using a Texas Instruments 960A minicomputer on-line. Pulses from the preamplifier were fed into a pulse accumulator in the computer and the number of photons $n(t_i)$ in a time interval $\Delta_t$ was recorded for 1000 consecutive periods. The full self-correlation function was then computed

$$C(t_i) = \sum_j n(t_j) n(t_i + t_j), \tag{12}$$

and this measurement was repeated and averaged 100 times. Typical parameters are a counting rate of $10^4$ photons/sec and $\Delta t = 10^{-3}$ sec so that shot noise was unimportant. However, one is measuring a random variable and it is necessary to time average for ~$10^4$ relaxation times to have a 1% accuracy in the correlation function. The correlation function is then normalized

$$\bar{C}(t_i) = \sum_{j=1}^{N} \frac{n(t_j) n(t_i + t_j)}{N \bar{n}^2} . \tag{13}$$

### C. Sample preparation

The sample of CBOOA used in the present experiment was obtained from Eastman (#11963). It was recrystallized once from a benzene-hexane mixture and dried by repeated melting in vacuum. The transition temperatures were: melting (73.2 °C); smectic $A$–nematic (82.995 °C); and nematic-isotropic (107.4 °C). We attempted to obtain higher purity materials by Shiff's base synthesis using recrystallized starting materials. However, we found transition temperatures comparable to those of the Eastman material and decided to use the Eastman material because it is commonly used. We have no adequate assay of impurity content at present. We do not believe that the smectic $A$–nematic transition temperature ($T_{SN}$) is an adequate indicator of sample purity since we have observed $T_{SN}$ to increase with aging. The last sample reported here was filtered through a 0.2-$\mu$m millipore filter to remove dust.

The samples were contained between microscope slides coated with Dow-Corning XZ-2-2300 to obtain homeotropic alignment. A $2\times10^{-3}$-in. Mylar film was used as a spacer to obtain a 50-$\mu$m thick sample; a 2–5 mm diameter hole in the Mylar film contained the liquid crystal. The edges of the microscope slides were sealed with vapor-free epoxy. This construction served to eliminate flow of the liquid crystal by containing it in a small volume; the small volume permitted equilibration of the distribution of impurities by diffusion so that the transition temperature would be uniform even though the samples may not be of high purity; finally the liquid crystal was isolated from the oxygen and water in the atmosphere so that chemical deterioration was minimized. After an initial equilibration time of a few days the transition-temperature drift was typically 5–10 °mK per day. The sharpness of the observed transition indicates that thermal gradients and transition-temperature gradients were less than 2 °mK over the 300-$\mu$m illuminated disk.

### D. Data reduction

Quantitative interpretation of the self-beating experiment is complicated by the cross over from homodyne to heterodyne detection. The theoretical expression for the correlation function (limit detection area ≪ coherence area) is

$$\bar{C}(t) = 2B(1-B)e^{-t/\tau} + B^2 e^{-2t/\tau} , \tag{14}$$

where $B = I_R/(I_R + I_{el})$; $I_R$ is the Rayleigh intensity,

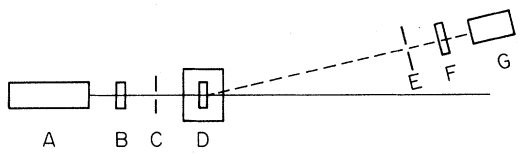


FIG. 1. Diagram of the light scattering apparatus: (a) HeNe laser; (b) polarizer; (c) 300 $\mu$m pinhole; (d) dample in hot stage; (e) 700 $\mu$m pinhole; (f) analyzer; (g) photomultiplier tube.

$\tau$ is the relaxation time and $I_{el}$ is intensity of elastically scattered light. The first term is the heterodyne term from beating of the Rayleigh light with the elastically scattered light. The second term is the homodyne term from beating of the Rayleigh light with itself.

