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Light-Scattering Study of Fluctuations in Blue-Phase II

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The lattice-paramater fluctuations seen in blue-phase II are studied by quasi-elastic light scattering. The spectrum in frequency and k-space, $I(q,\nu)$, is expressible as $S(\nu)A(q)$. In the range 4–3500 Hz, $S(\nu)$ could be fitted to a sum of two central lorentzians plus a constant. Below 4 Hz, there was excess noise with at least two more characteristic frequencies. The spectra show that the fluctuating quantity is neither a simple relaxation nor just a propagating wave, but something more complex.

1. INTRODUCTION

The "blue" phases are modifications of the well-known helical cholesteric mesophase in which the local molecular orientation shows three-dimensional periodicity.[1-3] The two "solid" blue phases (BP) have the symmetry of crystals. It has recently been shown that they exhibit a shear modulus over a range of frequencies, just as real crystals do.[4-6] However, almost nothing is known about the hydrodynamics of these phases. Thermal fluctuations have been detected in all three BP, so it seems reasonable to study these fluctuations in order to learn about the dynamic properties of the BP.[7] In this paper, I report the results of such a study, and show that the BP exhibits unexpectedly-complex bahavior.

When a single "crystal" (platelet, to use the common nomenclature) of a BP is illuminated with light whose wavelength is near, but not exactly on a Bragg resonance, the image appears to twinkle. To the eye, this scintillation resembles that found in a nematic observed in polarized light. It has been argued that the dominant contribution to the visible flicker is a fluctuation of the local lattice parameter.[7] As

the lattice fluctuates, parts of it become momentarily more reflective, parts less. These differences in reflectivity show up as a flickering contrast in back-reflection. The lattice-parameter of a typical BP is such that Bragg scattering at $2\theta \sim 180°$ is usually the most convenient way to observe the sample's optical properties. Now consider the optical field just below a sample illuminated from above as previously described. The varying reflectivities imply varying transmissions, so the sample acts like a screen with a flickering pattern printed on it. Thus, the fluctuations can scatter light in the forward direction, with small features scattering at large angles, just as in any simpler scattering experiment. Therefore, the angular dependence of the scattering should yield information about the system. Also, the frequency spectrum gives the same sort of information as one would get by measuring the scattering from a nematic. The main difference in the optics of the BP and nematic is that in the BP we are "diffracting off the diffraction", and thus must be near but not exactly on a Bragg reflection in order to get large effects. In this paper, I report the results of a measurement of $I(q, \nu)$ for the scattering from a BP.

2. EXPERIMENTAL DETAILS

To approach Bragg resonance, one can tune the illumination, the sample, or the geometry. The latter was limited by the hot-stage used, the illumination came from an argon laser with four wavelengths from which to choose, so I decided to tune the sample. The sample was made of 27.5 wt.% hexyloxycyanobiphenyl (60CB) in cholesteryl nonanoate (CN). The 60CB fraction was chosen to make the sample's Bragg reflection fall in the desired range. The CN-60CB mixture was placed between glass plates coated with a polyimide and rubbed to secure paralell alignment. This procedure produces good single platelets which last for a week or more before degrading into polycrystallinity. The sample was kept in a Mettler FP52 hotstage.

Fig. 1 is a schematic diagram of the optical setup. The laser L was a 15 mW air-cooled Ar laser with polarized output at 5145Å. Its output was focussed by lens L onto the sample. The focal spot was $\sim 200\mu$ in diameter. The irises I_1 and I_2 provided some spatial filtering. The diagonal mirror M directed the beam onto the sample at a near-right angle. The beam reflected off the sample hit M again and was stopped, but light scattered near the back-reflected beam was collected by dissecting microscope MI, which was used to monitor the state of the sample and to see where the beam hit. Polarizer P_1 was

