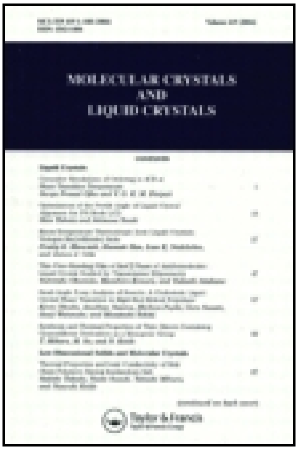

Molecular Crystals and Liquid Crystals

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

An Empirical Form for the Orientation-Ordering Intermolecular Potential in Para-Azoxyanisole

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To cite this article: S. K. Ghosh (1976): An Empirical Form for the Orientation-Ordering Intermolecular Potential in Para-Azoxyanisole, Molecular Crystals and Liquid Crystals, 37:1, 9-21

To link to this article: http://dx.doi.org/10.1080/15421407608084341

Mol. Cryst. Liq. Cryst., 1976, Vol. 37, pp. 9–21
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Printed in Holland

An Empirical Form for the Orientation-Ordering Intermolecular Potential in Para-Azoxyanisole†

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(*Received August 19, 1976*)

We demonstrate here that the angle-independent factor of the orientation-ordering intermolecular potential (OIP) U in para-azoxyanisole (PAA) can be well represented by an equation of the form: $u = A/T - B$, where A and B are positive and independent of temperature T but dependent on pressure P; u is defined as U/kT, where k is the Boltzmann constant. This form for u has been derived from experimentally observed temperature dependence of u at a constant P. In such a determination of u, use has been made of the long-range orientational order parameter Q measured by an NMR technique and a universal u–Q relation. This u–Q relation, formally similar to the one that can be derived from the Maier–Saupe theory, has been obtained from a phenomenological theory and the intermolecular interaction treated under the molecular field approximation. We apply this empirical form for u in understanding a few experimental results in PAA, and show that reasonable agreements can be obtained if certain other facts are also taken into proper consideration.

I INTRODUCTION

One of the characteristic properties of the nematic phase is the existence of long-range order, which is measured by a parameter Q defined as:[1]

$$Q = \langle(3\cos^2\theta - 1)\rangle/2 \tag{1}$$

where θ is the angle between the molecular axis and the average ordering direction or the director, and the angular brackets indicate the statistical average over the molecular ensemble. This order parameter Q decreases with increasing temperature T, and vanishes in the isotropic phase to which the nematic phase transforms at T_C. This nematic–isotropic (N–I) transition

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† Work financially supported by Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche.

is a weak first-order phase transition as evidenced by a small discontinuity in specific volume and a low latent heat at T_C. The sharp drop of Q to zero immediately above T_C does also suggest the N-I transition to be first order. Maier and Saupe[2] (MS) were the first to offer a microscopic theory to understand qualitatively these observations. Their theory is essentially based on the mean field or molecular field approximation (MFA) under which the orientation-ordering intermolecular potential (OIP) takes a simple single-particle form:

$$U_1 = -DQ(3\cos^2\theta - 1)/2V_n^2 \tag{2}$$

where D is a characteristic of the substance, and V_n is the specific volume in the nematic phase. This form for the OIP is derived on the assumption that the dispersion interaction is the principal source for orientational ordering. Although the MS theory has been fairly successful in qualitative understanding of many properties in nematic phase, quantitative agreement between the theory and experiments has not been quite satisfactory. In order to improve upon the MS theory, much effort has been made but with little success so far.[3] The general approach to such improvement has been mainly in two directions:

1) to incorporate other types of intermolecular interaction, both attractive and repulsive, besides the dispersion interaction

2) to remove the limitations of the MFA.

Unfortunately, none of these approaches has brought the theory and experiments appreciably closer.