In the experiment for the twist mode the laser beam is vertically polarized, the Rayleigh light is horizontally polarized, and the scattering vector lies in the horizontal plane. Most of the elastically-scattered light (from optical imperfections and dust) is vertically polarized and as we rotate the analyzer from horizontal to vertical we go from the homodyne to the heterodyne regime (as judged from the lifetime of the 1 exponential fit). The data are not consistent with (14) because we find a zero-time correlation function of about 0.75 rather than 1.0 in the homodyne limit. This effect could be caused by nonuniformities in the sample leading to a partial breakdown of the momentum conservation rule, or by any of a number of experimental problems. In order to analyze the data we use the following expression which we have verified experimentally:

$$\overline{C}(t) = C_0[2B(1-B)e^{-t/\tau} + B^2 e^{-2t/\tau}]. \qquad (15)$$

We measure the correlation function with horizontal analyzer (homodyne) and 45° analyzer (heterodyne) and can determine the three constants from two data sets. We can determine the lifetimes and intensities from the heterodyne measurement and correct for the known small amount of homodyne component. Or we can determine the intensity from the homodyne measurement and correct for the known small amount of heterodyne component. We have used both methods for the relative intensities and the results agree. The correction factors for the intensities and lifetimes are typically 10% or less. For the splay mode both laser beam and the Rayleigh light are horizontally polarized and we cannot reach the homodyne regime. We use $C_0 = 0.75$ to correct the splay data.

## III. EXPERIMENTAL RESULTS

We present data from two samples. The samples are annealed for several days in the nematic phase just above the phase transition. Twist-mode data are available for sample 1 from the phase transition to 0.45 °K above the transition. For sample 2 twist and splay mode data are available from the phase transition to 0.5 °K above and (in a separate run in a Mettler microscope hot stage) from 0.1 °K above to 20 °K above the phase transition. Two runs on sample 1 and one run on sample 2 reproduced each other within experimental error from the phase transition to 0.45 °K above the transition. Data from sample 1 was somewhat more stable and is used in the analysis. From 0.5 °K to 20 °K above the transition only the data from sample 2 are available. Since only relative intensities are measured it is necessary to match the intensity data for the two samples in the common range of temperature; the lifetimes are absolute and require no matching. The wave number is $q = 1.02 \times 10^4$ cm$^{-1}$.

The intensity of Rayleigh light scattered from the twist mode $I_t$ is shown over four decades of temperature $(T - T_c)$ in Fig. 2. The lower curve (a) shows the intensity from the transition region to 30 °mK above; curve (b) from the transition to 300 °mK above, curve (c) from the transition to 3 °K above, and curve (b) from the transition to 20 °K above. The vertical scale is the same for the four plots, and the temperature scale is expanded by a factor of 10 for successive curves. The solid line is the fit using mean-field theory and the dashed line is the fit using the helium-analog theory; the fitting is described in the next section. The intensity data are continuous and do not show a sharp drop (first-order transition). This is seen by plotting $I^2$ vs $T - T_c$ as in Fig. 3. One can also see that the second-order mean-field

