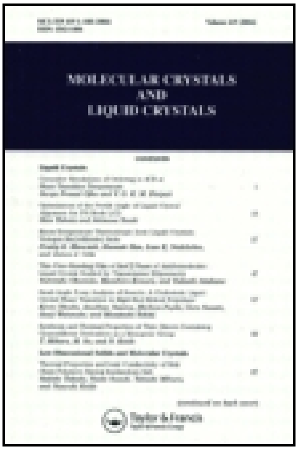

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Small Angle X-Ray Studies of Liquid-Crystal Phase Transitions
I. *p*-Azoxyanisole

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Abstract—Small angle X-ray scattering experiments have been performed on *p*-azoxyanisole in the isotropic liquid, nematic liquid, and solid regions. Measurements were carried out in a Hart-Bonse type small angle diffractometer with the sample maintained at temperatures controlled to ±0.003 °C. Premonitory phenomena were observed in the isotropic liquid at temperatures considerably above the nematic-isotropic transition temperature, T_c. As the nematic-isotropic transition was approached from above, the correlation length for molecular ordering increased from 300 Å at 15 °C above T_c to 1900 Å at T_c. Within the nematic liquid region the correlation length was found to be essentially constant down to several degrees above the nematic-solid transition, followed by an additional increase in correlation near the transition to the solid phase. The experimental results indicate that neither the Ornstein-Zernike nor Fisher theories of critical point behavior are adequate to explain the phase transition. The Frenkel heterophase fluctuation theory is in qualitative agreement with the temperature dependence of the correlation length.

To our knowledge no one-component liquid crystal system has been investigated using small angle X-ray scattering techniques. There are many reasons why this should be so, the main one being that the technique requires a high degree of experimental sophistication, since the measurements are made very close to the main beam, which must be confined to angles of the order of seconds of arc with attendant loss of incident intensity and consequently very low scattered intensity. Thus to attain good statistics long counting times are required, and when, in addition, accurate temperature controls are needed (as in the present study), stability problems become very severe since the measurements take weeks or even months to complete.

However, these difficulties are counterbalanced by the advantages of the method, which offers a direct means of measuring long-range order in liquids. In fact it is now possible to measure correlation phenomena out to 15,000 Å, and to measure the degree of intermolecular ordering both in the isotropic and liquid crystalline regions as a function of temperature, and get information about the physical phenomena occurring at and in the vicinity of the isotropic-nematic transition.

In this paper we present initial results of an investigation of the small angle scattering of *p*-azoxyanisole, which has a nematic range from 117 °C to 135 °C. This compound has been extensively studied and its isotropic-nematic transition is apparently first order, characterized by discontinuities in density and viscosity.[1-3] It has a heat of transition (178 cal/mole). A variety of measurements, notably ultrasonic absorption[4] studies, have been interpreted as indicating premonitory phenomena and attempts made to correlate them with the Frenkel heterophase fluctuation theory. Since this theory has been extensively discussed[5] we will not elaborate further on it, except to point out that the temperature dependence of small angle scattering can in principle give direct information about the ordering parameters explicit in the theory.

Theory

The scattering of electromagnetic radiation by liquids can be considered to be the result of local fluctuations in certain properties of a system. In particular, for visible light the scattering is caused by deviations in refractive index, and for X-rays by deviations in electron density. By straightforward application of Maxwell's equations, it can be shown that the scattered X-ray intensity is[6]

$$I = I_0C\iint\left\langle\left(\frac{\delta\rho}{\rho}\right)\left(\frac{\delta\rho'}{\rho}\right)\right\rangle_{av}\exp\{i[\mathbf{s}\cdot(\mathbf{r}-\mathbf{r}')]\}d\tau\, d\tau' \tag{1}$$

