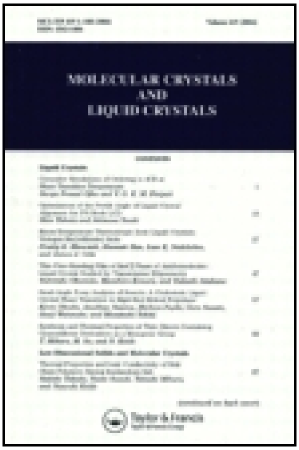

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Interpretation of Thermodynamic Derivatives Near the Liquid Crystal Phase Transition in p-Azoxyanisole

Richard Alben [a]

[a] Department of Engineering and Applied Science, Yale University, New Haven, Connecticut, 06520

Version of record first published: 08 Dec 2010.

To cite this article: Richard Alben (1970): Interpretation of Thermodynamic Derivatives Near the Liquid Crystal Phase Transition in p-Azoxyanisole, Molecular Crystals and Liquid Crystals, 10:1-2, 21-29

To link to this article: http://dx.doi.org/10.1080/15421407008083483

Molecular Crystals and Liquid Crystals. 1970. Vol. 10, pp. 21–29

Printed in Great Britain

Interpretation of Thermodynamic Derivatives Near the Liquid Crystal Phase Transition in *p*-Azoxyanisole

RICHARD ALBEN

Department of Engineering and Applied Science
Yale University
New Haven, Connecticut 06520

Received August 11, 1969; *in revised form November* 17, 1969

Abstract —A general theory of phase transitions described by a single order parameter is applied to the nematic liquid crystal PAA. From previously published results on expansivity, sound velocity, and specific heat, it is shown for the nematic–isotropic phase transition in this substance (a) the coexistence curve is a curve of constant order parameter, and (b) the order parameter slightly below the transition is a function of $V^{4.3}T$, where V is volume and T is temperature.

Many phase transitions have been successfully characterized in terms of an order parameter.[1] Provided there is just one such parameter it is possible to formulate a general theory which is independent of the detailed nature of the transition but still gives a few useful relations. We will apply such a theory to the nematic–isotropic phase transition in *p*-azoxyanisole (PAA) and show, within ± 10% that (a) the coexistence curve is a line of constant order parameter and (b) the variation of the order parameter with reduced volume is 4.3 times that with reduced temperature.

General Theory

Consider an order parameter (η) which appears in the free energy (g). The equilibrium (unconstrained) value of η, which minimizes

g at a particular temperature (T) and pressure (p), is $\eta(T, p)$. We assume that g is a well-behaved function of η, but that η is not a well-behaved function of T and p for ranges of T, p which constitute the phase transition region. In summary:

$$g = g(T, p, \eta) \tag{1}$$

$$\left.\frac{\mathrm{d}g}{\mathrm{d}\eta}\right|_{\eta = \eta(T,\, p)} = 0.$$

Differentiating the stationary condition with respect to T and p yields:

$$g_{\eta T} = -g_{\eta\eta}\eta_T,$$

$$g_{\eta p} = -g_{\eta\eta}\eta_p. \tag{2}$$

where the subscripted arguments denote partial differentiation. The stationary condition permits us to take for the entropy

$$S(T, p, \eta) = -g_T. \tag{3}$$

Thus the specific heat (at constant pressure) divided by the temperature is

$$C/T = \left.\frac{\mathrm{d}S}{\mathrm{d}T}\right|_{\eta=\eta(T,\, p)} \tag{4a}$$

$$= S_\eta \eta + S_{TT} \tag{4b}$$

$$= g_{\eta\eta}(\eta_T)^2 + S_T \tag{4c}$$

where the last equality follws from (2) and (3).

The first term in (4c) arises from a derivative of η; it might well be very large where η changes rapidly. We denote this term by $\Delta C/T$, where Δ denotes a " transition contribution " to the quantity in question. For the above identification to hold, it is not necessary that the transition be a critical one. What is required is that the Δ-quantity be large and rapidly varying enough to be distinguished from the non-transition background. According to present ideas liquid crystal transitions are not critical, but, as we shall see, there is region over which both pre- and post-transition effects in p-azoxyanisole are distinguishable.

