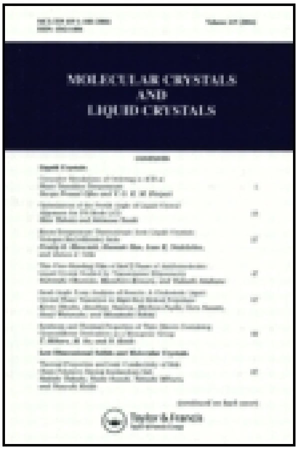

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

On a Characteristic of Nematic-Isotropic Phase Transition

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Version of record first published: 17 Oct 2011.

To cite this article: S. Kobinata, H. Yoshida & S. Maeda (1983): On a Characteristic of Nematic-Isotropic Phase Transition, Molecular Crystals and Liquid Crystals, 99:1, 139-144

To link to this article: http://dx.doi.org/10.1080/00268948308072035

Mol. Cryst. Liq. Cryst., 1983, Vol. 99, pp. 139–144
0026-8941/83/9904-0139/$18.50/0

On a Characteristic of Nematic-Isotropic Phase Transition

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(Received April 1, 1983)

Temperature dependence of the covariance of second orientational order, $\overline{(P_2 - \overline{P}_2)^2}$, has been investigated by using the second ($\overline{P}_2$) and fourth ($\overline{P}_4$) orientational order parameters in nematics. It was found out that the covariance always approaches ⅕ as the temperature increases toward the nematic-isotropic phase transition showing no appreciable first order discontinuity at T_{NI}.

I. INTRODUCTION

Recently, there has been considerable interest in the experimental determination of the higher order parameters of liquid crystals, mostly the fourth parameter $\overline{P}_4$ in nematics and smectics, besides the usual second parameter $\overline{P}_2$. $\overline{P}_4$ can be obtained, in principle, from the polarization characteristics of Raman scattering,[1-4] fluorescence,[5-7] ESR,[8] X-ray,[9] etc., though there still remain some essential difficulties in each method. We showed recently that the resonance Raman probe method can be very useful for the above purpose.[10-13]

Now, there may be various aspects to show the significance of $\overline{P}_4$ in describing the orientational behavior of liquid crystalline molecules. In the present paper, we notice that the covariance of the second order parameter, $\overline{(P_2 - \overline{P}_2)^2}$, is evaluated from $\overline{P}_2$ and $\overline{P}_4$. Then, the orientational behavior of individual molecules near the nematic-isotropic phase transition is discussed from the P_2 covariance point of view by using the $\overline{P}_2$ and $\overline{P}_4$ reported so far.

II. RESULTS AND DISCUSSION

The second ($\overline{P}_2$) and fourth ($\overline{P}_4$) order parameters of liquid crystalline state are defined as an orientational average of the second and fourth Legendre polynomials,

$$P_2(\cos\theta) = 1/2(3\cos^2\theta - 1)$$
$$P_4(\cos\theta) = 1/8(35\cos^4\theta - 30\cos^2\theta + 3), \qquad (1)$$

where θ denotes the angle between the director and molecular long axis. If $\overline{P}_2$ and $\overline{P}_4$ are given, we can evaluate the variance of P_2 by using the relation,

$$\overline{P_2^2} = (18/35)\overline{P}_4 + (2/7)\overline{P}_2 + 1/5 \qquad (2)$$

and hence the covariance of P_2,

$$\overline{(P_2 - \overline{P}_2)^2} = \overline{P_2^2} - (\overline{P}_2)^2 \qquad (3)$$

which is reduced to 1/5 in the isotropic phase and to 0 in a completely ordered phase. Besides, it is also equal to 0 in such a case as all the molecules are oriented with a definite θ and randomly otherwise, irrespective of $\overline{P}_2$ and $\overline{P}_4$. However, there exist ordered states for which $\overline{(P_2 - \overline{P}_2)^2}$ is equal to 1/5, as shown later. It should also be noted that $\overline{(P_2 - \overline{P}_2)^2}$ of Eq. (3) is simply the covariance in statistics, because it does not include any orientational correlation between different molecules directly, and hence is quite different from propagating fluctuations in usual statistical mechanics.[14]

