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The Effect of Compressibility on the Thermodynamic Properties of Liquid Crystals (I)

The Nematic-Isotropic Phase Transition

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The effect of liquid compressibility on the nematic-isotropic phase transition is investigated according to the method of Mattis and Schultz using a volume dependent Hamiltonian in a constant pressure partition function. The theory is able to account for the large difference in constant pressure and constant volume transition temperatures, and the volume change at the constant pressure transition for para-azoxyanisole.

I INTRODUCTION

The importance of both attractive and repulsive molecular forces for the nematic-isotropic phase transition has been demonstrated by Deloche and Cabane,[1] and by McColl and Shih.[2,3] McColl and Shih determined the orientational order parameter for para-azoxyanisole at constant volume. They report a constant volume (221 cm^3/mole) transition temperature of 437.5°K as compared to a constant pressure transition temperature, at one atmosphere, of 409°K. This large difference in transition temperatures certainly indicates that volume is a significant factor for the constant pressure phase transition. McColl and Shih also calculated a constant volume order parameter from a Landau expansion of the Helmholtz free energy containing both orientational and packing entropy terms. Their calculation gave good agreement with experimental values over a wide range of temperatures.

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The purpose of this paper is to investigate a simple method for determining the constant pressure thermodynamic properties of a nematic liquid from a constant volume statistical model. The method is based on a modification of the theory of Mattis and Schultz[4] who considered the effect of lattice compressibility on the ferromagnetic phase transition.

II THEORY

We assume that the ordering effects in a nematic liquid take place in a fluid background which is treated as a harmonic continuum. Furthermore, we assume that the background fluid is isotropic with respect to compression or extension so that the energy of compression can be described in terms of a single variable δ where $\delta = (V - V_0)/V_0$ is the fractional change in volume and V_0 is the volume of the liquid crystal in some stress free state. Following Mattis and Schultz we consider a Hamiltonian of the form

$$H = \frac{\delta^2 V_0}{2K_0} + f(\delta) H^0(V_0) \tag{1}$$

where $H^0(V_0)$ is the constant volume Hamiltonian of the liquid crystal taking account of the orientational order in the stress free state defined by V_0. K_0 is the compressibility of the background fluid and $f(\delta)$ is some function which expresses volume dependence of the orientational energy. The Helmholtz and internal energies appropriate to the constant volume system are, in terms of the usual thermodynamic relations,

$$F(V_0, \beta) = -\frac{1}{\beta} \ln \operatorname{Tr}(e^{-\beta H^0}) \tag{2}$$

and

$$U(V_0, \beta) = \frac{\partial}{\partial \beta} [F(V_0 \beta)] \tag{3}$$

where $\beta = (kT)^{-1}$. The Gibbs free energy is based on the trace of an isothermal-siobaric partition function and is

$$G(\beta, P) = -\frac{1}{\beta} \ln Z = -\frac{1}{\beta} \ln \operatorname{Tr} e^{-\beta(H + PV)} \tag{4}$$

where H is defined by (1). The partition function in (4) is evaluated by first summing with respect to the orientational variables only, treating δ as a parameter. This gives, after substituting for H from (1),

$$Z = \exp\{-\beta[\delta^2 V_0/2K_0 + P(1 + \delta)V_0 + f(\delta)F(V_0, \beta^*)]\} \tag{5}$$

where

$$T \equiv T^*[f(\delta)], \qquad \beta \equiv \beta^*/f(\delta) \tag{6}$$

The relations shown in (6) are identities which must be satisfied according to the expressions (2) and (5). They determine an effective thermodynamic temperature T^* defining the state of the system at constant volume V_0 in terms of the temperature T for the system at constant pressure P. The relations between T and T^*, or β and β^* provide one of two self consistency conditions which allow one to relate between the constant volume and constant pressure system. The second condition is obtained by specifying explicitly the volume dependence of the orientational energy $f(\delta)$ and then minimizing $G(\beta, P)$ with respect to δ. For $f(\delta)$ in a nematic liquid we shall assume that the attractive orientational forces are of the dispersion type and vary as $1/r$.[6] This is consistent with the assumptions of the Maier–Saupe[5] theory of the nematic phase and has been widely used by others in mean field calculations. $f(\delta)$ is then

