

## Pretransitional behavior of the density of the nematic phase

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Volume and temperature studies on pentylcyanobiphenyl, in a single-capillary dilatometer capable of a sensitivity in density of  $2 \times 10^{-6}$  g/cm<sup>3</sup> in a constant-temperature bath stable to  $\pm 0.2$  mK, are reported. The data in the nematic-phase pretransitional region have been fit by an equation of the form  $V = a + bT + c |1 - T/T_{SP}|^e$ , where  $T_{SP}$  represents the limit of mechanical stability of the nematic phase (where  $dp/dV=0$ ), and the "pretransition exponent"  $e = 0.50 \pm 0.01$ . To this accuracy, the nematic volume near the transition has the square-root behavior also suggested earlier by experimental results on *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) and other compounds. A new thermodynamic mean-field understanding of this behavior is presented and discussed. Tricriticality of a particular kind is also discussed.

The densities of nematic liquid-crystalline phases show strong pretransitional decrease as the transition to the isotropic phase is approached. Press and Arrott,<sup>1</sup> Chang,<sup>2</sup> Armitage and Price,<sup>3</sup> and others<sup>4-7</sup> have determined the changes of volume with temperature for MBBA, alkyl cyanobiphenyls, and 4,4'-azoxyanisole (PAA) among other nematics. These authors reached no definite conclusion as to the value of the "critical exponent" although a square-root behavior was strongly suggested for various, sometimes unrelated, reasons. We present here, volume-temperature data obtained on pentylcyanobiphenyl (5CB) in a nematic phase. As we discuss below, points in the two-phase region must be excluded from the data set used for finding the "pretransitional exponent."

We have used our dilatometric apparatus for detailed measurements on 5CB, reading 86 points spaced at about 50-mK intervals (or less) in a thermostatted bath stable to  $\pm 0.2$  mK. The  $T_{NI}$  of the sample as observed by microscopy was 37.5°C. The dilatometer consisted of a glass bulb 7 cm<sup>3</sup> in volume topped with a glass capillary of 1-mm internal diameter. The heights were read to 0.02 mm with the aid of a Wild cathetometer (Switzerland). Such measurements correspond to a sensitivity in density of  $2 \times 10^{-6}$  g/cm<sup>3</sup>.

The behavior expected from the mean-field theory is shown in Figs. 1(a) and 1(b). As the temperature is raised, the order parameter  $S$ , determined by  $\partial G/\partial S=0$ , decreases to its lowest possi-

ble value at the point  $L$  in Fig. 1(a), where the mean-field free energy  $G$  has a horizontal inflection,

$$\partial G/\partial S = \partial^2 G/\partial S^2 = 0.$$

For higher temperatures only isotropic solutions,  $S=0$ , are possible. Our earlier calculations,<sup>8</sup> now confirmed by the full solution of the Onsager integral equations,<sup>9</sup> show that the isotherm  $p=p(\rho)$  of the mesophase would have a slope of negative infinity at  $L$ , that is,  $\partial p/\partial \rho = -\infty$  meaning  $L$  marks the limit of orientational stability. Here,  $p$  is the pressure and  $\rho$  is the number density. Moreover, before orientational instability limit at  $L$  could be reached, the "spinodal" point, marked SP in Fig. 1(b), would have to be crossed. Because at SP  $\partial p/\partial \rho=0$  the nematic phase becomes mechanically unstable with respect to isotropic phase, but, is still orientationally stable because [see Fig. 1(a)]  $\partial^2 G/\partial S^2$  is positive. At SP the isotropic density fluctuations would be infinite since the isothermal bulk compressibility is infinite. At constant pressure this limit of mechanical stability of the nematic phase would correspond to some temperature  $T_{SP}$ , presumably higher than the true equilibrium transition temperature  $T_{NI}$ . The temperature  $T^{**}$  corresponding to  $L$ , the ultimate limit of the orientational stability of the mesophase, would probably be higher still. The low temperature limit for isotropic phase existence will be reached at  $T^*$ , when, for  $S$  still zero,  $\partial^2 G/\partial S^2=0$ . This limit, ex-