where I_0 is the incident intensity, C is a constant, ρ is the average electron density, and the integration is carried out over the whole irradiated volume. The other quantities and their physical significance can be briefly explained as follows: take any two volume elements $d\tau$ and $d\tau'$ at distances $\mathbf{r}$ and $\mathbf{r}'$ from any arbitrary point in the system. Suppose that there exist there electron density fluctuations $\delta\rho$ and $\delta\rho'$. Their product averaged over time results in an observable scattered intensity. The scattering vector $\mathbf{s}$ depends on the angle between unit vectors in the incident and scattered directions and its magnitude is $s = 4\pi/\lambda \sin\theta$ where λ is the wave length and θ is half the scattering angle. For $\mathbf{r}-\mathbf{r}' = 0$, $d\tau = d\tau'$ and the fluctuation average is $(\delta\rho/\rho)^2_{av}$. Debye[6] defines a correlation function $G(r)$ (where $r = |\mathbf{r}-\mathbf{r}'|$)

$$\left\langle\left(\frac{\delta\rho}{\rho}\right)\left(\frac{\delta\rho'}{\rho}\right)\right\rangle_{av} = G(r)\left\langle\left(\frac{\delta\rho}{\rho}\right)^2\right\rangle_{av} \tag{2}$$

which is dimensionless and measures the extent to which the fluctuations at $\mathbf{r}$ and $\mathbf{r}'$ are correlated. It is evident that $G(r) = 1$ for $r = 0$ and tends towards 0 for large r, where the fluctuations in the volume elements are uncorrelated.

Substituting (2) into (1) and integrating we obtain

$$I(s) = I_0CV\left\langle\left(\frac{\delta\rho}{\rho}\right)^2\right\rangle_{av}\int_0^\infty G(r)\frac{\sin sr}{sr}\,d\tau \tag{3}$$

where V is the irradiated volume.

Equation (3) is difficult to use for technical reasons which need not concern us here. Therefore, it is usual to expand the integral and restrict the expansion to very small values of s. Thus

$$\frac{I(s)}{I(s=0)} = 1 - \frac{\int r^2G(r)\,d\tau}{\int G(r)\,d\tau}\frac{s^2}{6} + \frac{\int r^4G(r)\,d\tau}{\int G(r)\,d\tau}\frac{s^4}{120} - \cdots \tag{4}$$

In the angular range of our experiments we can terminate the series at the second term. The coefficient of this term defines a length

$$L^2 = \frac{\int r^2 G(r)\, d\tau,}{\int G(r)\, d\tau} \tag{5}$$

the persistence or correlation length, the range over which the fluctuations in the two volume elements are correlated. Thus the initial region of the scattering curve should vary linearly with s^2 and have a slope of $L^2/6$.

An alternative approach is that of Guinier[7] who has shown that for discrete and widely separated particles of any shape the scattering at small angles is closely approximated by a Gaussian

$$I \propto e^{-s^2\bar{R}^2/3} \tag{6}$$

where $\bar{R}$ is the radius of gyration of the scattering particle. This leads automatically to an expression

$$\frac{I(s)}{I(s=0)} = 1 - \frac{s^2\bar{R}^2}{3} \tag{7}$$

which is equivalent to (4) with $L = \sqrt{2}\,\bar{R}$. Thus the data can be analyzed by using either (4) or (6). If one assumes that liquid crystalline systems contain regions in which the molecules are ordered over a finite distance with a characteristic shape then (6) can be used to characterize this region.

Experimental

The measurements were made with a modified Hart-Bonse type diffractometer.[8] The fore-crystal was eliminated because it gave no significant gain in intensity and its removal greatly facilitated the alignment of the two grooved crystals. A point source from a high intensity Philips Cu tube was used to decrease the vertical divergence and a notched slit was placed at the exit port to enable easy adjustment of the beam height. A stepping motor and printout system allowed automatic collection of data, and repeat scans were made from zero scattering angle out to approximately 10 minutes of arc. The step-scanning limits were set so that on every pass the main beam was traversed in steps of 0.5 seconds of arc, thus automatically determining the $2\theta = 0$ position. Carefully calibrated copper foils were inserted in front of the detector during this part of the scan to insure that the intensity did not exceed 10^4 cps, well within the linear response region of the detection system. The Hart-Bonse unit is the ideal instrument to use in the angular region of these experiments since it provides very high scattering intensity with very narrow resolution (9″ of arc).