$$f(\delta) = 1/(1 + \delta)^2. \tag{7}$$

Substituting (7) into (5) and maximizing with respect to δ gives

$$(1 + \delta)^3(\delta + K_0 P) = \frac{2K_0 U^0}{V_0}(\beta^*) \tag{8}$$

This is the second of the pair of self consistency relations for the thermodynamically stable states. The term U^0 refers to the internal energy of the system at constant volume V_0, and at the temperature T^*.

The theory of Mattis and Schultz is particularly useful for predicting qualitatively the behavior of the system in the region of the phase transition at constant pressure if the behavior at constant volume is known. This is illustrated schematically in Figure 1. We consider the expression

$$\phi = (1 + \delta)^3(\delta + K_0 P)$$

and express the self consistency conditions in terms of:

$$\phi_1 = 2K_0 U^0(\beta^*)/V_0 \tag{9}$$

$$\phi_2 = (\beta/\beta^*)^{3/2}[(\beta/\beta^*)^{1/2} - 1 + K_0 P] \tag{10}$$

The stable states are determined by a graphical construction as shown in Figure 1. ϕ_1 is determined by the compressibility of the background fluid and the internal energy, plotted as a function of β^*, which is assumed to be known from some constant volume theory. In Figure 1 we have shown ϕ_1 for three different situations corresponding respectively to a first order phase transition, a second order transition with a sharp change in U^0 in the

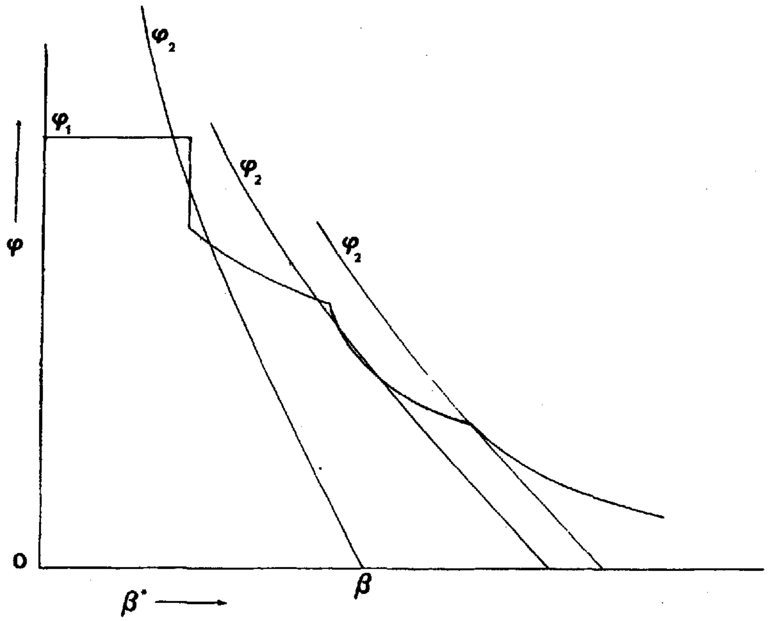

FIGURE 1 Plot of self-consistent equations ϕ_1 and ϕ_2 *vs* β^* at $P = 1$ atm. For ϕ_1 three different types of transition are shown schematically. A first order (constant volume) transition, a strong second order transition, and a weak second order transition. The intersection of ϕ_2 with the β^* axis determines the constant pressure temperature β. The transition temperature is determined by selecting the function ϕ_2 which cuts euqal areas on the ϕ_1 curve.

region of T_c^*, and a gradual change in U^0 in the region of T_c^*. ϕ_2 is also shown in each case for a single value of β (the constant pressure temperature of the system). In examples (1) and (2) ϕ_2 is chosen so that equal areas are cut in the two phase region†, and corresponds to the transition temperature at constant pressure. In example (1), the transition is first order but occurs at the temperature $\beta \neq \beta^*$ at constant pressure P. In example (2) the second order constant volume transition has become first order at constant pressure‡. In the third example the transition remains second order. We see that, in general, the behavior of the constant pressure system is determined by the magnitude

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† Mattis and Schultz have given proof of the equal area construction for a particular volume dependent Hamiltonian appropriate to the ferromagnetic phase transition. We have been able to prove the stability criteria and the equal area construction for any differentiable function $f(\delta)$.