Now, by using $\overline{P}_2$ and $\overline{P}_4$ values determined in some recent experiments on nematics and smectics, it is possible to evaluate the above covariance. In Figure 1, the covariance obtained from our results by resonance Raman probe method is plotted against the reduced temperature, $T^* = T/T_{NI}$, where T_{NI} is the nematic-isotropic transition temperature. Figure 1 shows a remarkable feature that the covariance approaches 1/5 as temperature increases towards T_{NI}, i.e., $T^* \rightarrow 1$. Note that 1/5 is the value properly applicable to the isotropic phase. The solid line in Figure 1 has been calculated from Maier-Saupe's theory.[15] As can be seen, Maier-Saupe's theory overestimates the covariance considerably and fails to reproduce the steep rise-up near T_{NI}. It definitely predicts, however, that the covariance is reduced to 1/5 at T_{NI}, showing no gap at that point, which is quite in accord with the experimental observation. This fact is rather unexpected because Maier-Saupe's theory predicts discontinuous changes of $\overline{P}_2$ and $\overline{P}_4$ at T_{NI}, that is, from 0.4293 and 0.1200 in nematic to both zero in isotropic, respectively. When $\overline{P}_4$ term is included to the molecular field potential as has been done by Luckhurst, *et al.*[16] then calculated value of $\overline{(P_2 - \overline{P}_2)^2}$ deviates 1/5 at T_{NI}. But deviation is considerably small for the reasonable range of contribution of $\overline{P}_4$ term to the molecular field potential, as can be seen later in Figure 3.

In Figure 2, the temperature dependence of $\overline{(P_2 - \overline{P}_2)^2}$, evaluated from other sources of data such as ordinary Raman and polarized fluorescence,

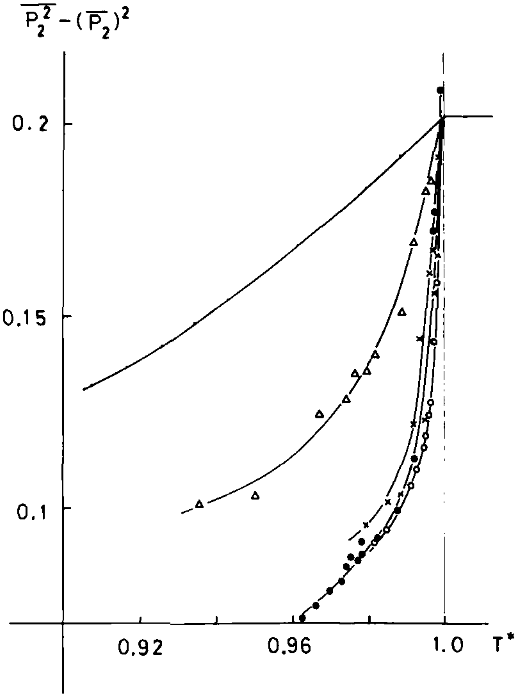

FIGURE 1 The covariance $\overline{(P_2-\overline{P}_2)^2}$ obtained from our results by resonance Raman probe method: —Δ—Δ—Δ—, MBBA, Ref. 10; —O—O—O—, 5CB, Ref. 11; —●—●—●—, 8CB, Ref. 13; —X—X—X—, 6CB, Ref. 13; and ————, Maier-Saupe's theory.

are shown. It shows essentially similar characteristics i. e. $\overline{(P_2-\overline{P}_2)^2} \to 1/5$ as $T \to T_{NI}$. A few stray points correspond to the ordinary Raman results, which may occasionally include considerable errors owing to assumptions and difficulties included in the analysis.