It seems to us that many of these discrepancies, if not all, arise from the use of a phenomenological theory, which is based on the Helmholtz free energy rather than on the Gibbs free energy, in relating experimental results with microscopic theories. The importance of using Gibbs free energy was also realised by Deloche *et al.*[4] in understanding their experimental results on the effects of pressure on T_C and Q_C in para-azoxyanisole (PAA). But they did not pursue the problem far enough, rather they concentrated their attention in understanding their results with a steric repulsion in addition to the attractive MS interaction. Similar conclusion was also arrived at later by McColl[5] from his studies on the pressure dependence of Q in PAA. The limitations of the MS form for OIP has been dramatically demonstrated by McColl and Shih[6] in extending the nematic range in PAA even if the specific volume is maintained constant. Any simple volume dependent OIP, even if it includes attractive and repulsive interactions, cannot explain this observation. Further evidence to this direction is provided by the recent observations of Baskakov *et al.*[7] on the possibility of transforming the first order N–I transition to second order, where the specific volume and latent heat are expected to vanish, by the application of pressure.

To understand all these observations, it is convenient to work with Gibbs free energy (G) rather than with Helmholtz free energy (F) which is usually simpler from computational viewpoint. To this end, we have developed recently a phenomenological model[8] which enables us to write G for the nematic phase as:

$$G_n(P, T, Q) = G_i(P, T) + G_{or}(P, T, Q) \tag{3}$$

where

$$G_{or}(P, T, Q) = F_{or}(V_n, T, Q) \tag{4}$$

The subscripts n, i and or stand, respectively, for nematic, isotropic and orientation-ordered.

The essential idea of our model is to consider the nematic phase as a mixture of two non-interacting fluids—one of which behaves like an isotropic liquid, represented by G_i, to which the nematic phase transforms at T_C, and the other is completely orientation-ordered represented by G_{or}. At the N–I transition the or-component vanishes leaving the i-component only. The equation (3) has been derived on the assumption that the volume of the or-component $V_n - V_i$ is negligibly small in comparison to the volume of the i-component V_i. In deriving quantitative results, we have calculated G_{or} or F_{or} under the MFA. For this purpose we have used the general two-body form for the OIP rather than restricting ourselves to the MS form or its improved versions. Such a potential has already been used with considerable success,[9] and the MS potential is a special case of this form. We discuss this potential with some necessary details in the next Section to bring out the inherent assumptions involved, and calculate G_{or} or F_{or} with this potential. We also discuss there how these results can be used to derive an empirical form for the OIP. In Section III, we derive an empirical form for the OIP in PAA from Q measured at different T and at a constant P. We also discuss there some problems of such determinations. In Section IV, we apply this empirical form to understand some existing experimental results. Finally, we conclude in Section V.

II ORIENTATION-ORDERING INTERMOLECULAR POTENTIAL

The general form for the two-body OIP can be written as:

$$U_{12}(\mathbf{r}_1, \boldsymbol{\omega}_1, \mathbf{r}_2, \boldsymbol{\omega}_2) = -U(\mathbf{r}_{12})(3\cos^2\theta - 1)/2 \tag{5}$$

where $\mathbf{r}_j$, $\boldsymbol{\omega}_j$ denote, respectively, the center of gravity and the orientation of the jth molecule; the molecules are assumed to be long rod-like with the length-to-breadth ratio much greater than unity. The angle-independent part $U(r_{12})$ is assumed to depend on the radial distance r_{12} $(=r)$ between the centers of gravity of two molecules. Such an assumption is, of course, not rigorously valid for complex molecular structure where the centers of gravity may change with different molecular configurations.[10] The other part of OIP is angle-dependent, and θ_{12} defines the angle between the two molecular axes. This is the first angle-dependent term for two-body OIP compatible to the symmetry of the problem. Under these conditions of two-body interaction and following Kirkwood,[11] we can write the orientational free energy as:

$$F_{or}(V, T, f(\omega)) = \frac{NkT}{V}\int f(\omega)\ln f(\omega)\,\mathrm{d}\omega\,\mathrm{d}V + \frac{N^2}{2V^2}\int f(\omega_1)f(\omega_2)n^{(2)}(r)U_{12}(r)\,\mathrm{d}\omega_1\,\mathrm{d}\omega_2\,\mathrm{dV}_1\,\mathrm{d}V_2 \tag{6}$$

where $f(\omega)$ is the single-particle orientational distribution function, and $n^{(2)}(r)$ is the pair distribution function. Here we have assumed these two distribution functions to be independent of each other. In addition to Eq. (6), $f(\omega)$ must also satisfy the following two conditions:

$$\int f(\omega)\,\mathrm{d}\omega = 1 \tag{7}$$

$$Q = \int(3\cos^2\theta - 1)f(\omega)\,\mathrm{d}\omega/2 \tag{8}$$

The first is the normalizing condition and the second the definition of the orientational order parameter, which is the same as Eq. (1).