‡ This is the type of behavior discussed by Mattis and Schultz showing that the ferromagnetic transition can be weakly first order depending on the extent of coupling between the spin variables and the lattice. The example in Figure 1 is only schematic and the first order behavior depends on the slopes of both ϕ_1 and ϕ_2. The slopes in turn depend upon the pressure and the compressibility. If the value of the compressibility is small, as in a solid phase, there will be little difference between constant pressure and constant volume behavior.

of the compressibility and the slope of the internal energy in the region of the transition.

The isobaric thermal expansivity and the temperature dependent compressibility are easily obtained from the temperature and pressure derivatives of δ. The expansivity is

$$\left(\frac{\partial\delta}{\partial T}\right)_p = \alpha_p = \frac{2K_0(1+\delta)C_v(\beta^*)}{(1+\delta)^3 + 3(1+\delta)(\delta + K_0 P)V_0 - 4K_0 C_v(\beta^*)t} \tag{11}$$

and the isothermal compressibility is

$$-\left(\frac{\partial\delta}{\partial P}\right)_T = K_t = \frac{(1+\delta)V_0\alpha_P}{2C_v(\beta^*)} \tag{12}$$

We can also express $C_P(\beta)$ in terms of $C_v(\beta^*)$. The result is

$$C_P(\beta) = (1 + 2\alpha_P T^*)C_V(\beta^*). \tag{13}$$

Finally, it should be pointed out that the method of Mattis and Schultz suffers the same limitations as any theory which results from minimizing the free energy function with respect to a single parameter. The limitations of mean field type calculations for the nematic-isotropic phase transition have been discussed extensively by Alben.[6] In particular the interpretation of the theory in the region of a phase transition is questionable because there is no provision for the important effect of fluctuations. The Mattis and Schultz theory has been criticized on this basis.[7] For certain properties of liquid crystals, however, such as the difference in the constant pressure and constant volume transition temperatures or the volume change at the transition, we shall show that the method described above gives results which compare favorably with experimental values.

III RESULTS AND DISCUSSION

The effect of compressibility will be determined from the constant volume measurements of McColl and Shih[2,3] on para-azoxyanisole. The order-disorder contribution to the internal energy is given by

$$U^0(\beta^*, V_0) = \frac{E}{2}(1 - S^2) \tag{14}$$

where $E/2$ is the molar internal orientational energy in the isotropic phase, and S is the constant volume order parameter. For E we take the value