The sample was maintained at temperatures controlled to ± 0.003 °C in a constant temperature cell described in another publication.[9] The sample holder was made of stainless steel with .01 mm thick mica windows. The thickness of the sample was 1 mm, chosen to give the optimum X-ray attenuation of 63%. British Supply House research grade *p*-azoxyanisole was used without further purification. The material exhibited some discoloration after the experiment was completed, but since the measurements were made over a period of about six weeks of continuous scanning, it is doubtful that the decomposition affected the results.

Results and Discussion

In Figs 1 and 2 the small angle intensity patterns are shown as a function of the scattering angle, 2θ. The ordinate scale is logarithmic, to encompass the large range of intensities measured. We point this out because on such plots the data sometimes appear to exhibit maxima which disappear in a linear plot, and have no physical significance. Figure 1 is included to show how the scan through the main beam is used to check any variation in position or intensity of the incident beam. As pointed out previously, calibrated attenuators are placed in the apparatus in the range

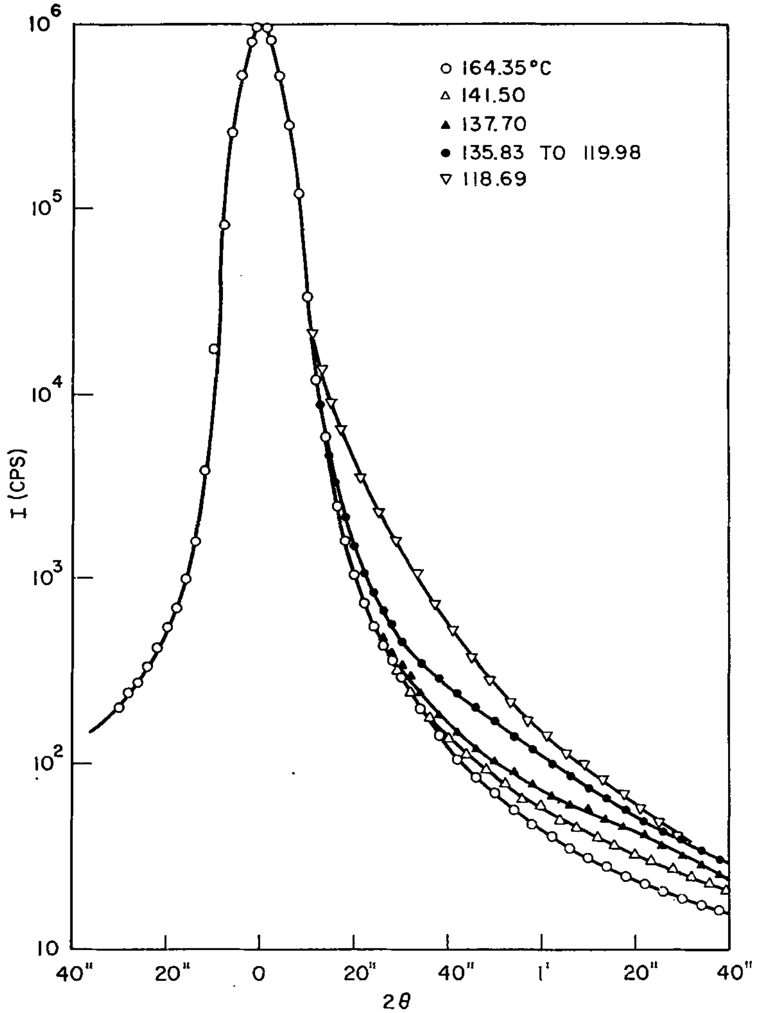

Figure 1. X-ray scattering intensity as a function of the scattering angle, 2θ (main beam area).

where the main beam is present and the ordinate has accordingly been scaled up to correspond with that of the outer part of the pattern. Figure 2 shows the data that we have used in our analysis. At the highest temperature, 164.35 °C there is no excess scattering,