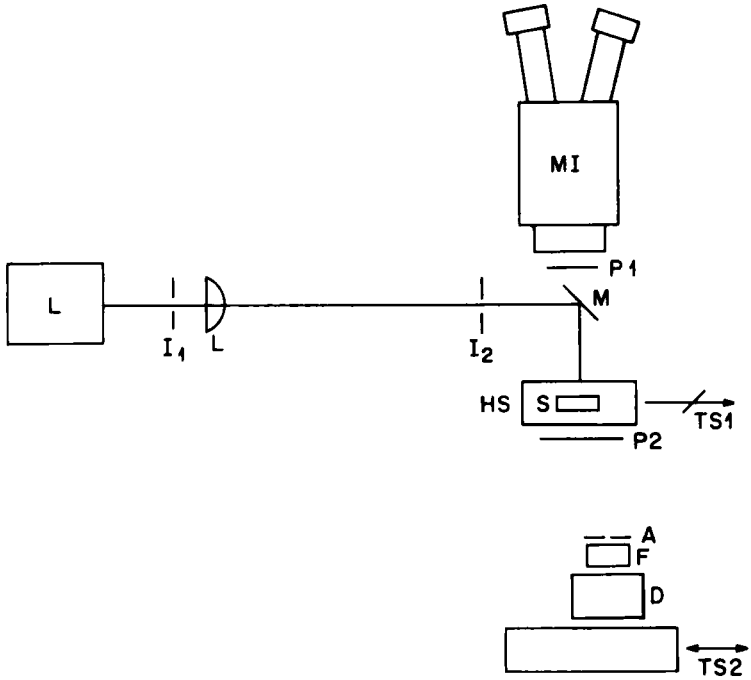

FIGURE 1 Schematic diagram of apparatus. See text for meaning of labels.

used to suppress extraneous scattering in MI and give maximum contrast. A white-light source (not shown) provided with a polarizer could be made to provide a broad beam along a path close to that of the laser beam. This white light allowed microscopic examination of parts of the sample not illuminated by the laser spot. The sample S was inside hot-stage HS, which was attatched to XY translator TS_1. The laser beam remained fixed; the sample moved under it so that a defect-free area of BP was illuminated. The active area was chosen so it was all BPII, of uniform color, and showed no dislocations or bright dust-specks within the laser spot. The transmitted beam went through the sample and polarizer P_2 to be intercepted by detector D. A 100μ pinhole A defined the angular resolution of the detector, and an interference filter F was used to cut out extraneous light. The detector was mounted on translation stage TS2, with which it could be scanned across the diffraction pattern. The signal from the detector (a PMT) went into an ADC interfaced to a PDP-11/23 computer. The computer took 2050 samples of the voltage and did an FFT on the resulting time series, saving the Fourier magnitudes. This process was repeated 100 times for each angle, and the results averaged. Since the

discrete Fourier transform of a noise signal is itself noisy (a fundamental theorem of stochastic processes—noise is intrinsically noisy), the signal averaging provided by the 100 repetitions was needed for good signal/noise ratio.

In any light-scattering experiment such as this, one has to know whether the experiment is done under homodyne or heterodyne conditions. To answer this question, I looked at the probability distribution of the intensity recieved at the detector. In the extreme heterodyne limit, the distribution should be Gaussian, while homodyne effects give rise to a skew distribution. The intensity at any time was assumed to be given by:

$$I = a + b(n + c)^2 \tag{1}$$

where I is the intensity, n a Gaussian random variable with zero mean and unity variance, and a, b, and c are constants to be fitted. The first term models incoherent background intensity. The n term represents the fluctuation signal, while the c represents any coherent background. Thus, the homodyne limit is represented by $c \ll 1$, while the heterodyne limit is given by $c \gg 1$. The fitted values of c ranged from 3–10, showing that the majority of the signal is from the heterodyne component, i.e. the cross-term $2ncb$. This assumption was used for normalization purposes. The intensity for each angle was divided by the average DC voltage. This normalization gives a quantity proportional to b if $a \ll bc^2$ and $c^2 \gg 1$.

The polarizer was set for minimum transmitted intensity in the BP. Data were also taken in the isotropic phase, with the polarizer set so that the average intensity was the same as in the BP. This procedure was repeated for each angle. By equalizing DC levels, I assure that the detector-related noise is the same for both phases, and thus cancels out when the isotropic-phase data are subtracted from the BP data.

The effect of vibrations and drifts of various quantities were assayed by looking at the signal in the isotropic phase with the beam hitting the edge of a large dust particle. The resulting signal was largely white noise, with some sharp peaks superimposed on it, and did not increase with decreasing frequency as did the low-frequency tails of the BP data.