$$E = 4.4876\, T_{N-I}(R)$$

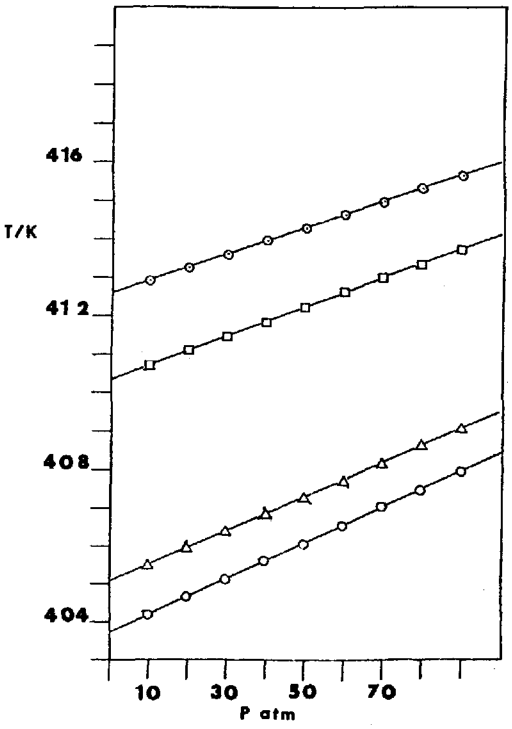

FIGURE 2 Constant Pressure transition temperature *vs* Pressure for various assumed values of the background fluid compressibility K_0.
⊙ $K_0 = 4.5 \times 10^{-11}$ cm^2/dyne, □ 5.0×10^{-11} cm^2/dyne,
△ 6.2×10^{-11} cm^2/dyne, ○ 6.6×10^{-11} cm^2/dyne

determined from the Maier–Saupe theory assuming constant volume. For the order parameter S we shall use the values reported by McColl and Shih determined from the two parameter Landau expansion at constant volume.†

In order to determine the transition temperature at constant pressure we need a value for the compressibility of the background fluid at the experimental molar volume $V_0 = 221$ cm^3/mole. This value is used to calculate ϕ_1 in equation (10). This is done by assuming a value for K_0 and determining the transition temperature at different pressures according to the graphical construction of example 1 in Figure 1. The actual calculations were done by

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† We could have chosen the order parameter calculated from the Maier–Saupe model (assuming constant volume) which neglects the packing and mixing entropy. The order parameter calculated from this theory is somewhat larger, particularly at lower temperatures, than the values determined by McColl and Shih. We have done the calculations for both models and find that the difference in constant volume S values has little effect on the constant pressure thermodynamic properties predicted by the method of Mattis and Schultz.

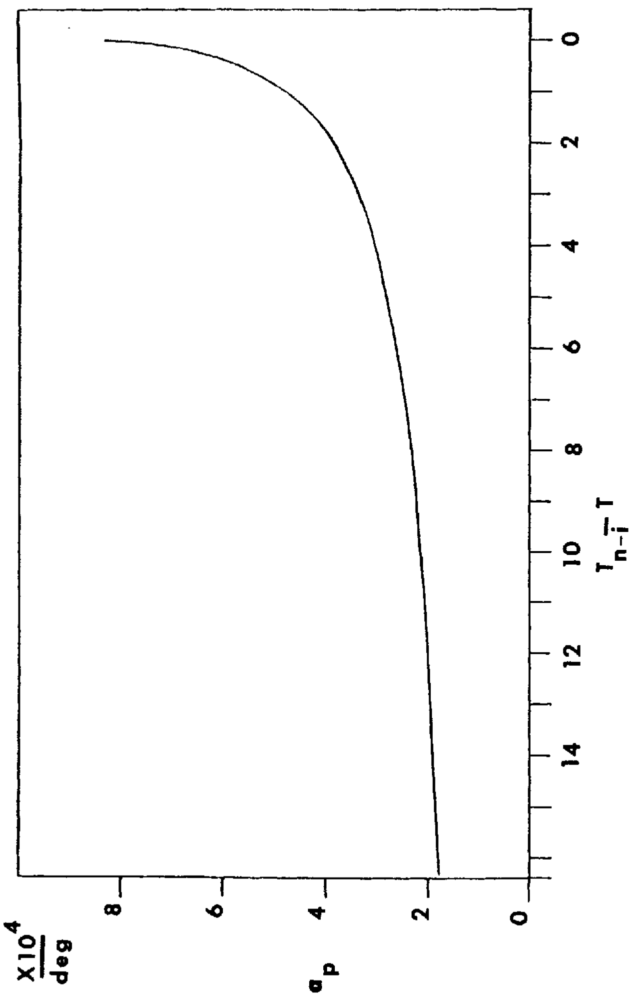

FIGURE 3 Order-disorder contribution to the isobaric expansivity *vs* $T_{N-I} - T$ for $K = 5.0 \times 10^{-11}$ cm^2/dyne at 1 atm.