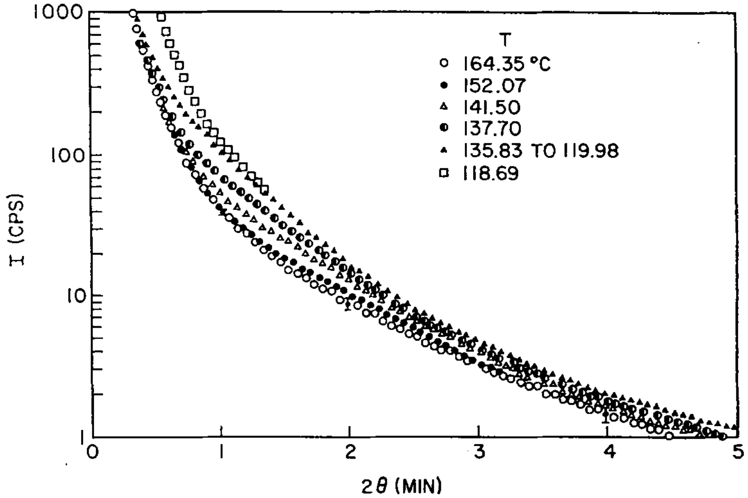

Figure 2. X-ray scattering intensity as a function of the scattering angle, 2θ

and the intensity pattern is that of the empty cell multiplied by the attenuation factor $e^{-\mu x}$ of the sample (μ is the absorption coefficient and x the cell thickness). We thus choose this as the background scattering.

The first indication of an excess scattering developing occurs at ~ 152 °C, some 16° above the phase transition temperature, T_c. Its magnitude is small, being just slightly larger than the error range of the background data. As we have seen, X-ray scattering results from differences in electron density in the liquid, and the region of s covered by small angle scattering results from long-range contributions to $G(r)$, as can be seen from Eq. 4; for the second term to have any influence on the angular dependence of I, $s^2L^2/6$ must be greater than $\sim 10^{-2}$. Since $0 < s < 0.01$ Å^{-1}, L must be greater than ~ 100 Å. This excess scattering is the first evidence of long-range molecular ordering and an indication that premonitory phenomena are taking place. The correlated fluctuations in electron density can only be interpreted as resulting from formation in parts of the liquid of a more densily packed molecular structure than in the bulk of the liquid.

A transition from a system of freely rotating molecules to one in which a nematic type of alignment is produced would indeed account for this local increase in electron density. It is worthwhile pointing out that if the entire system were to align in concert there would be no effect on the angular dependence of the scattering, because the correlation length would now encompass the whole sample, resulting only in a change of electron density of the total system.

Continuing our examination of Fig. 2 we note that as T approaches T_c the excess scattering increases in magnitude and moves towards smaller angles, indicating that the nematic type regions are becoming larger. The curves at 141.50 °C, 137.70 °C and 135.83 °C show this trend clearly. Below 135.83 °C the scattering patterns become nearly constant and superimpose throughout the nematic region, indicating that there is no further increase in molecular alignment and that the phase transition is complete, near or at this temperature. The temperature increments chosen were not small enough to exactly define T_c, but it is probably close to 135.83 °C. Finally, there is found to be a marked increase in scattering at or near the nematic-solid transition as indicated by the curve for 118.69 °C. Since our aim has been to study the isotropic-nematic transition, we will not further discuss at this time the nematic-solid transition.

Before proceeding to a quantitative analysis we show in Fig. 3 the actual scattering (I–I_B) for several temperatures above, near and below T_c. The total error of the measurements is indicated by the magnitude of the error bars. With reference to this we must signal the fact that all the curves were taken over a period of 6 weeks during which time the experimental arrangement was stable to 1%. We note that on a linear plot the increase in scattering is much more clearly displayed. Figure 4 shows Guinier plots (ln I vs s^2) of the data of Fig. 3 and it can be seen that good straight lines are obtained in all cases except for the lowest temperature (where the material is probably in the solid phase). At the two lowest temperatures in the nematic region where measurements were made (data not shown in Fig. 4) there