Under these conditions and again following Kirkwood, we can derive the single-particle distribution function

$$f(\omega) = C\exp[UQ(3\cos^2\theta - 1)/2kT] \tag{9}$$

where

$$C^{-1} = \int \exp[UQ(3\cos^2\theta - 1)/2kT]\,\mathrm{d}\omega \tag{10}$$

Here we have used for the single-particle potential

$$\frac{N}{V}\int f(\omega)n^{(2)}(r)U_{12}(r, \omega, \omega')\,\mathrm{d}\omega'\,\mathrm{d}V = -\tfrac{1}{2}UQ(3\cos^2\theta - 1) \tag{11}$$

where

$$U = \frac{N}{V}\int n^{(2)}(r)U(r)\,\mathrm{d}V \tag{12}$$

Without the knowledge of $U(r)$ and the pair distribution function $n^{(2)}(r)$, the integral in Eq. (12) cannot be evaluated. But it may be safely assumed that U is to be a function of V and T. Although our single-particle potential is formally identical with that of MS, we do not assume any specific form for U, which is to be determined from experiments. It is to be noted here that both attractive and repulsive interactions can be included in $U(r)$ and hence in U, since they are expected to be similarly dependent on the relative orientations of interacting molecules.

With the above form for $f(\omega)$, the orientational free energy per particle can be obtained as:

$$F_{or} = G_{or} = kT[-\ln Z + uQ(Q+1)/2] \tag{13}$$

where

$$Z = \int_0^1 \exp[3uQx^2/2]\,\mathrm{d}x \tag{14}$$

$$Q = Z^{-1}\int_0^1 (3x^2 - 1)\exp[3uQx^2/2]\,\mathrm{d}x/2 \tag{15}$$

and $u = U/kT$.

Now it is straightforward to show, as in the original treatment of MS, that the N–I transition is first order with $u_C = 4.5414$, and $Q_C = 0.42886$ at $T = T_C$. Using the expression for G_{or}, given in Eq. (13), the other values of Q and corresponding u can be calculated. The results of such a calculation yield a universal relation between u and Q, and are shown in Figure 1. It

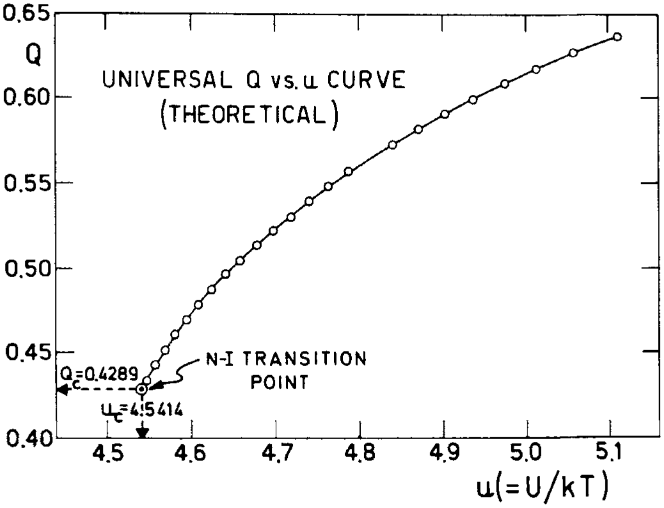

FIGURE 1 The universal u–Q curve.

is to be noted here that the universal relationship between Q and T/T_C as proposed by MS cannot be true in general, since U is a function of V and T (see Eq. (12)). This may be one of the reasons why so much scattering of experimental points are observed around the Q versus T/T_C curve.[12] This universal u–Q relationship can be used to determine u from the values of Q measured under different experimental conditions. In such determinations of u, absolute Q should be measured. It should be pointed out that u is expressible as a function of any two of the three thermodynamic variables[8,13] P, V and T. Hence, in order to determine the functional form of u, it will be convenient to measure Q varying one parameter and keeping the other constant. By repeating similar measurements, the complete functional form for u can be determined. Otherwise, one has to know the correct equation of state of the nematic phase.