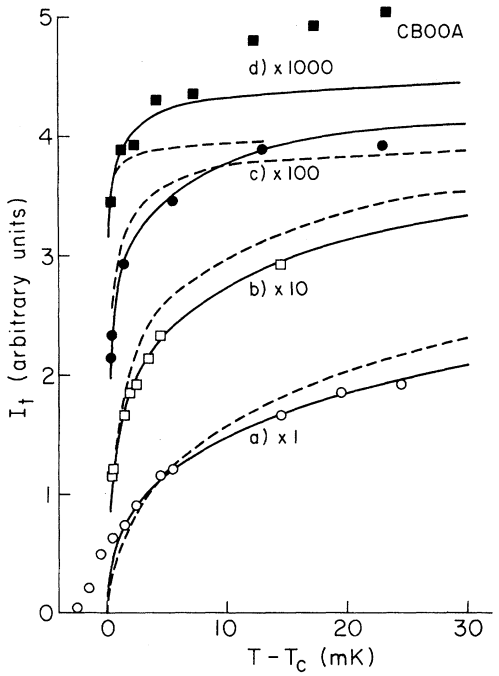


FIG. 2. Light-scattering intensity from the twist mode vs $T$-$T_c$: (a) open circles, 0–30 °mK; (b) open squares, 0–300 °mK; (c) filled circles, 0–3 °K; (d) filled squares, 0–30 °K. The solid line is a least-squares fit to the mean-field theory, and the dashed line is a least-squares fit to the helium-analog theory. Note expansion of the temperature scale by a factor of 10 for successive curves.

theory fits the data to within 1.5 °mK of $T_c$ and that the rounding of the phase transition is ≈2 °mK. This rounding could be due to thermal gradients, inhomogeneities of $T_c$, or to the fact that the correlation length gets long enough near $T_c$ that $q\xi$ is no longer small and one moves out of the hydrodynamic regime. If the phase transition were first order with $T_c - T^* < 3$ °mK, the first-order drop in the intensity might be obscured by the rounding of the transition. We can place an experimental upper limit of 3 °mK on $T_c - T^*$ ($T^*$ is the extrapolated critical temperature and $T_c$ is the actual first-order transition temperature).

The lifetime of the twist mode is plotted in Fig. 4 over decades of temperature with the upper curve being from the transition to 30 °mK above. The data show a moderately strong slowing down within 30 °mK of the transition. The data are in qualitative disagreement with the prediction of the helium analog that the twist mode should speed up near the phase transition. The lower curve from the transition to 20 °K above shows the slowing down at low temperature expected from the normal temperature dependence of a viscosity.

The intensity and lifetime of the splay mode from the transition to 20 °K above are shown in Fig. 5. These results are interesting for a number of reasons. The data from the intensities and lifetimes from 10 °mK above the transition to 2 °K above are constant within experimental error and show no hint of a pretransition effect. This is of course expected theoretically. At higher temperatures as one approaches the nematic-isotropic phase transition the splay-mode intensity increases. From the simple theory[20] one expects $K_{11}$ to be proportional to $S(T)$ ($S(T)$ is the Maier-Saupe[21] orientational order parameter) and $\Delta n$ to be proportional to $S(T)$ so that $I_s \propto \Delta n^2/K_{11}$ should be temperature independent; it is not. We can anticipate that $\Delta n^2/K_{22}^0$ may show a similar temperature dependence.

Both $\gamma_1$ and $\gamma_s$ are expected to show the usual temperature dependence of a liquid viscosity. This complicates the subtraction of the background term $\gamma_1^0$ in Eq. (9). We plot the ratio $\gamma_1/\gamma_s \propto I_t\tau_s/I_s\tau_t$ in Fig. 6. Since we measure only relative intensities the absolute magnitude of the ratio is unknown and the vertical scale is arbitrary. The ratio goes to a constant at high temperature and show the strong pretransition increase of $\gamma_1$ near the smectic $A$–nematic phase transition. The solid line is the fit to mean-field theory and the dashed line is the fit to the helium-analog theory.

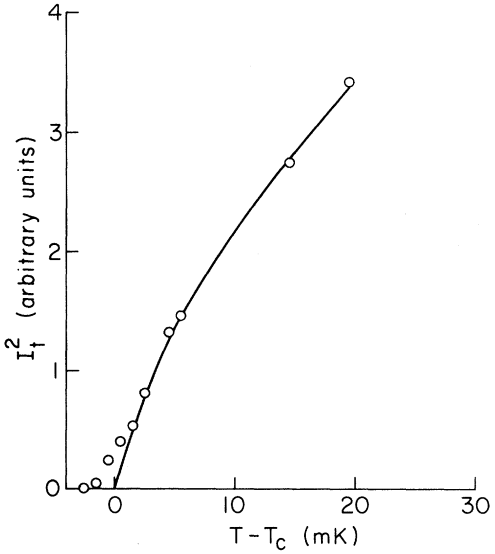


FIG. 3. Twist-mode intensity squared vs $T-T_c$ near the transition. The data show no first-order drop at the phase transition. The solid line is drawn as a guide to the eye.