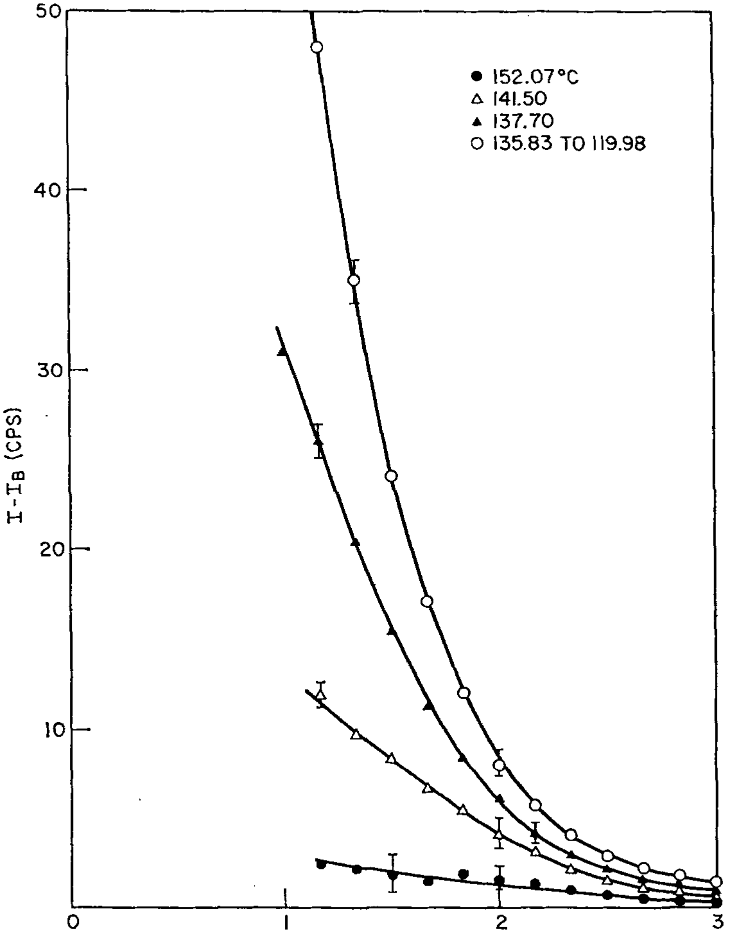

Figure 3. Excess scattering for temperatures above and within the nematic region.

is suspicion of a slight curvature developing, but it is within experimental error and we do not feel justified in interpreting this as evidence for another premonitory effect as the nematic-solid transition is approached. From these plots values of *L* were determined, and they are displayed as a function of temperature in Fig. 5, and the numerical values listed in Table 1.

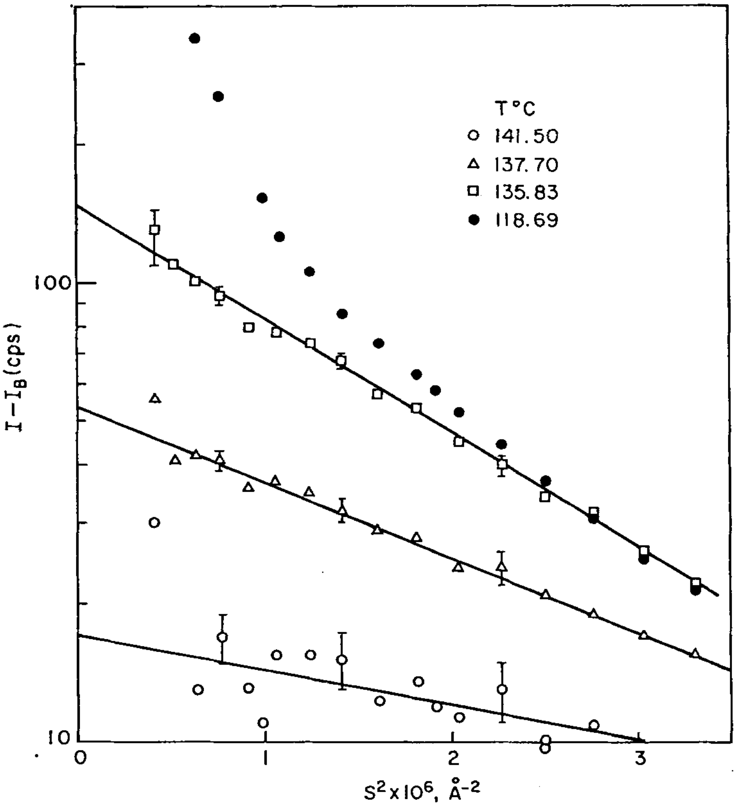

Figure 4. Guinier plots for representative scattering data. $s = 4\pi/\lambda \sin\theta$.