3. RESULTS

Data for the range 4–3500 Hz, and for various angles are shown in Fig. 2. Each curve has the same shape, but with different intensity. In

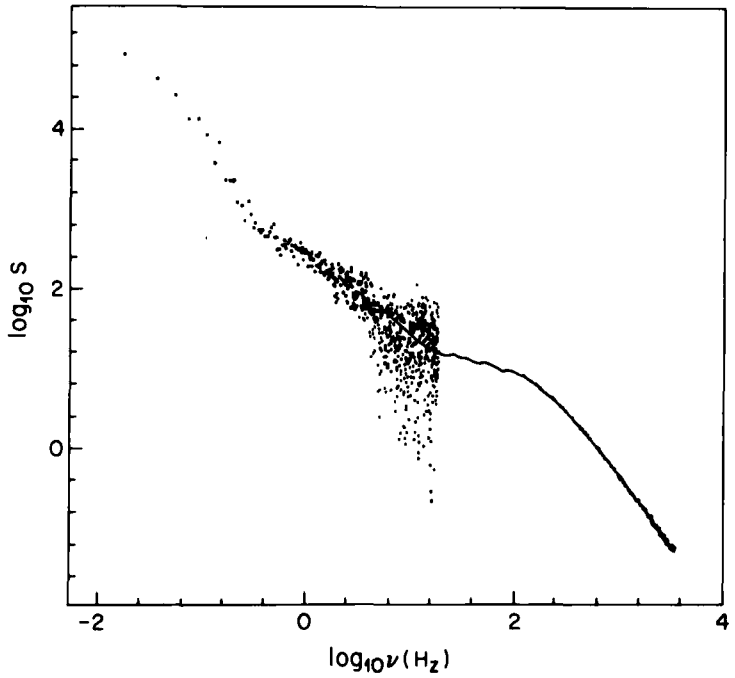

FIGURE 2 $S(\nu)$ (normalized) vs. ν for $q = .027, .175, .349, .524, .888\mu^{-1}$, in order from top to bottom curve.

other words,

$$I(q,\nu) = A(q)S(\nu) \tag{2}$$

The data were summed together to get a form for $S(\nu)$, which is shown in Fig. 3. The solid line is a fit to the form:

$$S(\nu) = \text{const.}\left(\frac{1}{1+(\nu/125)^2} + \frac{.214}{1+(\nu/360)^2} + .00113\right) \tag{3}$$

This fit works quite well at the high end, but fails for lower frequencies. Changing either of the frequencies in the denominators by 10–20 Hz produced a doubling of the sum of squared residuals. The low frequencies could be probed by putting a delay in the data-gathering loop, with results shown in Fig. 4, in which the results from a single angle ($q = .35\mu^{-1}$) are scaled for comparison with the average shown in Fig. 3. It can be seen that there are at least two frequencies in the low-frequency tails, in addition to the two at the high end.

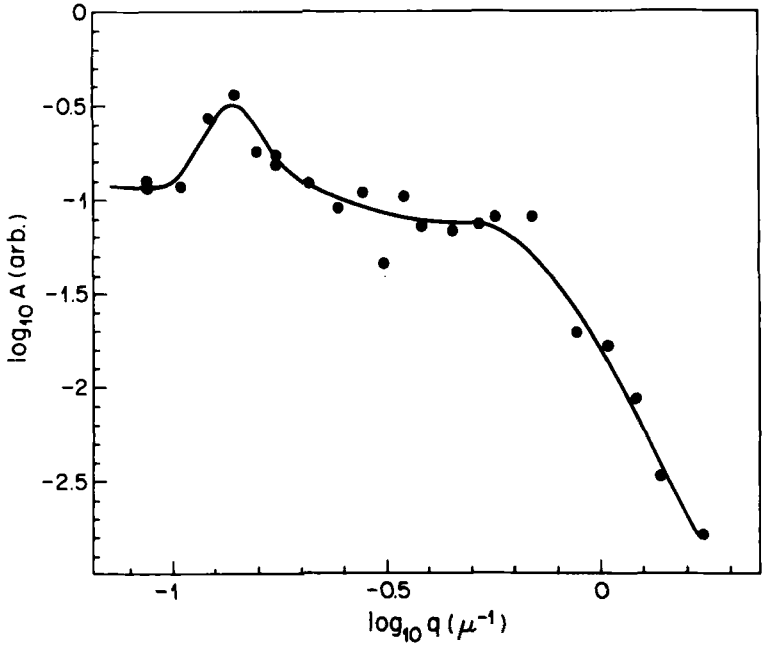

FIGURE 3 Summed data ($S(q)$) vs. ν (dots) and 2-lorentzian fit (solid curve).

The angular dependence of $A(q)$ is shown in Fig. 5. The scatter may be due to incoherent background light which would affect the normalization discussed above. The sharp cutoff at the higher angles is real and not an artifact of the interferance filter used, which cuts off at somewhat higher angles.