## IV. QUANTITATIVE DATA ANALYSIS

In this section we perform a quantitative test of the theoretical expressions for $\gamma_1$ and $K_{22}$. We

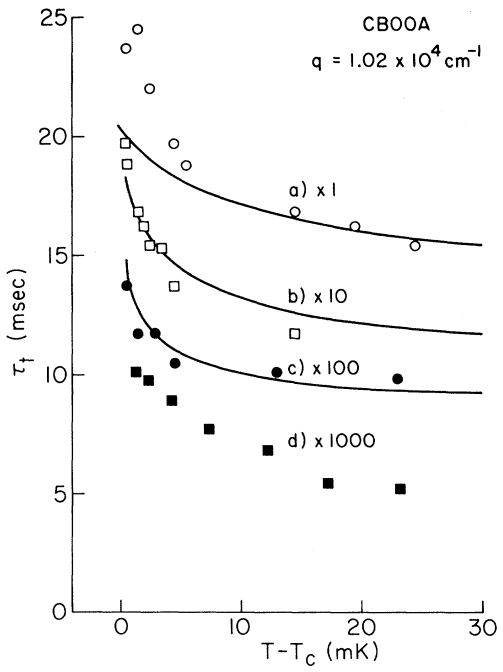


FIG. 4. Lifetime of the twist mode vs $T-T_c$ for $q=1.02 \times 10^4$ cm$^{-1}$; (a) open circles, 0–30 °mK; (b) open circles, 0–300 °mK; (c) filled circles, 0–3 °K; (d) filled squares, 0–30 °K. The solid line is taken from the fit of $K_{22}$ and $\gamma_1$ to the mean-field theory and is plotted from 0 to 3 °K where the temperature dependence of $\gamma_1^0$ is unimportant. The temperature scale is expanded as in Fig. 2.

find, somewhat to our surprise, that the data for both $\gamma_1$ and $K_{22}$ are entirely consistent with the mean-field theory and are clearly inconsistent with the helium analog.

We begin with a fit of the twist-mode intensity data from Fig. 2. For the intensity at temperature $T$ we use the expression

$$I^{-1} = I_0^{-1}\{1 + [\Delta T_2/(T - T_c)]^{\alpha_2}\}, \tag{16}$$

and the mean-square error

$$\sigma \equiv \frac{1}{N}\sum_{i-1}^{N} (I_i^{-1} - I_0^{-1}\{1 + [\Delta T_2/(T_i - T_c)]^{\alpha_2}\})^2/I_i^{-2}, \tag{17}$$

with equal weighting for all data points. Minimizing $\sigma$ with respect to three parameters ($I_0^{-1}$, $\Delta T_2$, $T_c$) produces the usual nonlinear least-squares fit. We first fix $\alpha_2 = 0.5$ or 0.67 and do a three-parameter fit. Since we expect a temperature-dependent background at high temperature which is omitted from (16), we remove points from the high-temperature end of the data until $\sigma$ does not decrease further. Since we expect rounding of the phase transition near $T_c$ we remove points from the low-temperature end of the data until $\sigma$ does not decrease further. When this is done we find for $\alpha_2 = 0.5$, $\sigma = 2.6\times10^{-4}$, $\Delta T_2 = 45$ °mK, 1.6 °mK $< T - T_c < 7.3$ °K; the rms statistical error in the data is 1.5%. This fitted curve is the solid line in Fig. 2 and it fits the data well. For $\alpha_2 = 0.67$ and the same temperature range we find $\sigma = 1.6\times10^{-3}$, a factor of 6 larger, and therefore a poor fit. The value of $\alpha_2$ which minimizes $\sigma$ is 0.47; $\sigma$ is twice as large for $\alpha_2 = 0.40$ and 0.54 ($\chi^2$ test) and we feel justified in claiming $\alpha_2 = 0.47 \pm 0.07$. The exponent is stable if we delete more of the high-temperature data; fitting the data from 1.6 °mK to 450 °mK we find $\alpha_2 = 0.48 \pm 0.08$. Thus we believe that the temperature-dependent background, which clearly present well above the phase transition, does not bias the exponent.