III MEASUREMENT OF u AND ITS EMPIRICAL FORM

We have used the universal u–Q relation, shown in Figure 1, in measuring u for which we need to know the absolute values of Q. These Q in PAA were measured at different T and at a constant P from the NMR spectra of ring protons obtained by Fourier transform spectroscopy. The center of gravity of such a spectrum, measured from the spectral center, is related to the order parameter Q by a simple relation.[14] Experimental details and results of such measurements have been reported earlier.[15] We have used here these Q to determine u at different T and at a constant P. Corresponding to each measured, Q we obtain a u related to Q through the universal u–Q relation as shown in Figure 2. These u are fitted to an equation of the following form by the method of least squares:

$$u = A/T - B \tag{16}$$

where A and B are constants independent of T but may depend on P, since the measurements have been made at a constant P. At the moment we do not know the pressure dependence of A and B, but we shall see shortly that a reasonable form can be derived from other experimental results. The least squares fits are excellent as can be seen in Figure 3, and the values for the constants are: $A = (4.94 \pm 0.06) \times 10^3$ °K, and $B = 7.58 \pm 0.15$. Using these values of A and B, and the theoretical value of u_C in Eq. (16), we obtain T_C to be 408.1°K. This value of T_C is in excellent agreement with the directly observed one for our sample. The reliability of the value of T_C, deduced above, was also checked by fitting the data to the following equation by the method of least squares:

$$u - u_C = A(1/T - 1/T_C) \tag{17}$$

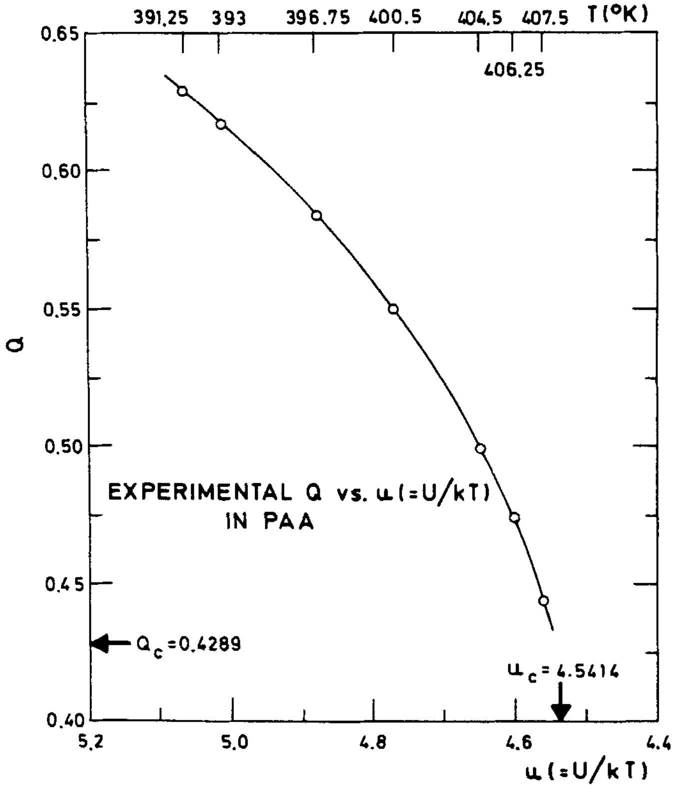

FIGURE 2 Determination of u from experimental Q in PAA; the open circles represent experimental Q with corresponding T shown on the top scale. The smooth line represents the universal u–Q relation similar to that shown in Figure 1.

The agreement between the constants in Eqs. (16) and (17) was excellent.