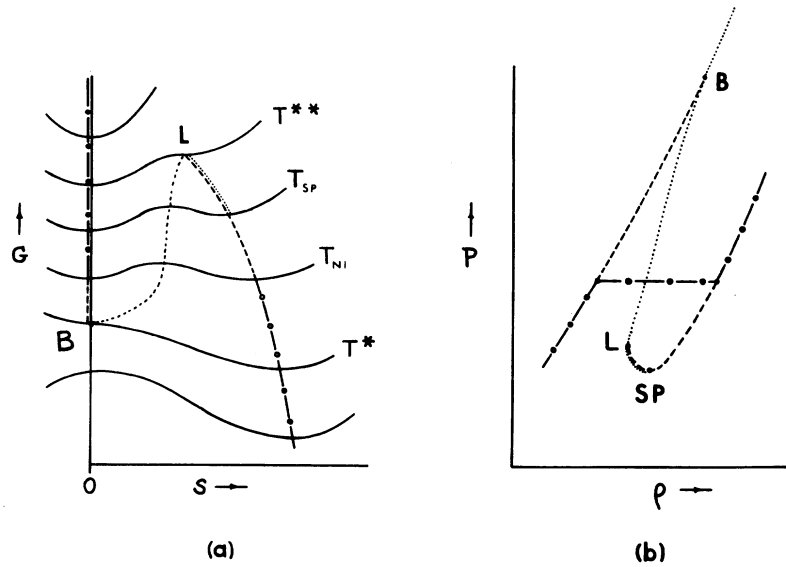


FIG. 1. (a) Mean-field free energy as function of the order parameter. The mesophase occurs at  $T \leq T^*$ . (b) The pressure-density isotherm calculated in Ref. 8. Before  $L$  is reached the nematic becomes mechanically unstable at SP, where  $dp/dV=0$ . The dashed line is the inaccessible locus of maxima in the free energy which joins the isotherm of the isotropic phase at the bifurcation point  $B$ .

pected to be below  $T_{NI}$ , was introduced in early mean-field theories and its existence is indirectly supported, for example, by birefringence data. Temperature  $T^*$  corresponds to the bifurcation point  $B$  in Fig. 1. These four temperatures,  $T^*$ ,  $T_{NI}$ ,  $T_{SP}$ , and  $T^{**}$ , can be discerned within the mean-field theory of the first-order nematic isotropic transition. Pursuing the consequences of the mean-field theory, let us concentrate on the properties of the right-hand side of the lower isotherm in Fig. 1(b), describing the compression of the mesophase. Considering a Taylor's expansion about a point  $p_{SP}$ ,  $V_{SP}$  at constant pressure, we have

$$(p - p_{SP}) = \left. \frac{\partial p}{\partial V} \right| (V - V_{SP}) + \frac{1}{2} \left. \frac{\partial^2 p}{\partial V^2} \right| (V - V_{SP})^2 + \dots \quad (1)$$

At the spinodal point, SP,  $(dp/d\rho) = (dp/dV) = 0$ , and we see immediately that the isotherm behaves like  $(V - V_{SP})^2$ , that is quadratically. This means  $(dp/dV) = \text{const}(V - V_{SP})$ . Since

$$\left. \frac{dV}{dT} \right|_p = - \frac{(\partial p / \partial T)_V}{(\partial p / \partial V)_T}, \quad (2)$$

and assuming further that the numerator of (2) is

well behaved and smooth, we can integrate Eq. (2) between two states at the same pressure, to conclude that the volume will vary as  $(T_{SP} - T)^{1/2}$  and that the thermal expansion  $dV/dT$  will diverge as  $(T_{SP} - T)^{-1/2}$ . The constant pressure curve  $V = V(T)$  should look like the dashed line shown in Fig. 2 for a hypothetical absolutely pure substance. Integrating Eq. (2) and allowing for a linear background term, we obtain

$$V = a + bT + c |1 - T/T_{SP}|^e, \quad (3)$$

with  $e=0.5$ . Similar equations have been used in Refs. 1 and 3, but with a different explanation of the origin of the exponent and the position of the asymptote to the  $dV/dT$  vs  $T$  curve. Here the exponent is  $\frac{1}{2}$ , simply because the isotherm  $p-V$  is quadratic, as derived above. One might expect the experiment to deviate from this prediction. The experimental pattern, as shown by the solid line in Fig. 2, is complicated by the fact that no ideally pure liquid crystal exists so that the single clearing point  $T_{NI}$  in reality splits into two temperatures  $T'$  and  $T''$  delimiting the two-phase region. The latter region *must be excluded from the analysis* since in that region  $dV/dT$  is due to the changing proportion of the two phases as well.

Figure 3 shows the deviations from experiment obtained using Eq. (3) with the constants

$$a = 241.6808 \text{ cm}^3 \text{ mol}^{-1},$$

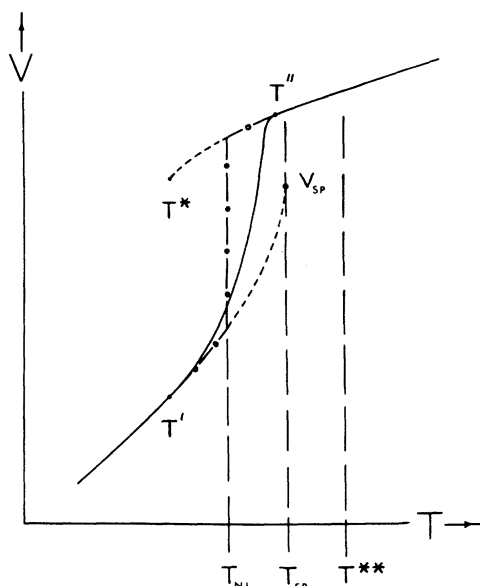


FIG. 2. Volume as a function of temperature of the nematic two-phase and isotropic regions for a substance which is not absolutely pure. At  $T'$  the first drop of the isotropic phase appears and at  $T''$  the last drop of the nematic disappears.  $T_{SP}$  is above  $T'$ . The nematic was extrapolated about  $T'$  and has a cusp at  $T_{SP}$  corresponding to a volume  $V_{SP}$ .