We analyze the $\gamma_1/\gamma_s$ data in a similar way. We write

$$\gamma_1/\gamma_s = R\{1 + [\Delta T_1/(T - T_c)]^{\alpha_1}\}. \tag{18}$$

A three-parameter fit with $\alpha_1 = 0.5$ from 1.6 °mK to 17.3 °K yields a mean-square error of $1.6\times10^{-3}$ and $\Delta T_1 = 330$ °mK; with $\alpha_1 = 0.33$ we find $\sigma = 1.2 \times10^{-2}$ a factor of 7 greater. From a four-parameter fit and a $\chi^2$ test (just as above) we find $\alpha_1 = 0.52 \pm 0.08$. Restricting the temperature interval to 1.6 °mK to 450 °mK we find $\alpha_1 = 0.51 \pm 0.09$.

Fitting the two data sets for $I_t$ and $\gamma_1/\gamma_s$ independently give a transition termperature for each data set and the transition temperatures are not equal. For the fit to mean-field theory the transition temperature for the $\gamma_1/\gamma_s$ data is 0.7 °mK higher than the transition temperature for the $K_{22}$ data. For the fit to the helium-analog theory the

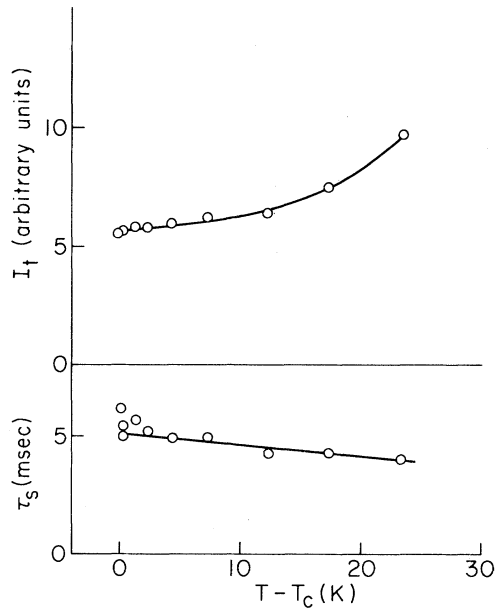


FIG. 5. Light-scattering intensity and lifetime of the splay mode vs $T$-$T_c$.

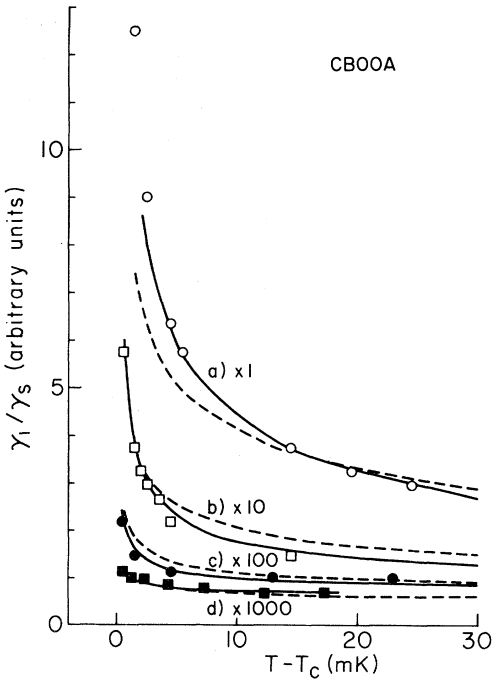


FIG. 6. Ratio of the twist viscosity to the splay viscosity vs $T$-$T_c$: (a) open circles, 0–30 °mK; (b) open squares, 0–300 °mK; (c) filled circles, 0–3 °K; (d) filled squares, 0–30 °K. The solid line is the fit to the mean-field theory for the enhancement of $\gamma_1$, and the dashed line is the fit to the helium-analogy theory. The temperature scale is expanded as in Fig. 2.