TABLE 1

T(°C)	L(Å)	N_s
152.07	$300 \pm {}^{400}_{300}$	$< 10^3$
141.50	$1000 \pm {}^{150}_{300}$	8×10^4
137.70	1500 ± 150	2×10^5
135.83 to 129.93	1850 ± 75	10^6
122.10	1900 ± 150	—
119.98	$1900 \pm {}^{300}_{200}$	—

There are some striking features of these results which should be noted. The first, of course, is the unequivocal demonstration that premonitory phenomena do in fact exist at temperatures above the isotropic-nematic transition. Thus the correlation length of 300 Å which is first observed at $T - T_c = 16.24\,°C$ increases rapidly as the temperature is lowered reaching a value of ~ 1850 Å at the transition temperature. Equally interesting is the fact that almost all through the nematic region the correlation appears to be constant. This implies first, that the nematic phase is not all ordered, but consists of widely separated regions whose actual volume V_0 is small when compared to the average volume available to each region, V_1. For instance if $8\,V_0/V_1$ becomes greater than approximately 0.1 a visible change would be evident in the Guinier plots, definitely not exhibited by our results.[10] This is very much in agreement with the experiments of Williams[11] who found that when the nematic phase of *p*-azoxyanisole was viewed under a microscope it consisted of small dark spots, widely separated. Secondly, this result appears to be in conflict with those deduced from measurements by other techniques in that the premonitory effects are completely asymmetrical; that is we see them on the high temperature side of the transition, but they are completely absent below the transition. This suggests that perhaps some other mechanisms than hetrophase fluctuations are responsible for the effects observed by other methods below T_c.

An estimate of N_s, the number of molecules in the correlated regions can be obtained from the measured correlation lengths. Assuming that the shape of the ordered region is an ellipsoid of revolution of the same axial ratio as that of the individual molecule a straightforward calculation gives the number of molecules in the ordered regions. It is interesting that our estimates for the minimum size, $< 10^3$ molecules, and the mean size of the aggregates in the nematic phase, 10^6 molecules, are in good agreement with the estimates of Hoyer and Nolle[1] for the former and of Ornstein and Zernike[12] for the latter. We point out, however, that the ordered regions must be regarded as dynamic entities, with constant change of molecules between the ordered and disordered regions. However to a first approximation the results are highly suggestive of an ordering scheme similar to that proposed by the early workers in the field. We point out again that further experiments, which we are now doing in the region of the small angle pattern where peaks characteristic of the shape of these coordinated regions should be evident, will allow a much more definite estimate of the ordering scheme in the nematic region.

Although we have not as yet been able to extract any further parameters relevant to heterophase theory, our experiments appear to settle one very important point that has been the subject of much uncertainty in the past. That is, briefly, whether the isotropic-nematic phase transition is a critical point phenomenon, or a truly first-order transition, as evidenced by the transition heat. The evidence of heterophase fluctuations within a supposedly isotropic phase near the transition temperature has been clearly established. Our data definitely rule out the possibility that this is due to critical point behavior. This possibility