In addition to the above form for u, we have also tried the following:

$$u = B - AT \tag{18}$$

This form for u does also fit the experimental data fairly well, although with a slightly reduced T_C but not with appreciably different correlation coefficients. Both the forms for u, given by Eqs. (16) and (18), are the simplest. We prefer the former to the latter on the following considerations. From the definition of u ($= U/kT$), the first and second terms in both forms for u can be identified with the attractive and repulsive interactions, respectively. In the first form, the attractive part is independent of T under constant P while the repulsive part increases with increasing T. In the second form, both attractive and repulsive parts increase with increasing T under constant P.

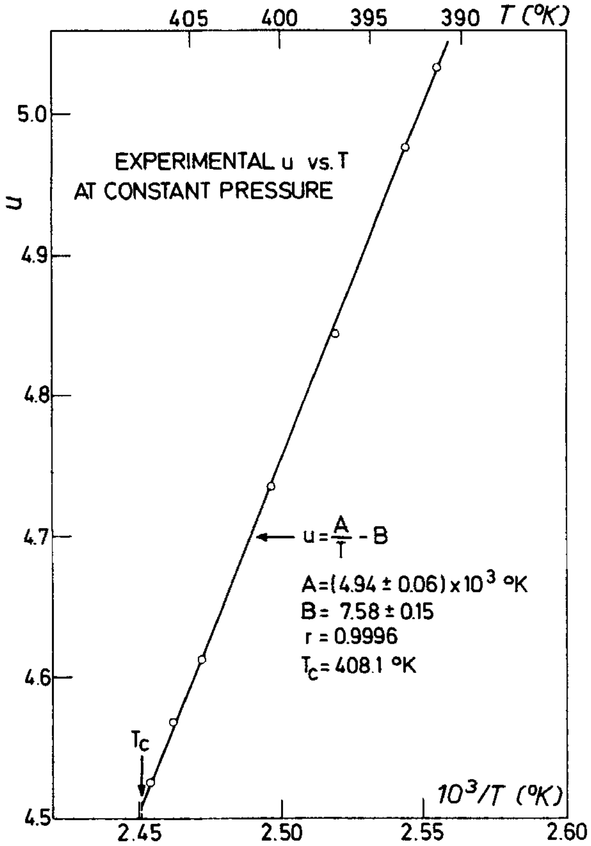

FIGURE 3 u versus $1/T$ plot. The straight line shows the least squares fit to Eq. (16).

The increase of repulsive interaction with increasing T can be understood qualitatively from the steric models,[16,17] since less number of molecules can be accomodated in a given volume with increasing disorder. But we do not find any plausible reason for the increasing attractive interaction with increasing T. Furthermore, our computations of the specific volume in the nematic phase at different T suggest also that the former form for u is more acceptable.[18] It can be noted that both the attractive and repulsive interactions are same order in magnitudes, although very large for only two molecules interacting among themselves. We shall come to this point shortly in the next Section.

Here we would like to stress the importance of measuring the absolute Q in determining u as functions of T, V or P. In this respect we may note that our Q are obtained by taking into account properly the angle (10°) between the molecular axis and the para-axis of benzene rings. If this angle is not taken into consideration, then u obtained from these Q give a completely unacceptable T_C. This fact may be used to determine the molecular geometry which is not very easily accessible in the nematic phase. In principle, Q and hence u should be measurable from the different parts of molecules, from the molecule as a whole or from bulk quantities, such as electric and magnetic susceptibilities. Particular attention should be paid in relating the measured Q with absolute Q, since such a relation may not be always unambiguous. At least from this point of view, it seems that NMR measurements of absolute Q from the spectra of ring protons is most suitable. Problems of such measurements have been discussed earlier.[14]

IV SOME APPLICATIONS AND DISCUSSIONS

In this Section, we apply the empirical form for u (Eq. (16)) in understanding some of the existing experimental results.

It is well known that T_C increases with increasing P. This suggests that U should also increase with increasing P, since u_C $(=U_C/kT_C)$ remains the same for all T_C. Hence at a constant T $(<T_C)$, Q increases with P as it increases with increasing u shown in Figure 1. But no change in Q_C is expected, in accord qualitatively with experimental observations.[4–6] On similar arguments, we can also understand qualitatively the observations of McColl and Shih[6] that the nematic range is considerably extended with pressure even if the specific volume is maintained constant. Any simple volume dependent OIP, such as that of MS or its improved versions, cannot explain this observation. In order to be more quantitative, we need to know the pressure dependence of A. Unfortunately, no such measurements exist till now. We shall see shortly that the pressure dependence of A can be derived from the experimental results of Baskakov *et al.*[7] Prior to presenting these results, we show below that the latent heat and specific volume discontinuity for which we can apply directly our measured A can be reasonably understood.