transition temperature for the $\gamma_1/\gamma_s$ data is 3.3 °mK higher than the transition temperature for the $K_{22}$ data. The lifetime and intensity data were taken simultaneously and it is unphysical to use different transition temperatures in fitting $I_t$ and $\gamma_1/\gamma_s$. If we fix the transition temperature halfway between the transition temperatures determined from the three-parameter fits, and vary the remaining two parameters to fit the data, the mean-square errors are all approximately doubled. The mean-field theory still fits the data 6 or 7 times better than the helium-analog theory. The transition temperature found from the mean-field fit to the intensity data lies in the middle of the fitted transition temperatures and we now fix $T_c$ at that value. A two-parameter fit of mean-field theory ($\alpha_2 = 0.5$) to the intensity data is shown as a solid line in Fig. 2 and is clearly a good fit from 1.6 °mK to 7 °K above the phase transition. A two-parameter fit of the helium analog ($\alpha_2 = 0.67$) to the intensity data is shown as a dashed line in Fig. 2 and the fit is poorer with deviations up to 10%. A two-parameter fit of mean-field theory ($\alpha_1 = 0.5$) to the viscosity data is shown as a solid line in Fig. 6 and is again clearly a good fit from 2.5 °mK to 17 °K above the phase transition. A two-parameter fit of the helium analog ($\alpha_1 = 0.33$) to the viscosity data is shown as a dashed line in Fig. 6, and again the fit is poorer with deviations up to 17%. These deviations for the helium analogy are well outside the experimental error of about 3%–5%.

We can make a stronger case against the helium analog by examining the twist lifetime which is measured directly. Near the transition temperature where the temperature dependence of $\gamma_1^0$ and $K_{22}^0$ are unimportant, the twist lifetime varies as

$$\tau_t = \tau_0 \left( \frac{1 + [\Delta T_1/(T - T_c)]^{\alpha_1}}{1 + [\Delta T_2/(T - T_c)]^{\alpha_2}} \right). \tag{19}$$

With the parameters $\Delta T_i$, $\alpha_i$ from the two-parameter fit of the previous paragraph we show the lifetime versus temperature in Fig. 7 for the mean-field theory (solid line) and the helium analog (dashed line). The qualitative behavior of the helium-analog lifetime is wrong within 60 °mK of the phase transition. The mean-field theory fits the data within experimental accuracy to within 3 °mK of the phase transition. Given the observed rounding of the transition we cannot claim the data within 3 °mK of $T_c$ are significant. Thus we find no experimentally significant deviations from mean-field theory from 3 °mK to 7 °K above the phase transition.

## V. THEORETICAL ESTIMATES

If the mean-field theory is in fact correct for CBOOA we should be able to calculate the magnitude of the pretransition effects provided enough parameters are known. For $K_{22}$ one need know only the smectic interplanar spacing $d$ and the correlation lengths

$$K_{22} = K_{22}^0 + \frac{\sqrt{2}\pi}{6} \frac{kT\xi_1^2}{d^2 \xi_{\parallel}}, \tag{20}$$

all of which can be found from the x-ray experiment.[2] That experiment may have been incorrectly analyzed (the analysis did not produce mean-field exponents). If we ignore the analysis and take the measured correlation lengths at 88.8 °C where instrumental smearing is unimportant we find $\xi_{\parallel} = 184$ Å, $\xi_{\parallel}/\xi_{\perp} = 4$. Now assuming a mean-field temperature dependence we find