The second term in (4c) is a derivative at constant η. It is tempting to associate this with a background, not sensitive to the transition. However, S_T is a function of η and rapid changes in η will create bumps in the background. The bumps are an intrinsic difficulty with this whole approach; they cannot be defined away, and they create ambiguities in identifying the η-derivative Δ-quantities. Since it is only the η-derivative quantities about which general statements can be made, we must further require that non η-derivative Δ-quantities must be much smaller than their η-derivative conterparts.[‡]

Proceeding as in (4) with regard to α, the isobaric thermal expansion coefficient and β, the isothermal compressibility, we may complete the list of η-derivative Δ-quantities.

$$\begin{aligned} \Delta C/T &= S_\eta \eta_T = g_{\eta\eta}(\eta_T)^2, \\ -V\Delta\alpha &= -V_\eta \eta_T = g_{\eta\eta}\eta_p\eta_T, \\ V\Delta\beta &= -V_\eta \eta_p = g_{\eta\eta}(\eta_p)^2 \end{aligned} \tag{5}$$

where V is the volume. From (5) follows a "scaling law" relation which will provide a check on the applicability of the theory.

$$(\Delta\alpha)^2 = \Delta\beta \times \Delta C/TV \tag{6}$$

Little has been said of the physical meaning of η because the results of this analysis do not involve a physical theory. Note that nothing would be changed if for η was substituted some arbitrary (but well-behaved) function of η. There is nothing in this formulation which gives the functional form of $\eta(T, p)$ or even the order of the transition.

[‡] Consider for example the ambiguity in the specific heat per unit volume which occurs because of the transition effect on the volume:

$$\left(\frac{1}{V}\Delta\frac{C_p}{T} - \Delta\frac{C_p}{TV}\right) = \frac{1}{V}\Delta\frac{C_p}{T}\left(\frac{\Delta V}{V}\right) \bigg/ \frac{\Delta C_p}{C_p}.$$

$\Delta V/V$ is the relative change in a non-derivative quantity; for PAA it is always less than 2×10^{-3}. $\Delta C_p/C_p$ is the relative change in a derivative quantity; it reaches about 0.2. Thus the ambiguity in $(1/V)(\Delta C_p/T)$ is less than 1%.

There are physical theories of liquid crystals which are of the type discussed above; we discuss them briefly as examples of what the order parameter might be. The molecular-statistical theory of Maier and Saupe[2] defines a long-range order parameter for the pre-transition region.

$$S = \tfrac{1}{2} < 3 \cos^2\theta - 1 > \tag{7}$$

θ is the angle between the long axis of a given molecule and the average nematic axis, and $< >$ denotes expectation value. That S may be found by minimizing a suitable g is easily checked since self-consistency and minimum free energy are equivalent conditions in this sort of " molecular field " approximation.[3]

For the post-transition region the Frenkel heterophase fluction theory has been employed.[4] This is not usually presented as a single order parameter theory. However, it is possible to force it into such a form using, for example, the total number of molecules in the ordered phase as an order parameter.‡ Thus it is not surprising that the predicted heterophase contribution to the thermodynamic derivatives follows the scaling law (6).[4]

‡ The Gibbs free energy may be written as:

$$g = tr\rho(\mathscr{H} + p\mathscr{V}) + kT\, tr\, \rho \ln \rho$$

where $\mathscr{H}$ is the Hamiltonian, $\mathscr{V}$ is the volume operator (giving the volume associated with each state), the trace includes integration over continuous variables and ρ is an operator of unit trace to be specified by minimizing g. The actual minimum occurs when ρ is the true density matrix.

In the Frenkel theory,[10] $\rho(p, T)$ specifies a distribution of molecules between the disordered phase and among groups which have characteristics of the ordered phase. We may imagine $\rho(p, T)$ as some $\rho(p, T, \eta)$ evaluated at $\eta = \eta(p, T)$ where $\eta(p, T)$ minimizes g. For η take N_A, the total number of molecules in ordered phase. Introducing this self-consistency leaves considerable freedom of form for $\rho(p, T, N_A)$ but one way might be to scale the latent heat by some complicated function of N_A, p, and T such that $N_A = tr\, N_A\, \rho(p, T, N_A)$. The scale factor would also have to become 1 for $N_A = N_A(p, T)$ so that we are led back to the Frenkel disruption at equilibrium. Now it is readily verified that $N_A(p, T)$ varies rapidly near the transition. Also variation of g at constant N_A will not lead to dramatic effects. Thus we have the elements necessary for a single order parameter theory.

Results for PAA

p-azoxyanisole is the most completely studied nematic liquid crystal system; it is the only one for which reasonably accurate measurements of the three second derivatives of g have been published. (β is derived from measurements of sound velocity.) A review of these data is shown in Fig. 1. The background is taken as the dotted curves. The implied Δ-quantities both above and below the transition are listed in Table 1. T_r is the transition temperature.

TABLE 1 Transition contributions to thermodynamic derivatives. These are the heights-above-background estimated from Fig. 1. The accuracy is about ±10% below T_r and ±25% above.

