Temperature Dependence of Orientational Order in a Nematic Liquid Crystal at Constant Molar Volume*

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(Received 2 May 1972)

Results on the temperature dependence of orientational order at constant molar volume in the nematic liquid crystal p-azoxyanisole are reported for the first time. These results clearly indicate the failure of theories of the nematic phase which do not include both energetic and steric intermolecular interactions.

In this Letter, we report the first constant-volume measurements of long-range orientational order in a nematic liquid crystal. These measurements make possible the first realistic assessment of the respective roles of attractive and repulsive interactions as the microscopic origin of this order.

The long-range molecular alignment, characteristic of nematic systems, is considered to be due to anisotropic intermolecular interactions. Since nematics consist of molecules whose shape and structure are inevitably rather complicated there is very little *a priori* information available about these interactions. Also, most thermodynamic measurements on nematics are carried out at constant pressure (1 atm), so that as temperature is varied, the molar volume also varies as a result of thermal expansion. Thus, it has been difficult to have confidence in comparisons of experimental results with theory, because theoretical calculations are encumbered with an unknown Hamiltonian varying in an uncontrolled manner.

Measurements at constant volume obviate one of the worst of these problems in that, at constant molar volume, radial averages of the intermolecular interactions should be constant in a first approximation. Thus, in comparing constant-volume measurements with theory, the Hamiltonian can be characterized by a small number of constant parameters.

In addition, we believe that the experimental quantity that may best be compared with present theory is the long-range–order parameter S, defined as

$$S = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle, \qquad (1)$$

where θ is the angle between the longest axis of a molecule and the unique axis of the uniaxial nematic phase.[1] Other thermodynamic quantities, such as heat capacity and latent heat of transition, are expected to be far more sensitive to *short*-

range order than S is, and thus are much less amenable to calculation.

In this Letter, we first present measurements of S at constant molar volume for the nematic liquid crystal p-azoxyanisole (PAA). We then show that existing theoretical models for the nematic phase fail to account for our results. The failures are due to wrong assumptions rather than poor approximations. The basic interactions required in future rigorous theories are then revealed by the construction of an approximate mean-field theory which accounts well for the data on S. The most important result is that the roles of both energetic attractions and steric repulsions are very clearly demonstrated. We then briefly present the volume dependence of S in PAA.

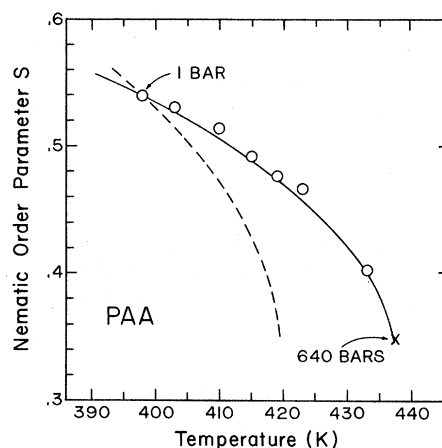In Fig. 1 are shown the data on the variation of S with absolute temperature T at a constant mo-

FIG. 1. Nematic order parameter S versus absolute temperature T at the constant molar volume 221 cm³/mole. Circles, experimental data from Ref. 2 and the PVT equation of state; cross, experimental transition value of S. Dashed curve, Weber-Maier-Saupe universal curve for constant volume (Refs. 4 and 5); solid curve, model with balance of steric and energetic effects as discussed in text.

lar volume V of 221 cm^3/mole. These data were collected from two sets of experiments. The first experiment, briefly reported earlier,[2] is on the variation of S with temperature and pressure in PAA. The second experiment is on the temperature and pressure dependences of the molar volume in PAA, which will be reported in depth in a longer publication elsewhere. Combining the two sets of data permitted a determination of the data in Fig. 1.[3]

One aspect of Fig. 1 that immediately shows the the importance of volume change with respect to order is the enormous increase in the thermal range of the nematic phase of PAA at constant volume as compared with constant pressure. For example, at a constant pressure of 1 atm, the solid-nematic phase transition occurs at 390 K and the nematic-isotropic liquid phase transition occurs at 408 K. By contrast, at a constant molar volume of 221 cm^3/mole the solid-nematic transition occurs at 390 K while the nematic-isotropic liquid transition temperature increases to 437.5 K. Thus, the thermal range of the nematic phase of PAA is increased from 18 K at constant pressure to 47.5 K at constant volume, more than a factor of 2.5!

We now show that the data of Fig. 1 cannot be explained by either of two models that have been proposed for the nematic state. The first of these models, due to Weber[4] and Maier and Saupe,[5] assumes that anisotropic attractive intermolecular interactions are responsible for orientational order. The statistical mechanics are handled in a "mean-field" approximation. One feature of this type of model is that it is necessary to postulate the radial dependence of this interaction, but, at constant density, radial averages should be approximately constant, so that the more basic assumption—that orientational order is driven by energy—can be tested in our experiments, independently of the form assumed for the radial dependence of the interactions. The result of the Weber-Maier-Saupe calculation is shown as the dashed curve in Fig. 1. Clearly, the data are not well explained by this model, which yields a nematic thermal range of only about half of the experimental value.