$$\xi_{\parallel} = \frac{24}{(T/T_c - 1)^{1/2}} \text{ Å}, \tag{21}$$

$$\xi_{\perp} = \frac{6}{(T/T_c - 1)^{1/2}} \text{ Å}. \tag{22}$$

Taking $d = 35$ Å we calculate

$$K_{22} = K_{22}^0 + \frac{0.44 \times 10^{-8}}{(T/T_c - 1)^{1/2}} \text{ cgs}. \tag{23}$$

In order to normalize our experimental $K_{22}$ data we take the value of $\gamma_1$ at 90 °C from Huang *et al.* ($\gamma_1 = 0.47$ P) and our lifetime $\tau_t = 7.7 \times 10^{-3}$ sec, $q = 1.02 \times 10^4$ cm$^{-1}$ and an 8% enhancement and find $K_{22}^0 = 0.55 \times 10^{-6}$ cgs at 90 °C. The normalized experimental enhancement of $K_{22}$ is

$$K_{22} = K_{22}^0 + \frac{0.7 \times 10^{-8}}{(T/T_c - 1)^{1/2}} \text{cgs}, \tag{24}$$

which is in satisfactory agreement with the magnitude of the theoretical enhancement.

The full theoretical expression for $\gamma_1$ is

$$\gamma_1 = \gamma_1^0 \left( 1 + \frac{\pi \gamma_3 kT \xi_{11}}{32 \gamma_1^0 C_{11} d^2} \right). \tag{25}$$

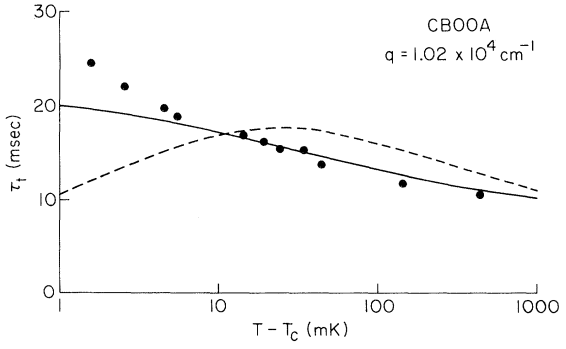


FIG. 7. Lifetime of the twist mode vs $\log(T-T_c)$. The solid line is taken from the fit of $K_{22}$ and $\gamma_1$ using the mean-field theory and the dashed line is taken from the fit of $K_{22}$ and $\gamma_1$ by the helium-analog theory.

Here $C_{11}$ is the coefficient of the longitudinal gradient term in the smectic free energy[3]; it has been determined from the x-ray work. However, there is no information on $\gamma_3$ so that we cannot check this theoretical expression. We can use it to get an estimate of $\gamma_3/\gamma_1^0$. According to the x-ray work $C_{11}=5NkTd^2/(2\pi)^2$, where $N$ is the molecular density. From the experimental magnitude of the enhancement of $\gamma_1$ and the above parameters we estimate $\gamma_3/\gamma_1^0 \approx 8$. If there were a measurement of $\gamma_3$ by a fluid permeation experiment or by a measurement of the lifetime of smectic order parameter fluctuations we could have a quantitative test of (25).

## VI. CONCLUSIONS

Our conclusions are that the smectic order parameter fluctuations in the nematic phase of CBOOA are mean-field-like and that the phase transition is truly continuous (second order). Since these conclusions fly in the face of almost all previous experimental work, a discussion of previous work is in order.

We consider first the question of whether the phase transition is first order or second order. The previous experiments are the density measurements of Torza and Cladis[16] and the heat-capacity measurement of Djurek *et al.*[17] In both these measurements the temperature resolution was one to two orders of magnitude poorer than in our work. In addition, both measure the integrated effects of a number of modes, whereas we measure the long-wavelength behavior of the modes directly responsible for driving the transition to first order (according to the theory). We believe that our observations are more sensitive and that our conclusions are correct.