4. DISCUSSION

What can we infer about the fluctuations, given the information above? First, the fluctuations are not simple, diffusive modes, such as in the nematic.[8] There, the width of the frequency spectrum goes as q^2, which is not the case in the BP. The intensity dependence on q suggests the presence of some characterisitic size of order 8μ, or 50 times the lattice parameter, within which the material fluctuates in a correlated way on all times scales from 4–3500 Hz. At the very low frequencies, there is data from only one angle, so it may be that below 4 Hz, this assumption does not hold, but at the frequencies for which there is data at all angles, the fluctuating quantity appears to follow a relaxation behavior correlated over 50 unit cells.

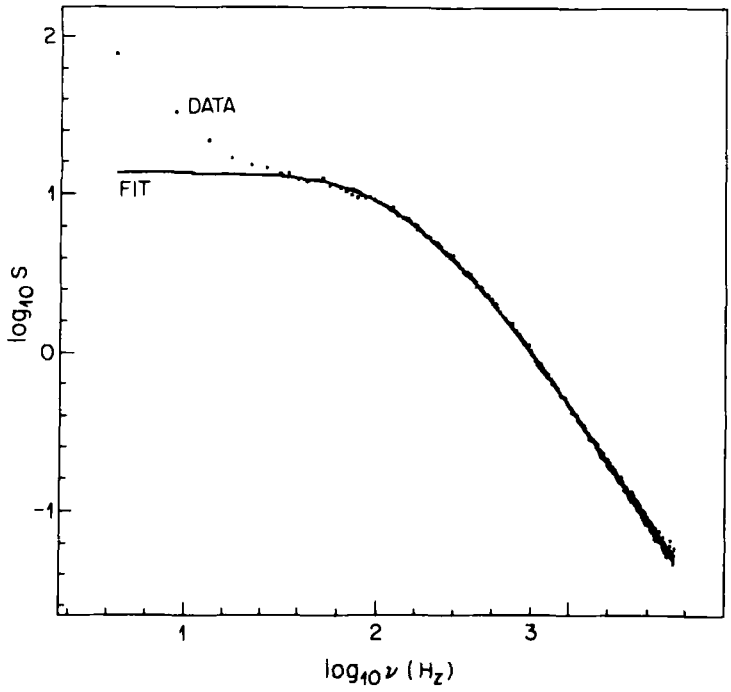

FIGURE 4 LF spectrum for $q = .35\mu^{-1}$ (unnormalized) compared with scaled, summed high-frequency spectrum.

In a previous paper,[7] it was argued that the scintillations are mainly due to lattice-parameter fluctuations. Some shear modulus has to be of order 1 erg/cm^3 or less in order to account for the observed intensity. How can this low value be reconciled with the large (several hundred to several thousand erg/cm^3) values observed in mechanical experiments? Remember that a cubic crystal has two independent shear moduli. Suppose one of these were $O(10^4 \text{erg/cm}^3)$, and the other $O(1 \text{ erg/cm}^3)$. We would like to know what the effective shear modulus found in a mechanical measurement on a polycrystal would be. This problem has never been rigorously solved. The conventional wisdom in metallurgy is that the effective modulus is the geometric mean of the two constants $\mu_1 = C_{44}$ and $\mu_2 = \frac{1}{2}(C_{11} - C_{12})$. However, this formula is an empirical rule valid for $\mu_1/\mu_2 \in [.1, 10]$. Suppose one of the moduli, say μ_2 vanishes. The above formula predicts a zero shear modulus for the whole sample, implying that each grain deforms only in its soft direction, which cannot be true because adjacent grains would pull away from or penetrate each other. Thus, for large