The second type of model is radically different. In the *steric models*, nematic orientational order is attributed to repulsive interactions associated with the shape of molecules.[6,7] By steric effect, it is meant that there are always more ways to pack aligned than unaligned molecules. Since steric effects are entropic rather than energetic

in nature, the predictions for S in these models are independent of temperature, and depend only on molar volume. Thus, steric models would predict that S is constant at constant molar volume, so that they also fail to account for the variation of S shown in Fig. 1.

We reconcile the failure of both of these models to explain our data by attributing nematic order in PAA to both energetic and steric effects. That both effects should be important has been recognized before,[8-10] but our data allow the first reliable estimate of the relative importance of the two effects. To illustrate this, we calculate the solid curve in Fig. 1 using an approximate mean-field theory outlined by Deloche, Cabane, and Jerome.[10] Specializing their treatment to the case of constant molar volume, we write the free energy of orientation[11] as

$$\Delta F = -AS^2 - TBS^2 - T\Sigma_{\mathrm{mix}}(S). \tag{2}$$

The last term in Eq. (2) is the usual mixing entropy. The A term represents internal orientational energy; A is constant since it depends only on molar volume. The B term represents "packing entropy," i.e., the entropy due to steric repulsions that favor molecular alignment. An expression for Σ_{mix} is given by Deloche, Cabane, and Jerome.[10] The equilibrium value of S is then calculated by the requirement that ΔF in Eq. (2) be minimum. The solid curve in Fig. 1 results from adjusting the values of A and B to obtain a fit to two points. Let T_k represent the nematic-isotropic liquid transition temperature. The relative importance of steric and energetic effects is assessed by computing the value of $BT_k/(A+BT_k)$. The value used for computing the solid curve in Fig. 1 is 0.45. Thus, our data, interpreted in terms of a highly approximate mean-field theory, indicate that steric and energetic effects each contribute about equally to molecular alignment.

Despite the obvious shortcomings of mean-field theories, we believe that this result is probably not far wrong, because the one quantity that mean-field theories, which neglect short-range order, may be expected to account for reasonably well is the long-range order itself. All previous estimates of the relative importance of energetic and steric effects have relied on experimental values of other thermodynamic quantities which surely depend sensitively on short-range order, or else they have relied on untestable assumptions about the volume dependence of intermolecular interactions.[2]

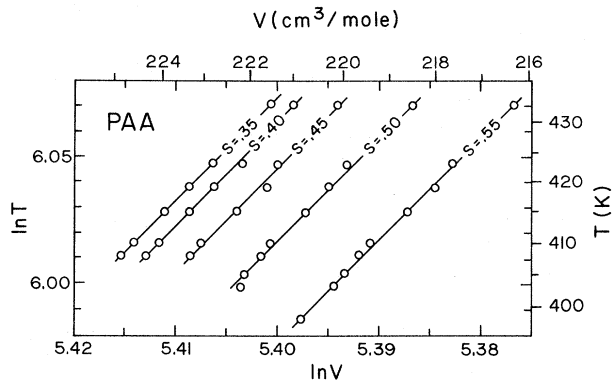We now turn to a second way of displaying our

FIG. 2. Curves of constant nematic order parameter S versus $\ln V$ and $\ln T$.

results. This is done in Fig. 2, where curves of constant S are plotted versus $\ln T$ and $\ln V$. Notice that the curves of constant S displayed this way are very nearly straight lines. The slope of these curves,

$$\gamma = -\,[\partial \log T / \partial \log V]_S,\qquad(3)$$

is a measure of the relative importance of temperature and volume changes in affecting nematic order. The values of γ are constant within experimental accuracy with a mean value of 4.0 ± 0.1. We now allow A and B in Eq. (2) to have a volume dependence. Constant values of S, then, result from constant values of $A/T + B$, so that, in this mean-field approximation, values of γ are given by

$$\gamma = -\frac{\partial \log A}{\partial \log V} - \frac{BT}{A}\frac{\partial \log B}{\partial \log V}\,.\qquad(4)$$

The dependences of A and B on V are of course unknown, but if we assume along with Maier and Saupe that $A \propto V^{-2}$, and further postulate that $B \propto V^{-m}$, then the value of m consistent with these results is $m = 2.5 \pm 1$.

To summarize, we have presented new results on the temperature and volume variation of the nematic orientational order parameter S in PAA. These data make possible the first reliable estimate of the relative importance of anisotropic attractions and steric repulsions as the microscopic origin of the orientational order in nematic liquid crystals. Both effects are about equally important. The volume dependence of S is also presented. We hope that these results will pave the way for more realistic statistical treatments of liquid crystallinity.

We wish to thank Richard Alben for helpful discussions and for reading the manuscript.

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