The physical mechanism suggested by HLM to drive the first-order transition is very interesting. The entropy of the bend and twist thermal fluctuations is a function of the smectic order parameter $\psi$ and when one integrates out the director modes one is left with a $\psi^3$ term in the free energy in addition to the usual $\psi^2$ and $\psi^4$ terms. The $\psi^3$ term makes the transition weakly first order. For the type-I case HLM showed that the first-order phase transition occurred far enough above the extrapolated critical temperature $T^*$ that renormalization of the elastic constants was unimportant. In CBOOA we observe the opposite behavior; the renormalization of the elastic constants is large and the first-order phase transition has not taken place. One could argue that 3 °mK is not close enough to the phase transition and that the transition might be first order with $T_c - T^* < 3$ °mK. However, the coefficient of the $\psi^3$ term is inversely proportional to an elastic constant to the $\frac{3}{2}$ power and the pretransition increase in the elastic constants will reduce the magnitude of the $\psi^3$ term. Thus if one gets close enough to the transition that these pretransition effects are important the forces driving the transition first order weaken and it seems unlikely that the transition will be first order no matter how close one gets. This is the case of CBOOA and we believe that the phase transition in CBOOA is truly second order. This contradicts the HLM prediction that the smectic $A$–nematic phase transition is weakly first order.

The second question is whether the phase transition is mean-field-like or helium-like (or none of the above). The analysis of the early x-ray work[2] did not agree with either model. The analysis did not include the effects of director fluctuation on the liquid-structure factor and it should be repeated. The theory of the effect of director fluctuations on the liquid-structure factor has not been worked out yet. It would also be interesting to have this experiment repeated with the full resolution of single-crystal techniques. In Freederick's transition work Cheung *et al.*[5] found the helium exponent for $K_{33}$, while Cladis[6] found the classical exponent. Samples distorted by a field exhibit a "striping" phenomena[5] near the phase transition and it is not possible to use this method very close to $T_c$. The pretransition anomaly is much stronger in $K_{33}$ than in $K_{22}$ and it is important to extend the measurements of $K_{33}$ much closer to the transition temperature. The temperature dependent background is clearly a problem in the measurements of $\gamma_1$ by Huang *et al.*[14]; that may be the entire source of discrepancy between their work and ours. Our measurements were extended two decades closer to the phase transition than theirs and are therefore much less sensitive to background subtraction problems. In addition, taking the ratio $\gamma_1/\gamma_s$ apparently removes the temperature dependence of the background. The recent measurements of Durand and coworkers[18] of the lifetime of the twist mode are in qualitative agreement with ours, while their older intensity measurements,[7] which were not performed in their new hot stage, gave the helium exponent. Their intensity measurements in the new hot stage are in progress; it will be of great value to have these experiments performed in two laboratories. In short we believe that our results for the critical behavior are more reliable than previous work because our measurements extend much closer to the phase transition. It is important to repeat or reanalyze much of this experimental work to find out if it is in fact consistent with the mean-field model. One should be cautious in accepting the results of this type of quantitative analysis until

it is confirmed by other experiments.

de Gennes's helium analogy is an elegant attempt to predict the critical behavior of the smectic $A$–nematic phase transition and one is reluctant to give it up. Since helium mixtures exhibit classical behavior near the tricritical point, and since CBOOA may be in some sense near the tricritical point, the classical results for CBOOA may not be in conflict with the analogy to liquid helium. One would want to study the tricritical point using mixtures of CBOOA and a longer homolog, and to move as far from the tricritical point as possible perhaps using mixtures of CBOOA and its shorter homologs. Rayleigh scattering is an ideal tool for this work.

Another problem which deserves attention experimentally is the assay of impurities and the study of impurity effects on the phase transition.

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