If the covariance reduces to 1/5 at T_{NI}, following relationship is satisfied by $\overline{P}_2$ and $\overline{P}_4$ at the transition point

$$\overline{P_4^{NI}} = (5/18)\overline{P_2^{NI}}(7\overline{P_2^{NI}} - 2). \tag{4}$$

The validity of Eq. (4) is examined by using $\overline{P_2^{NI}}$ and $\overline{P_4^{NI}}$ reported so far or those estimated by extrapolation of some data. The results are shown in Figure 3, where a solid curve represent Eq. (4). Figure 3 includes theoretically calculated results together with the experimental plot. Most points are located near the curve of Eq. (4), suggesting that the convergence of the covariance to 1/5 as $T \to T_{NI}$ can be an essential attribute of the nematic-isotropic phase transition.

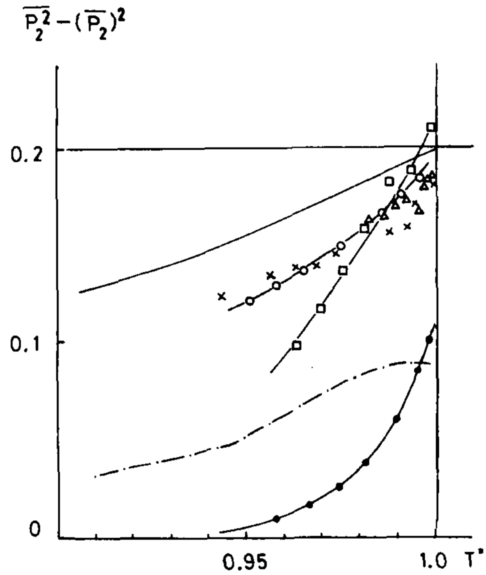

FIGURE 2 The temperature dependence of $\overline{(P_2 - \overline{P}_2)^2}$ evaluated from data by ordinary Raman (R) and polarized fluorescence (F): —□—□—□—, methoxyamyltolane, (R), Ref. 4; —△—△—△—, 4-amino-4′-nitrobiphenyl in 5CB, (F), Ref. 7; —X—X—X—, 4-dimethylamino-4′-nitrostilbene in MBBA (F), Ref. 5; —O—O—O—, 7CB, (R), Ref. 3; —●—●—●—, 5CB, (R), Ref. 2; —·—·—·—, BBCA/MBBA, (R), Ref. 1; and ————, Maier-Saupe theory.

This observation may be compared to Lindemann's melting law,[17] which states that melting occurs at such a temperature as the mean amplitude of lattice vibration attains a definite part of lattice constant. That is, the above observation suggests that nematic-isotropic phase transition occurs at such a temperature as the covariance of P_2 reaches ⅕.

The nematic-isotropic phase transition is known to be thermodynamically first order, and most physical quantities show the first order discontinuity at T_{NI} except some fundamental quantities such as the total mass and the free energy of the system.

In Maier-Saupe theory, the free energy per molecule (f) is given as

$$f(P_2) = 1/2\nu P_2^2 - kT \ln Z(P_2),$$
$$Z(P_2) = \int_0^1 \exp[\nu P_2 P_2(\cos\theta)/kT]\, d(\cos\theta) \qquad (5)$$

where the second order parameter P_2 is included as a running parameter, and ν is a measure of the strength of intermolecular interaction. The average of $\overline{P_2^n}$ is given by