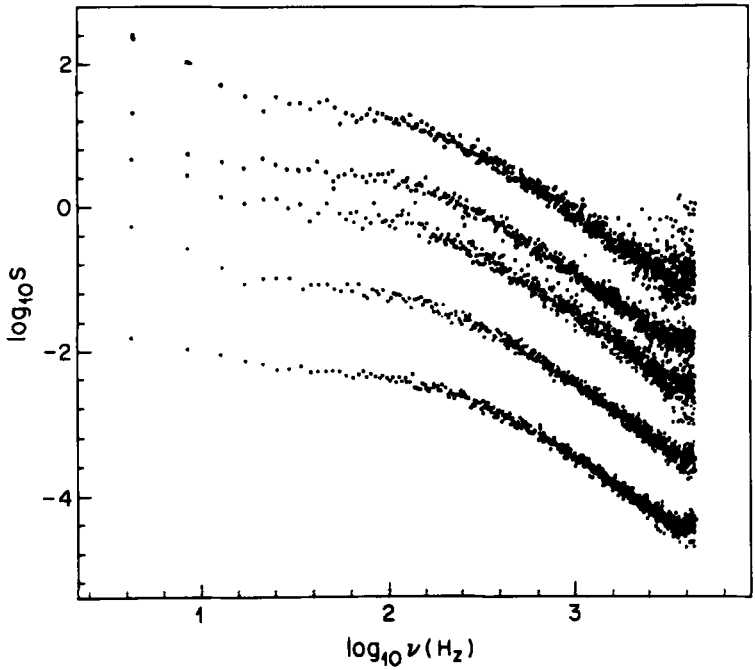

FIGURE 5 $A(q)$ vs. q.

anisotropies, the geometric mean is a lower bound. On the other hand, we can calculate the work required to deform the sample in such a way that each grain deforms in the same way, relative to the coordinate system of the sample. This deformation satisfies the boundary conditions, but is clearly not the lowest-energy state, so the modulus calculated therefrom is an upper limit. This limit is given by $2/3\mu_1 + 1/3\mu_2$. If we take one modulus to be 10^4 erg/cm^3 and the other as 1 erg/cm^3, we find that the lower bound is 100 erg/cm^3, and the upper bound is 3333 or 6666 erg/cm^3, depending on which modulus is soft. The experimental values fall nicely in between the lower limit and the lower value of the upper limit. The value of 10^4 erg/cm^3 for the hard modulus is the Kq_0^2 value referred to in Ref. 7.

There are other possible explanations for the flicker, which were not considered in Ref. 7. Suppose the fluctuating quantity is a local circular birefringence. This birefringence would shift the Bragg line just as a change in lattice parameter would, and this is consistent with the evidence presented in the previous paper. I tested this notion by placing a sample (CB15-E9 mixture with a BPII at 29.2°C) between 90% reflecting mirrors and illuminating with He-Ne laser light. The

Bragg wavelength is in the green, so lattice-parameter fluctuations cause little index shift at the red wavelength. To cause the .2% apparent lattice-parameter shift, we need an index shift of about the same magnitude. For a 50μ sample, this translates into a 1000Å path difference, or about 1/3 of a fringe. The Fabry-Perot formed by the mirrors and the sample had a finesse of about 10, so any such shift should have been quite visible. No such effect was found, to within about half the width of a fringe, or 15% of the predicted value.

The other possible source of the flicker is a fluctuating form factor. Imagine a sample thinner than the extinction length, and consider its reflectivity as a function of wavelength. As the sample gets thin, the curve of reflectivity vs. wavelength changes from the flat-topped Darwin form to one in which the reflectivity peaks at some wavelength. A fluctuation in the lattice parameter is equivalent to a shift of wavelength, so the intensity of the flicker will scale as the derivative of reflectivity vs. wavelength. This quantity is zero at the wavelength of peak reflectivity. The flicker would be strong at either edge of the Bragg band, and zero in the middle, much as for the thick sample. However, if the form factor is fluctuating, the reflectivity at all wavelengths fluctuates, leading to strong flicker at the peak wavelength.

To check for the possible influence of form-factor fluctuations, I used a thin sample of a pure compound (terepthaloyloxy-bis-4-(2′-methoxybutyl) benzoate), observed by reflection microscopy. This compound has a temperature-dependent lattice parameter. The sample was a smear of material on a glass slide, with the upper surface free. Thus, I could look at areas of varying thicknesses, and verify that the selected area was thin in the sense of having a peak reflectivity much less than that of thicker areas. The light source was a mercury lamp with a 5460Å interference filter. Even in the thinnest areas, the flicker always went away when the sample was brightest, reappearing when the temperature was adjusted so that the sample was dimmer than its peak brightness. It was necessary to look at a thin sample, because the flicker is predicted to vanish in thick ones for both lattice-parameter and form-factor modes.

I conclude that the identification in Ref. 7 of the source of the flicker as lattice-parameter fluctuations is correct, and so the above analysis concerning limits to moduli is relevant. Thus, we are left with an enormous elastic anisotropy as the only known explanation for both the mechanical and optical results.

The source of the intense, low-frequency noise is unknown, as is the lower cutoff frequency, if there is one. This LF noise is so intense that

the amount of scattering can change by a factor of three over tens of minutes.

It is clear that the dynamics of the BP remain a mystery, and are unlike those of normal solids.

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