$$b = 0.144436 \text{ cm}^3(\text{°C})^{-1}\text{mol}^{-1},$$

$$c = -0.470472 \text{ cm}^3(\text{°C})^{-0.5}\text{mol}^{-1},$$

$$T_{SP} = 37.5554 \text{ °C} \pm 0.0005,$$

and

$$e = 0.50 \pm 0.01.$$

Therefore, the compressibility divergence exponent is equal to its mean-field value  $e = \frac{1}{2}$ . This is our principal result. It is not really understood because if the transition is simply first order the mean-field reasoning requires a continuation into a region of metastable states up to the divergence of the isothermal compressibility of the nematic and that can hardly be accepted, except provisionally. The same path at the liquid-vapor critical isotherm corresponds to the exponent delta, but here, we are on an isotherm which can be likened to the liquid isotherm well below the critical point.

Recently Keyes<sup>10</sup> has suggested that tricritical values may be assigned to exponents related to orientational instability of the isotropic phase at  $T$ . Priest and Lubensky<sup>11</sup> have applied renormalization-group theory to orientational ordering of liquid crystals but not to the mechanical instability of the nematic, which governs the thermal expansion divergence. Recent specific-heat measurements of Anisimov *et al.*<sup>12</sup> support this idea of a tricritical behavior. Let us examine what tricritical behavior could mean in our context. We can see from Fig. 1(a) that a tricritical point in the  $G$ - $S$  relationship corresponds to the disappearance of the (unstable)  $B$ - $L$  part containing maxima of  $G$  vs  $S$ , thus to the merging of points  $B$  and  $L$ . If  $B$  is dis-

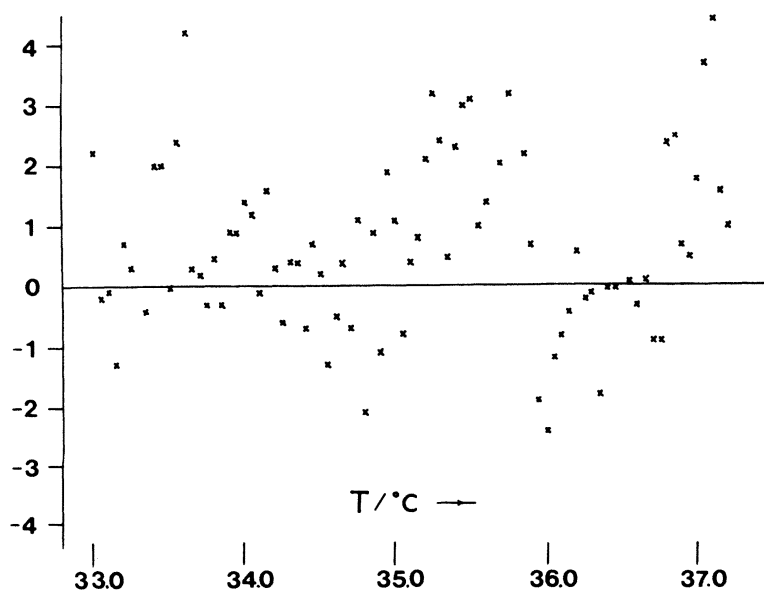


FIG. 3. The deviation plot of our experimental results and Eq. (1) in arbitrary units. Roughly 1 on the graph corresponds to  $1 \times 10^{-4}$  % change in the total volume.

tinct from  $L$ , the transition is first order, and if only  $B$  appears and no  $L$ , the transition is second order. However, a closer examination of the isotherm, Fig. 1(b), shows that the relationship between  $G$  and  $S$  represents only a part of the picture. Even after  $L$  has come closer to  $B$  and then disappeared from the diagram, the transition may still be first order if the isotherm of the mesophase starts from  $B$  with a negative slope,  $dp/d\rho < 0$ . The points between  $B$  and SP will still be unstable and the transition, first order. The transition becomes second order with  $dp/d\rho > 0$  at  $B$  both for the isotropic and for the mesophase only after SP has merged with  $B$ . We had such a case in our calculations<sup>13</sup> for a two-dimensional system where a tricritical point of the kind has been found. There, the changeover from a first-order to a second-order transition occurred in relation to the slope of the  $p$ - $\rho$  isotherm, whereas the  $G$ - $S$  relationship predicted a second-order transition in all cases. Such a tricritical point has a horizontal slope,  $dp/d\rho = 0$  at  $B$ . Moreover, for  $dp/d\rho < 0$  the transition becomes first order. Near such a tricritical point, the

tricritical point is the same point as  $B$  and the spinodal point, Eq. (1) also applies. Thus our results are explained by a proximity to the spinodal point which may, in fact, be a tricritical point. This is perhaps a more satisfactory statement since a spinodal point is never accessible experimentally while such a tricritical point might be. It remains to await for a deeper explanation as to why a tricritical behavior should be expected at all. To date there is no theory molecular or otherwise which would produce such a point, with a possible exception of Ref. 13 which, however, deals only with  $d = 2$ .

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