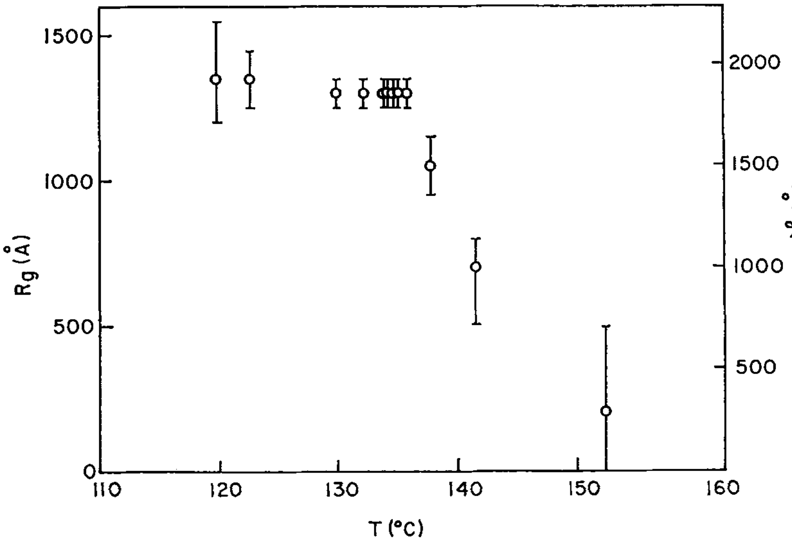

Figure 5. Temperature dependence of the radius of gyration, R_g, and the persistence length, L.

has been considered because the thermodynamic discontinuities are so small. Indeed Edmonds and Orr[4] have tried to interpret their ultrasonic measurements on the basis of the Ornstein-Zernike theory of second order phase transitions as modified by Fixman. Small angle X-ray scattering offers a unique test of critical phenomena. The intensity of the critical scattering has been shown[13] to be given by an expression of the form

$$I(s) \sim 1/(\kappa^2 + s^2)^{1-\eta/2} \tag{8}$$

where $\kappa \sim (\mathrm{T} - \mathrm{T_c})^{\nu}$ is a reciprocal correlation length, with ν a constant. The term η in the exponent is a measure of the deviation from the classical Ornstein-Zeinike behavior; the classical expression is of course obtained when $\eta = 0$. This expression

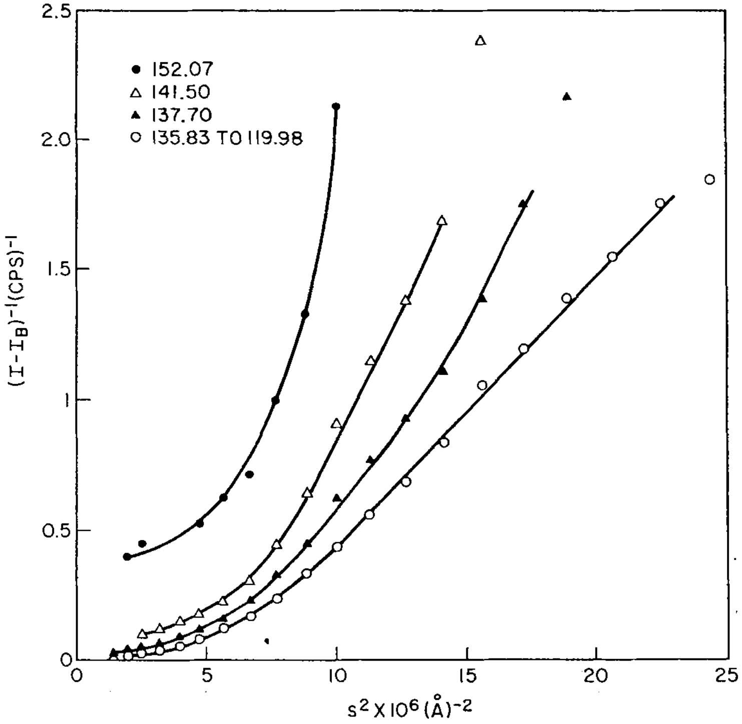

Figure 6. Ornstein-Zernike plot of scattering data.

has been experimentally verified.[14] Thus a plot of I^{-1} against s^2 would in the classical case give a series of straight lines. In the nonclassical case such plots would be concave *downwards* at small values of s^2. Figure 6 shows such a plot of our data and it is evident that the curves are concave *upwards* throughout the whole temperature range. This would imply that η is negative, which is physically impossible, and therefore the transition cannot be a critical point phenomenon.

Thus in sum, we have demonstrated that the heterophase fluctuation theory is valid on the high temperature side of the transition, and have measured the extent of the fluctuations. Our results rule out the possibility of a second or higher order (critical) transition, and in conjunction with the latent heat measurements strongly indicate that it is first order. We will report in the future on the effect of electric fields on the scattering behavior. Finally, it has not escaped our attention that in these X-ray transmission measurements, where the cell thickness is fairly small, that surface effects may be a contributing factor to our results.

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