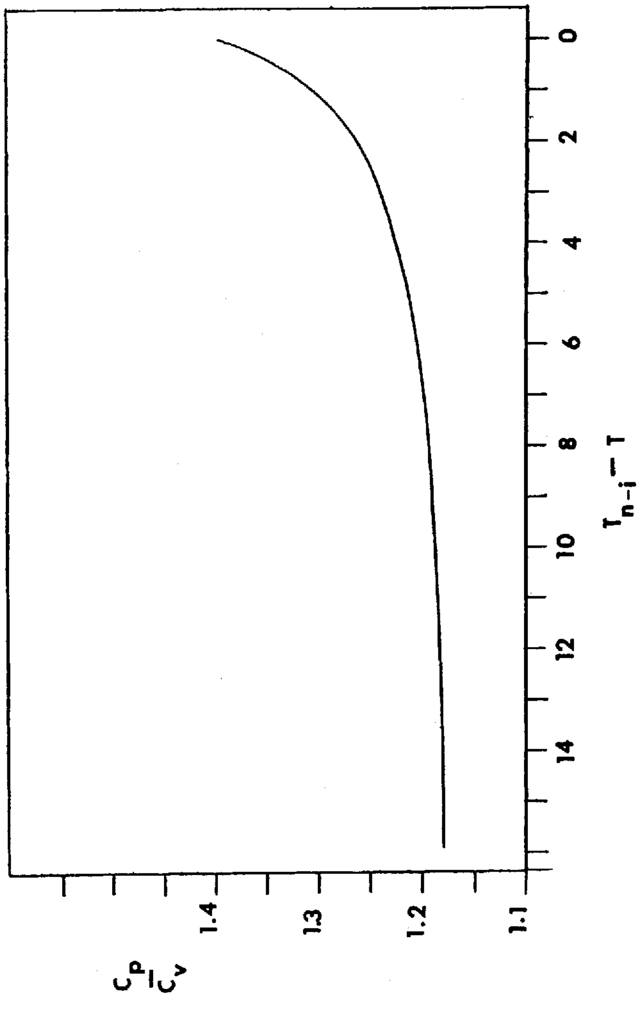

FIGURE 4 Order-disorder contribution to C_p/C_C *vs* $T_{N-I} - T$ at 1 atm.

simultaneous computer solution of the self consistent equations. A plot of the transition temperature as a function of pressure for several different values of K_0 is shown in Figure 2. The slope of this curve is known for para-azoxyanisole from the data of Tikhomirova *et al.*[8] who report a value of 0.03235 deg/atm for dT_{N-I}/dP. From the slopes of the curves in Figure 2 we find the best value for $K_0 = 5.0 \times 10^{-11}$ cm^2/dyne. The transition temperature at 1 atm. is 410.4 K in good agreement with the experimental value of 409 K.

The relative volume change $\Delta V/V$ for the transition at 1 atm. is found to be 0.0044. Again this value is in fair agreement with the experimental value of 0.0035 reported by Maier and Saupe.[9] The enthalpy change at the transition is 303 cal/mole as compared to the experimental value of 143 cal/mole obtained from the heat capacity data of Arnold.[10] Alben[6] has shown that the enthalpy change determined from mean field calculations is characteristically too high. The value we obtain is somewhat lower than that obtained from the Maier–Saupe theory because the constant volume order parameter is smaller ($S = 0.345$) at the transition.

The order disorder contribution to the coefficient of thermal expansion (α_P) and the ratio C_P/C_V are shown in Figures 3 and 4. These are included only to illustrate how the temperature dependence of these quantities can be determined from the theory of Mattis and Schultz. They are not compared with experimental data because the effects of fluctuations have not been included in the calculations and because it is difficult to separate out the order-disorder contributions from the remaining degrees of freedom.

In summary, we can conclude that the method of Mattis and Schultz can be used effectively for qualitative predictions of constant pressure behavior of nematic liquids from a constant volume model. The method can be extended to other types of mesophase transitions some of which are believed to be second order. In that case it is possible for a constant volume model which predicts a second order transition, such as the McMillan[11] theory for the smectic A-nematic transition to become first order at constant pressure. These results will be the subject of a later communication.

Acknowledgements

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