$T - T_r$ (K°)	$\Delta C/TV$ (erg deg^{-2} cm^{-3})	$\Delta\alpha$ (deg^{-1})	$\Delta\beta$ (cm^2 dynes^{-1})
-6	0.18×10^4	0.18×10^{-3}	6.1×10^{-12}
-5	0.22	0.20	7.8
-5	0.29	0.23	9.5
-3	0.29	0.27	11.5
-2	0.55	0.34	14.0
-1	0.87	0.47	21.0
-0.5	1.10	0.62	30.0
-0	1.68		
$+0$	0.84		
$+0.5$	0.42	0.15	
$+1$	0.31	0.10	6.0
$+2$	0.19	0.06	3.3
$+3$	0.11	0.04	2.1
$+4$	0.07	0.02	1.0
$+5$	0.04	0.01	0.6

The transition effects stand well above the background from about 5° below to 3° above the transition. Beyond these limits any small shift in what is called the background significantly alters the Δ-quantities. On the other hand, close to the transition temperature most measurements become less accurate. In particular the expansivity is necessarily averaged over a temperature increment of several tenths of a degree. This averaging

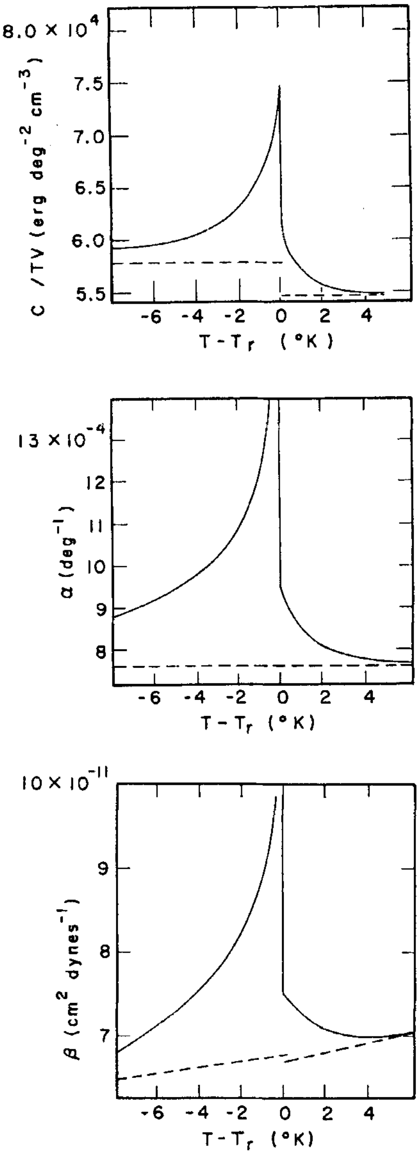

Figure 1. Experimental values of C, α, β in PAA. In all cases the temperature scale was set by taking the maximum effect as occurring at T_r. Dotted lines are the estimated non-transition background.

(a) C/TV from numerical results of Arnold[3] on C combined with density measurements of Maier and Saupe[5], $T_r = 135.3\,^\circ$C.

(b) α from a graph by Maier and Saupe[6], $T_r = 136\,^\circ$C.

(c) β from a graph by Kapustin and Bykova,[6] $T_r = 132\,^\circ$C. (These results agree with those of Hoyer and Nolle.[7])

introduces significant errors as the transition temperature is approached. Sound velocity measurements have been made in a frequency regime where attenuation near the transition seems to limit the accuracy of the compressibility results. The region from 1° to 3° from the transition probably contains the most precise information. A pessimistic estimate is that the errors are about $\mp 10\%$ below, $\pm 25\%$ above.

The only genuinely physical quantity which the Δ-quantities enable us to calculate is the ratio η_T/η_p. From (5) there are three ways to calculate this (only two are independent). The various results are given in Table 2. If the scaling law (6) were fulfilled the three values at a given temperature would agree. The fact that they apparently do not for the post-transition region is an indictment of the Frenkel theory, along with the whole class of single order parameter theories for that region. The pre-transition region provides a more encouraging picture. At each temperature the mean value of η_T/η_p is about 2×10^7 dyne/K°.

TABLE 2 The ratio η_T/η_p computed in three ways for temperatures near the transition. The values for each temperature would agree if the scaling law Eq. (6) were obeyed.