Under the condition of the N–I transition to be first order and according to our model for this transition,[8] the latent heat and specific volume discontinuity at T_C are given by:

$$\Delta H = \tfrac{1}{2}kT_C^2 Q_C^2(\partial u/\partial T)_P^C, \quad \text{and} \quad \Delta V^C = -\tfrac{1}{2}kT_C Q_C^2(\partial u/\partial P)_T^C \tag{19}$$

where the subscripts and superscripts C indicate the values at T_C. Using Eq. (16), these can be reduced to:

$$\Delta H = -kQ_C^2 A/2, \quad \text{and} \quad \Delta V^C = -kQ_C^2 A m_C/2T_C \tag{20}$$

where $m_C = dT_C/dP$. From these expressions, we get $\Delta H = 3800$ J/mole, and $\Delta V^C = 3.0$ cm^3/mole, where we have used $m_C = 0.0325$°K/atmos.[7] In fact, a wide range of values for ΔH and ΔV^C exist in the literature.[19] Hence no definite comparison between our values and those obtained by more direct methods can be made. But it should be pointed out that both these calculated values are in general about 4 to 5 times of the corresponding directly measured ones. This probably supports the long-standing view of MS that the molecules in the nematic phase exist in microclusters rather than individuals. Such an idea is also compatible with large values of U observed. We have also calculated specific volume in the nematic phase at different T, and these values are in excellent agreement with the experimental results of MS throughout the whole nematic range when the idea of clusters is taken into consideration.[18] In this calculation of specific volume, we have used

$$A = K(P_{cr} - P)T_C \tag{21}$$

derived from the observations of Baskakov *et al.*[7] that ΔV^C is expected to vanish at the critical pressure P_{cr}. They obtain, $P_{cr} = 2450$ atmos. in PAA. We have used this A also for calculating u at different P and at constant temperatures. These u are then used to obtain Q at different P and at constant temperatures. The results are shown in Figure 4. These curves are in qualitative agreement with the results of McColl,[5] particularly for low T, but in gross disagreement in details. This disagreement is not yet fully understood. But a few points may be noted.

1) McColl's method of measurement for Q yields consistently much low values. This is also noted when his Q are compared with the corresponding values reported by others.[15,20]

2) His data show the nematic phase existing where PAA should be in the solid phase.[4,7] The broken line in our Figure 4 shows such a solid–nematic transition line computed from the data of Baskakov *et al.*[7]

3) The purity of his sample; his sample has lower T_C than that of Baskakov *et al.*, and the departure increases with increasing pressure.

4) The pressure dependence of A may be more complex than that given by Eq. (21).

Since this A yields an excellent agreement between theoretical and experimental specific volumes in the whole nematic range, the point 4) as the source of disagreement can almost be ruled out. For all these reasons, we have not included the data of McColl in our Figure 4; we have only shown Q–P curves based on the observations of Baskakov *et al.* according to which the N–I transition is expected to transform to second order with respect to