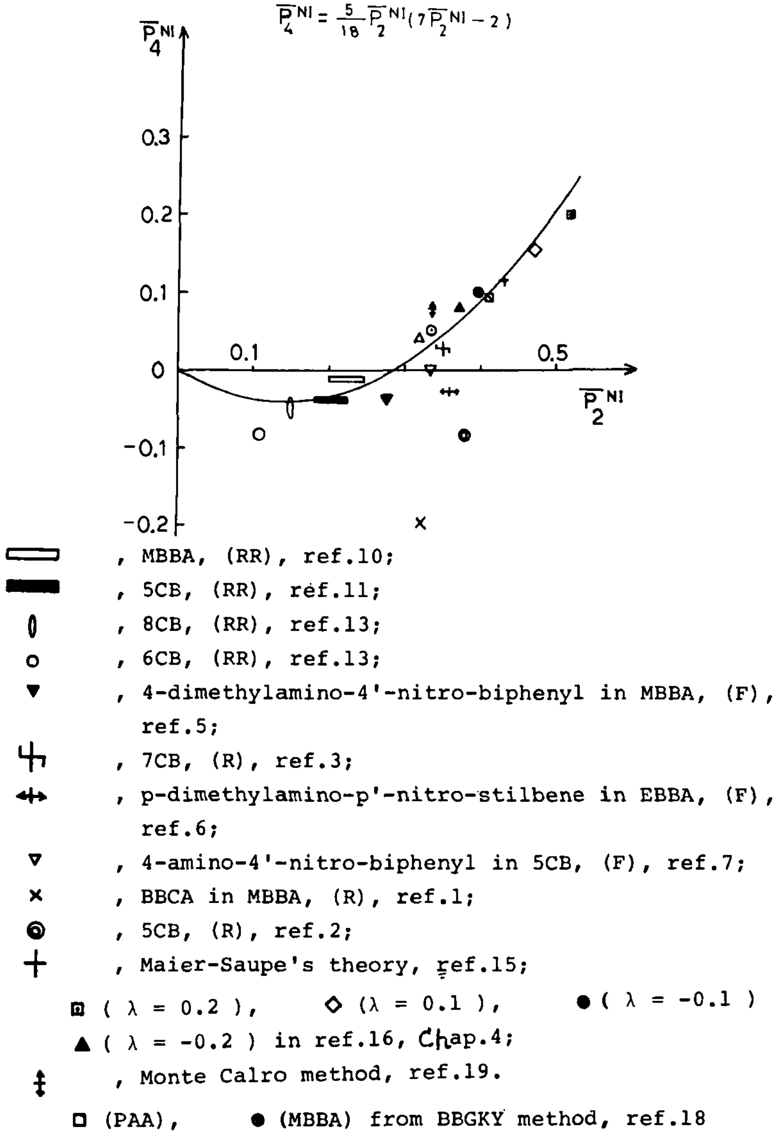

FIGURE 3 P_4^{NI} vs P_2^{NI} plot. Solid line represents Eq. (4). In the below, RR denotes resonance Raman, R and F means ordinary Raman and fluorescence respectively:

$$\overline{P_2^n} = \int_0^1 P_2^n(\cos\theta)\exp[\nu\overline{P}_2 P_2(\cos\theta)/kT]\,d(\cos\theta)/Z(\overline{P}_2) \tag{6}$$

By using the relations,

$$\nu = -2f(1), \qquad \partial^2 f/\partial^2 P_2 = \nu - (\nu^2/kT)(\overline{P_2^2} - (\overline{P}_2)^2) \tag{7}$$

and $\overline{P_2^2} = 1/5$ for $\overline{P}_2 = 0$, we obtain a simple expression,

$$\overline{(P_2 - \overline{P}_2)^2} = 1/5 - (kT/(4f(1)))[(\partial^2 f/\partial P_2^2)\overline{P}_2 - (\partial^2 f/\partial P_2^2)_0]. \tag{8}$$

which expresses the covariance in terms of the derivatives of free energy at $P_2 = \overline{P}_2$ and $P_2 = 0$. It is noticed that Eq. (8) does not maintain any features peculiar to Maier-Saupe theory.

Let us investigate the following Landau expression of free energy,[14]

$$f(P_2) = \alpha(T - T_c)P_2^2 + BP_2^3 + CP_2^4, \tag{9}$$

which is known to result in the first order phase transition for $B \neq 0$. T_c is the virtual second order phase transition temperature. We obtain, after simple calculations,

$$(\partial^2 f/\partial P_2^2)_0 = 2\alpha(T_{NI} - T_c) = (\partial^2 f/\partial P_2^2)\overline{P_2^{NI}}, \tag{10}$$

$$T_{NI} = T_c + B^2/4C, \qquad \overline{P_2^{NI}} = B/2C.$$

Thus, Landau theory of the first order phase transition expressed as Eq. (9) predicts the continuity of the covariance of P_2, i.e. $\overline{(P_2 - \overline{P}_2)^2} = 1/5$ at T_{NI}. The above discussions give support to the conjecture that the last fact is universally valid for N-I transition.

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