$T - T_r$	$\dfrac{\Delta C/TV}{\Delta\alpha}$	$\dfrac{\Delta\alpha}{\Delta\beta}$ (dynes deg^{-1} cm^{-2})	$\left[\dfrac{\Delta C/TV}{\Delta\beta}\right]^{1/2}$
-3	1.4×10^7	2.4×10^7	1.8×10^7
-2	1.6	2.4	2.0
-1	1.9	2.2	2.0
-0.5	1.8	2.1	1.9
$+0.5$	2.9		
$+1$	3.1	1.7	2.3
$+2$	3.1	1.8	2.4

The first useful interpretation of η_T/η_p follows from

$$\left.\frac{\partial\eta}{\partial T}\right|_p \Big/ \left.\frac{\partial\eta}{\partial p}\right|_T = \left.\frac{\partial p}{\partial T}\right|_\eta \tag{8}$$

Thus η_T/η_p is the slope of a line of constant order parameter.

The slope of the coexistence curve between liquid crystal and isotropic liquid states is, to about 2%, 2×10^7 dynes/K°.[8] Thus within the 10% accuracy of η_T/η_p the coexistence curve is a line of constant order parameter.‡

The second relation we can get from η_T/η_p is the change of the order parameter with temperature compared with its sensitivity to volume. For a small variation of temperature and volume around V_0, T_0, near but not including the transition, we may expand:

$$\eta(V, T) = \eta(V_0, T_0) + V\frac{\partial\eta}{\partial V}\left(\frac{V}{V_0} - 1\right) + T\frac{\partial\eta}{\partial T}\left(\frac{T}{T_0} - 1\right)\dots, \qquad (9)$$

and then define

$$n = V\frac{\partial\eta}{\partial V}\Big/\frac{\partial\eta}{\partial T}. \qquad (10)$$

n will be our measure of relative sensitivity. To first order in deviations (9) is equivalent to:

$$\eta = \eta^{V_0T_0}(V^nT). \qquad (11)$$

where the superscripts imply that the functional form depends on the point around which we expand. For the physical model of ordering due to molecular dispersion forces n is 2.§

It is straightforward thermodynamics to reduce (10) to

$$n^{-1} = aT[\beta/a(\eta_T/\eta_p) - 1] \qquad (12)$$

---

‡ The Maier and Saupe theory predicts that η will change along the coexistence curves. However, the change would be a subtle one, depending weakly on variation of the transition volume dialation and not be sensible within the accuracy of our determination.

§ Maier and Saupe, who proposed the molecular dispersion model, computed predictions for transition value of the order parameter[5] as a function of the transition volume change. Ideally such predictions could be used to check the value of $n = 2$ or alternatively to find n. Actually, however, the predicted change in S is too small for NMR and other techniques to measure.

For PAA with α and β evaluated at 1 °K below T_r we get $n = 4.3$. The 2 °K values for α and β give $n = 4.6$. It is to be noted that n as given by (12) is well behaved as T_r is approached from below even though α and β both change rapidly.

The value of 4.3 for n implies that the interaction responsible for ordering increases as the 13th power of the average intermolecular center of mass separation ($V^n = r^{3n}$). This is then evidence for a role for short range shape dependent[9] forces in the liquid crystal state.

In summary, we have proposed a " theory independent " approach to the nematic liquid crystal-isotropic phase transition in PAA. Especially below the transition, it seems that a single order parameter can self-consistently describe the transition anomalies in α, β and C. Thus we have been able to employ relationships among experimental data to argue the constancy of the transition order parameter and determine the incremental variation of the ordering energy with change in volume.

REFERENCES

1. Landau, L. D. and Lifshitz, E. M., *Statistical Physics* (Pergamon Press Ltd., London, 1958), p. 430 ff.; Boccara, N., *Solid State Commun.* **7,** 331 (1969).
2. Maier, W. and Saupe, A., *Z. Naturforsch,* **142,** 882 (1959).
3. Radcliffe, J. M., *Phys. Rev.* **165,** 635 (1967).
4. Hoyer, W. A. and Nolle, A. W., *J. Chem. Phys.* **24,** 803 (1956); Torgalkar, A., Porter, R. S., Barrall, E. M. II and Johnson, J. F., *J. Chem. Phys.* **48,** 3897 (1968).
5. Arnold, H., *Z. Phys. Chem.* (Leipzig) **226,** 146 (1964).
6. Maier, W. and Saupe, A., *Z. Naturforsch.* **15a,** 287 (1960).
7. Kapustin, A. P. and Bykova, W. T., *Sov. Phys. Crystallogr.* **11,** 297 (1966).
8. Robberecht, J., *Bull. Soc. Chim. Belg.* **47,** 567 (1938).
9. Saupe, A., *Mol. Cryst.* **1,** 527 (1966).
10. Frenkel, J., *Kinetic Theory of Liquids* (Dover, 1955), p. 382.