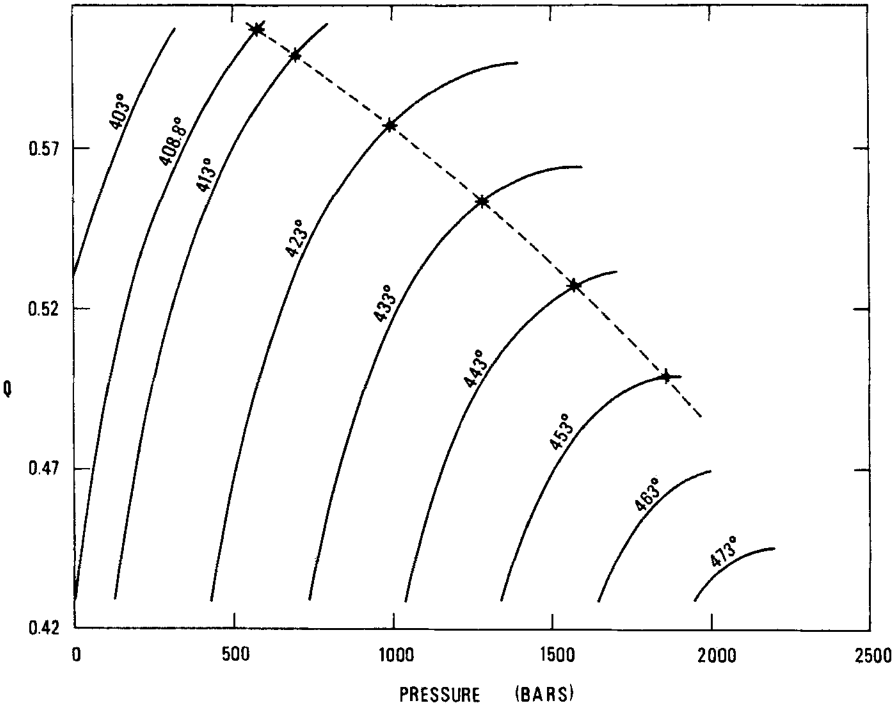

FIGURE 4 Expected pressure dependence of Q at different constant temperatures (continuous lines). All lines start from the N–I transition point with $Q_C = 0.429$. The broken line at the top shows the expected solid–nematic transition line computed from the data of Ref. 7.

the volume change and latent heat at some critical temperature (T_{cr}) and critical pressure (P_{cr}). Our Q–P curves clearly show that even at this critical point Q_C remains constant. In other words, with respect to the behavior of Q the N–I transition still remains first order at this critical point. At $T = T_{cr}$, our Q–P curves will reduce to a point (not shown in the figure), and as the pressure is increased the liquid will have a direct transition to the solid phase without going through the nematic mesophase. The detailed nature of this interesting critical point will be discussed in a future publication.

V CONCLUDING REMARKS

We have shown here that a reliable form for the OIP can be derived from the measurement of the long-range order parameter Q under various experimental conditions. Such studies are expected to reveal dependences of the OIP on different parameters and hence the nature of interactions involved in the ordering processes in liquid crystals in general, and in nematic liquid crystals in particular. Our studies demonstrate such an aspect in PAA in deriving the OIP from Q measured at different T and at a constant P. The OIP derived from such measurements are found to be fairly successful in understanding many physical properties in PAA not only qualitatively but also quantitatively. This may raise the question why the MFA on which our analysis is based is so successful here? It may not be surprising when we consider the following facts. The long-range order parameter is a thermodynamic average quantity averaged here under the MFA. It is well known that the MFA does not take into account the fluctuations in order or the so-called short range order effects. It seems that the effects of fluctuations on Q is small here, since Q is fairly large even at T_C. Such an argument is, of course, not valid for systems showing the second order phase transition, since the order parameter near T_C is extremely small; the fluctuations in such cases may even be larger than the order parameter itself. This is probably the reason why the effects of fluctuations on order parameter is felt extremely close to T_C, away from T_C the MFA is fairly good.[21] Particularly, the quantities like the order parameter and specific volume which essentially depend on thermodynamic averages not very sensitive to fluctuations or their correlations are so well represented by the MFA. But this is not the case with quantities, such as specific heat, which are sensitive to fluctuations. This may be the reason why we do not get good agreement with specific heat results.[22] The general nature of the temperature variation of the specific heat is reproduced, but the variation is not as fast as observed experimentally.[23]

Further, we would like to comment on the existence and nature of microclusters in the nematic phase as original postulated by MS. From the good agreement between experiments and the theory as discussed earlier, it does not seem that the concept of microclusters is an artifact of the MFA. In such a case, we would expect an increase in average number of molecules with lowering of temperature in the nematic phase. As a result, we would expect an increasing lowering of computed specific volume from the experimental values with decreasing temperature. But this is not observed. In fact, the results presented here and those on specific volume[18] suggest that the microclusters in the nematic phase are formed of near neighbor molecules. More observations are needed prior to coming to a solution of this problem.

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